Lec.1

Different Types of Chemical Bondes

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What is a chemical bond ?

A chemical bond is defined as the attractive force that holds various constituent particles (atoms, ions or molecules) in different chemical species.

Why do atoms combine together? — Cause of chemical bonding.

The atoms combine together for the following reasons:

1. **Concept of lowering of energy of combining atoms.** When two atoms combine together to form a bond, there is an overall decrease in the potential energy of the combining atoms, *i.e.*, a system having bonded atoms has lower energy than that having the unbonded atoms. This implies that the system of bonded atoms having lower energy is more stable than that of unbonded atoms having higher energy. *From this it, therefore, follows that the process of chemical bonding between the atoms decreases the energy of the combining atoms and gives rise to the formation of a system which has lower energy and hence has greater stability.*

2. **Octet rule or rule of eight : Electronic theory (or octet theory) of valency.** Lewis, Kossel and Longmuir (1916) tried, for the first time, to explain *why atoms combine together* on the basis of the electronic configuration of noble gasses as given here : He (Z = 2) → 2; Ne (Z = 10) → 2, 8; Ar (Z = 18) → 2, 8, 8; Kr (Z = 36) → 2, 8, 18, 8; Xe (Z = 54) → 2, 8, 18, 18, 8; Rn (Z = 86) → 2, 8, 18, 32, 18, 8. They assumed that since the atoms of noble gases do not normally react with other atoms to form compounds, it is reasonable to assume that the outermost shell configuration of the atoms of noble gases is a stable configuration of 8 electrons which they called an *octet.* They also concluded that the two electrons in case of helium (called *duplet*) is also as stable as an octet present in other noble gases. *Since the octet of electrons is so stable in the gases, one can reasonably assume that when atoms of other elements combine to form a molecule, the electrons in their outermost orbits are arranged between themselves in such a way that they achieve an octet of electrons which is stable and thus a chemical bond is established between the atoms.*

The tendency of the atoms to have eight electrons in their outermost shell is known as **octet rule** or **rule of eight**. Since helium atom has only two electrons, this rule is called **doublet rule** or **rule of two** in case of helium. Octet rule was given in the form of a theory which is known as *octet theory of valency* or *electronic theory of valency* which states that:

(*i*) Atom with 8 electrons in the outer most shell (2 in case of helium) are chemically stable and hence are incapable of chemical combination.

(*ii*) An atom having less than 8 electrons in its outer-most shell is chemically active and hence has a tendency to combine with other atoms. The atoms possessing less than 4 electrons in their ultimate shell usually tend to lose them, while those having more the 4 electrons in the outermost

shell tend to gain the electrons during the chemical combination or bond formation to attain stable configuration of the nearest inert gas.

(*iii*) Atoms combine chemically as a result of transferring of electrons from the outer-most shell of one atom to that of the other or by sharing one, two or three electron pairs between the valence-shell of both the combining atoms. The transfer of electrons or sharing of electron pairs gives a stable configuration of 8 electrons to the valence-shell of both the atoms.

(*iv*) The tendency of an atom for transference or sharing its electron pairs is a measure of its chemical activity.

Types of bonds

Main types of bonds are *ionic bond* (also called *electrovalent bond*), *covalent bond* and *coordinate covalent bond*. In addition to these bonds, *hydrogen bond, odd electron bond, metallic bond* and *van der Waals forces (inter-molecular forces*) are also known. In this chapter we shall discuss all these bonds.

Ionic Bond

What is ionic bond?

An ionic bond (also called electrovalent bond) is that bond which is formed when one or more electrons from the valence-shell of an atom (usually a highly electropositive element) are completely transferred to the valence-shell of another atom (usually a highly electronegative element). Thus an ionic bond is established between the two atoms whose electronegativity difference is very high.

The atom that loses electrons becomes positively-charged (cation) while the atom that accepts electrons becomes negatively-charged (anion). The cations and anions thus obtained are then attracted towards each other by the electrostatic force of attraction and are thus linked together by an ionic bond. Thus an ionic bond can also be defined as the electrostatic force of attraction existing between the cations and anions of an ionic compound. In the formation of an ionic bond or ionic compound energy is released. The cations and anions obtained by the loss or gain of electrons attain the nearest noble gas configuration.

Formation of ionic bonds in some ionic compounds

How an ionic bond is formed in ionic compounds can be explained by considering the formation of NaCl, MgO, CaF_2 and Al_2O_3 molecules. The formation of each of these molecules consists of three steps shown below:

NaCl

(a) Na (2, 8, 1) $\xrightarrow{-e^-}$ Na^+ (2, 8) + e^-

(b) Cl (2, 8, 7) $\xrightarrow{+e^-}$ Cl^- (2, 8, 8)

(c) Na^+ (2, 8) + Cl^- (2, 8, 8) $\longrightarrow$ Na^+Cl^-

MgO

(a) Mg (2, 8, 2) $\xrightarrow{-2e^-}$ Mg^{2+} + $2e^-$

(b) O (2, 6) $\xrightarrow{+2e^-}$ O^{2-} (2, 8)

(c) Mg^{2+} (2, 8) + O^{2-} (2, 8) $\longrightarrow$ Mg^{2+} O^{2-}

CaF_2

(a) Ca (2, 8, 8, 2) $\xrightarrow{-2e^-}$ Ca^{2+} (2,8,8) + $2e^-$

(b) F (2, 7) $\xrightarrow{+e^-}$ F^- (2,8)

(c) Ca^{2+}(2, 8, 8) + $2F^-$ (2, 8) $\longrightarrow$ $Ca^{2+}.2F^-$ or $Ca^{2+}(F^-)_2$

Al_2O_3

(a) Al (2, 8, 3) $\xrightarrow{-3e^-}$ Al^{3+} (2, 8) + $3e^-$

(b) O (2, 6) $\xrightarrow{+2e^-}$ O^{2-} (2, 8)

(c) $2Al^{3+}$ (2, 8) + $3O^{2-}$ (2, 8) $\longrightarrow$ $(Al^{3+})_2$ $(O^{2-})_3$

Favourable conditions for the formation of an ionic bond in M^+X^- ionic crystal

We know that the formation of the ionic crystal, M^+X^- takes place through the following steps:

(*i*) When energy equal to ionisation energy of atom M is supplied to it, it loses an electron and is converted into M^+ cation.

$$M^+ + \text{Ionisation energy of M} \rightarrow M^+ + e^-$$

(*ii*) Now the atom X takes up the electron given up by M and is converted into X^- anion. In the formation of X^- ion, energy equal to the electron affinity of X is released.

$$X^+ + e^- \rightarrow X^- + \text{Electron affinity of X.}$$

(*iii*) Now M^+ and X^- ions combine together due to the electrostatic force of attraction existing between them and form M^+X^- ionic crystal. In this process, energy equal to lattice energy of M^+X^- ionic crystal is released.

$$M^+ + X^- \rightarrow M^+X^- \text{ (ionic crystal)} + \text{Lattice energy of } M^+X^-$$

Different steps shown above indicate that the favourable conditions for the formation of an ionic bond or an ionic compound can be described as follows:

(*i*) *Low ionisation energy of atom M*. The ionisation energy of atom M should be low so that this atom may lose the electron readily to form the cation, M^+.

(*ii*) *High electron affinity of atom X*. The electron affinity of atom X should be high so that this atom may accept the electron (lost by M) readily to form the anion, X^-.

Since the elements lying on the extreme left of the periodic table (*i.e.*, metals of groups IA and IIA) have the lowest ionisation energies and the elements lying on the extreme right of the periodic table (*i.e.*, non-metals of groups VIA and VIIA) have the highest values of electron affinity, the formation of ionic bond is favoured between metals and non-metals, *i.e.*, the combination of metals and non-metals gives ionic compounds.

(iv) *Electronegativity difference between M and X atoms very high.* The electronegativity difference between M and X atoms should be very high so that complete transfer of electron(s) form M (less electronegative atom) to X (more electronegative atom) may be possible.

Covalent Bond

Introduction

According to Lewis-Langmuir (1919), a covalent bond is that bond which is formed between the two combining atoms by the mutual sharing of one, two or three electron pairs between them. By the mutual sharing of electron pair(s) each of the two combining atoms attains stable noble gas configuration. One electron of each electron pair is contributed by one atom while the other electron is contributed by the other atom. Thus both the combining atoms have equal claim on the shared electron pair.

The covalent bond formed by the sharing of *one*, *two* or *three* electron pairs between the participating atoms is called *single* (represented as —, *e.g.* H – H, Cl – Cl), *double* (designated as = *e.g.* O = O) and *triple* (designated as ≡, e.g. N ≡ N) covalent bond respectively. Double and triple covalent bonds are collectively called *multiple covalent bonds*. The formation of single covalent bond in H_2, double bond in O_2 and triple bond in N_2 molecules can be illustrated as follows:

H× · H or H — H, Ö×× : Ö or Ö = Ö , N ×× : N or N ≡ N

The compounds containing covalent bonds are called *covalent compounds*.

Factors favouring the formation of covalent bond between A and B atoms

The factors which favour the formation of a covalent bond between the two atoms A and B are given below:

(i) A and B atoms should have higher values of ionisation potential. A and B atoms should have higher values of ionisation potential so that none of them should be able to lose electron(s) and form cations. Thus, when the elements having high values of ionisation potential combine together, they form covalent bond between them (*e.g.* Cl — Cl, F — F etc.).

(ii) Electronegativity of A and B atoms should be equal or slightly different from each other. When two identical atoms (*i.e.*, the atom having the same electronegativity) combine together, a covalent bond is formed between them, since they have the same electronegativity. Due to the same electronengativity of the atoms, the electrons pair being shared by both the atoms is attracted equally by those atoms and hence lies exactly at the mid point of the distance between the two identical linked atoms. Thus a symmetrical distribution of the electron pair between the two atoms is obtained. This symmetrical distribution gives rise to the formation of a purely covalent bond between the two atoms. When the electronegativities of A and B are slightly different from each other, a polar covalent bond is formed between them. If B is more electronegative than A, polar covalent bond is represented as $A^{\delta+} - B^{\delta-}$ and if the electronegativity of A is more than that of B, the polar covalent bond is represented as $A^{\delta-} — B^{\delta+}$.

(*iii*) Colvalent bond is formed between A and B atoms when they equally share one (single bond), two (double bond) or three (triple bond) pairs of electrons with each other. Thus for the formation of covalent bonds between the two atoms, electron pairs must be shared equally between them.

(*iv*) In terms of overlap of atomic orbitals, a covalent bond is obtained by the overlap of only those atomic orbitals of the valence-shell which contain unpaired electrons only and these unpaired electrons must have opposite spins. If the electrons have the same (*i.e.*, parallel) spins, due to the repulsion between them, the overlap of orbitals will increase the potential energy of the system and the system will become unstable, *i.e.*, no bond will be established.

Important properties of covalent compounds

Some of the properties of covalent compounds are summarised below:

(*i*) *Physical state*: The covalent compounds are usually made up of discrete molecules which are held together by van der Waals forces which are very weak. Due to the weak nature of these forces, the covalent compounds usually exist in all the three states, namelly solids (*e.g.* I_2), liquids (*e.g.* Br_2) and gases (e.g. Cl_2) at ordinary temperature.

(*ii*) *Crystal structure*. The crystals of covalent compounds are of three types.

(*a*) Those in which the molecules are small and held together by van der Waals forces. Organic compounds and sulpher (S_8) are the examples of such type of crystals. Since the van der Waals forces are very weak, very small work is required to separate these molecules and hence the crystals of this type are soft, easily fusable and volatile.

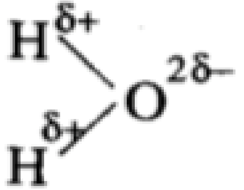
(*b*) Those in which every atom is united with the other by covalent links forming infinite three dimensional covalent structures called giant molecule. In these molecules strong forces operate in all the directions and hence these compounds are very hard and have high melting points. Diomond and silica are the examples of such type of covalent compounds.

(*c*) Those which consits of separate layers. Graphite is an example of such type of covalent crystals.

(*iii*) *Melting and boiling points*. Due to the existance of very weak van der Waals forces, energy required to break these weak forces is low and hence the melting points and boiling points of covalent compounds, excepting those which form giant molecules, are comparatively low.

(*iv*) *Electrical conductivity.* When an electric current is passed through a covalent compound in its liquid or fused state, due to the absence of free electrons and ions in them, the conduction of electric current does not take place and hence these compounds act as bad conductors of electricity. Graphite which is a net work covalent compound is an exception, since, due to the presence of free electrons in its structure, it is a good conductor of electricity.

(*v*) *Solubility in polar and non-polar solvents.* Most of the covalent compounds are insoluble in polar solvents, since covalent malecules do not contain ions and hence do not interact with the dipolar solvent

molecules  to form a hydrated ions. Due to the non-formation of hydrated ions, no hydration energy is released. Covalent compounds are soluble in non polar solvents (*e.g.* C_6H_6, CCl_4 etc.), because they have got merely the same molecular structures, *i.e.*, because both of them are of covalent nature. High polymeric covalent compounds and those forming gaint molecules are virtually insoluble in any solvent.

(*vi*) *Moleculer reactions.* The aqueous solution of covalent compounds donot contain any ions and hence donot undergo ionic reactions as ionic compounds do. These compounds, however, undergo moleculer reactions which are very slow and need a control of temperature and pressure.

(*vii*) *Soft and waxy.* Covalent compounds are soft and waxy, since they consist of separate molecules.

(*viii*) *Directional nature of covalent bonds, geometry and isomerism in covalent compounds.* Covalent bonds are directed in particular directions in space, *i.e.*, covalent bonds are directional and rigid. It is due to the directional nature of covalent bonds that covalent compounds have definite geometry (*e.g.* linear, trigonal planar, tetrahedral etc.) and hence show space isomerism. Mainly organic compounds which are covalent show isomerism.