Chemical Bonding

2-4 @ JEE Main/Advanced

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Types of chemical bond

On the basis | strength

(A) Strong bond

(B) Weak bond

Strong bond:
- (i) Ionic bond
- (ii) Covalent bond
- (iii) coordinate bond
- (iv) metallic bond

Weak bond:
- (i) Hydrogen bond
- (ii) Vander Waal forces
- (iii) Inter molecular forces

4.1. General Introduction— Molecules and Chemical Bond

Atoms are usually not capable of free existence but groups of atoms of the same or different elements exist as one species, e.g., H_2, O_2, P_4, S_8, H_2O.

A group of atoms existing together as one species and having characteristic properties is called a molecule.

Obviously, there must be some force which holds these atoms together within the *molecules*.

This force which holds the atoms together within a molecule is called a chemical bond.

A number of questions now arise :

 (*i*) Why do atoms combine ?

 (*ii*) Why are only certain combinations possible, *e.g.*, hydrogen exists as H_2 and not as H_3 ?

(*iii*) Why do some atoms combine while certain others do not, *e.g.*, two H-atoms combine to form H_2 but two helium atoms do not combine to form He_2 ?

(*iv*) Why do molecules possess definite shapes, *e.g.*, CO_2 is linear but H_2O is a bent molecule (V-shaped) ? Similarly, BF_3 is planar but NH_3 is pyramidal.

To look into the reasons for the answers to the above questions, different theories have been put forward from time to time. These are :

1. Kossel-Lewis approach   2. Valence Shell Electron Pair Repulsion (VSEPR) theory

3. Valence Bond Theory   4. Molecular Orbital Theory.

In this unit, we shall discuss each of these one by one.

4.2. Why do Atoms Combine ? –Kossel-Lewis Approach To Chemical Bonding

A number of attempts were made to explain the formation of chemical bonds in terms of electrons, but it was only in 1916 when Kossel and Lewis succeeded independently in giving a satisfactory explanation. Since their theory was based on the electronic concept of atom, so it is referred to as *Electronic Theory of Valency*. Whereas Kossel's field of study was largely limited to inorganic compounds, Lewis focussed his attention mainly to organic compounds.

The study of noble gases, earlier called inert gases, (Group 18 elements) suggests that neither they combine chemically with any other element nor among themselves, *i.e.*, they are chemically inert. Further, their electronic configurations are as follows :

Noble gas	Atomic No.	Electronic Configuration
Helium	2	2
Neon	10	2, 8
Argon	18	2, 8, 8
Krypton	36	2, 8, 18, 8
Xenon	54	2, 8, 18, 18, 8
Radon	86	2, 8, 18, 32, 18, 8

From the study of electronic configurations of the noble gases, it is clear that they have 8 electrons in their outermost orbit except in case of helium which has 2. Thus, noble gases are inactive or stable because they have 8 electrons in the outermost shell (called **octet**) or 2 electrons in case of helium (called **duplet**). Hence, it was suggested that they possess stable electronic configurations. In case of all other elements, the number of electrons in their outermost shell is less than 8 and hence they are chemically reactive. This led to the following conclusion, called **octet rule** :

The atoms of different elements combine with each other in order to complete their respective octets (i.e., 8 electrons in their outermost shell) or duplet (i.e., outermost shell having 2 electrons) in case of H, Li and Be to attain stable nearest noble gas configuration.

4.3. How do Atoms Combine ? (Modes of Chemical Combination)

As discussed above, atoms combine together in order to complete their respective octets so as to acquire the stable inert gas configuration. This can occur in two ways :

1. *By complete transference of one or more electrons from one atom to another.* This process is referred to as **electrovalency** and the chemical bond formed is termed as **electrovalent bond** or **ionic bond**.

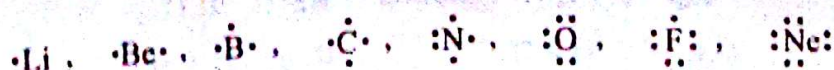2. *By sharing of electrons.* This can occur in two ways as follows :

(a) *When the shared electrons are contributed by the two combining atoms equally, the bond formed is called* **covalent bond**.

(b) *When these electrons are contributed entirely by one of the atoms but shared by both, the bond formed is known as a* **coordinate bond**, *also called* **dative bond**.

4.4. Lewis Symbols – Representing the Valence Electrons

In the formation of a molecule, only the outer shell electrons are involved and they are known as *valence electrons*. The inner shell electrons are well protected and are generally not involved in the combination process. It is, therefore, quite reasonable to consider the outer shell electrons, *i.e.*, valence shell electrons while discussing chemical bonds.

G.N. Lewis introduced simple symbols to denote the valence shell electrons in an atom. The outer shell electrons are shown as dots surrounding the symbol of the atom. These symbols are known as **Lewis symbols** or **electron dot symbols**. These symbols ignore the inner shell electrons. A few examples are given below :

$$\cdot Li \;,\quad \cdot Be\cdot \;,\quad \cdot \overset{\cdot}{B}\cdot \;,\quad \cdot \overset{\cdot}{\underset{\cdot}{C}} \;,\quad :\overset{\cdot}{N}\cdot \;,\quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \;,\quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}: \;,\quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Ne}}:$$

Significance of Lewis symbols. The number of dots around the symbol gives the number of electrons present in the outermost shell. This number of electrons helps to calculate the *common valency* of the element. That is why these electrons are called *valence shell electrons*.

The common valency of the element is either equal to the number of dots in the Lewis symbol (if these are ≤ 4) or 8 minus the number of dots (if these are > 4)

For example, Li, Be, B and C have valencies 1, 2, 3, and 4 respectively, *i.e.*, equal to the number of dots whereas valencies of N, O, F and Ne are 3, 2, 1 and 0 respectively, *i.e.*, 8 minus the number of dots.

Now, we shall discuss each type of bond one by one.

4.5. Electrovalent or Ionic Bond

When a bond is formed by complete transference of electrons from one atom to another so as to complete their outermost orbits by acquiring 8 electrons (i.e., octet) or 2 electrons (i.e., duplet) in case of hydrogen, lithium etc. and hence acquire the stable nearest noble gas configuration, the bond formed is called **ionic bond or electrovalent bond.**

Explanation of the formation of ionic bond. Atoms are electrically neutral. Therefore, they possess equal number of protons and electrons. On losing an electron, an atom becomes positively charged since now the number of protons exceeds the number of electrons.

$$A \longrightarrow A^+ + e^-$$
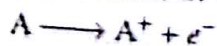
On the other hand, in case of atom, gaining the electron, the number of electrons exceeds the number of protons and thus the atom becomes negatively charged.

$$B + e^- \longrightarrow B^-$$

The oppositely charged particles formed above attract each other by electrostatic forces of attraction. The bond thus formed is known as *electrovalent or ionic bond.*

Such a type of bond is formed only when one of the atoms can easily lose electrons while the other can gain electrons and thus each acquires the stable electronic arrangement of the nearest noble gas.

Examples :

(1) Formation of sodium chloride. Sodium (atomic number = 11) has electronic configuration 2, 8, 1. By losing one electron of its outermost shell, it acquires the inert gas configuration of neon and changes into sodium ion.

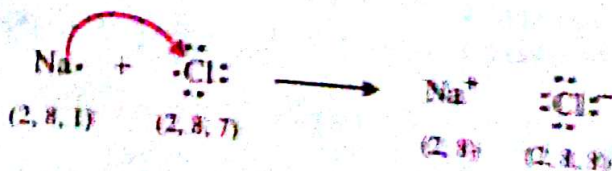$$\underset{2, 8, 1}{Na \cdot} \longrightarrow \underset{2, 8}{Na^+} + e^-$$

On the other hand, chlorine (atomic number = 17) having electronic configuration 2, 8, 7 accepts one electron released by sodium to complete its octet and acquire stable configuration of argon. In this process, chlorine is converted into chloride ion.

$$\underset{(2, 8, 7)}{:\overset{..}{\underset{..}{Cl}}\cdot} + e^- \longrightarrow \underset{(2, 8, 8)}{\left[:\overset{..}{\underset{..}{Cl}}:\right]^-}$$
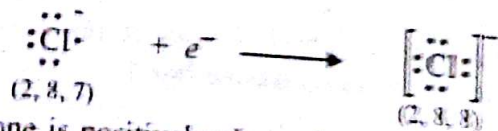
Now, we have two species, one is positively charged sodium ion and the other is negatively charged chloride ion. As they approach each other, they are held together by strong electrostatic forces of attraction. Thus, formation of sodium chloride takes place.

$$[Na]^+ + \left[:\overset{..}{\underset{..}{Cl}}:\right]^- \longrightarrow [Na]^+ \left[:\overset{..}{\underset{..}{Cl}}:\right]^-$$
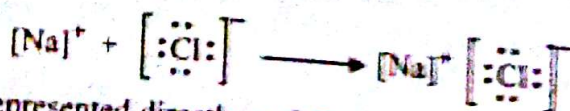
The above steps may be represented directly as follows :

$$\underset{(2, 8, 1)}{Na \cdot} + \underset{(2, 8, 7)}{:\overset{..}{\underset{..}{Cl}}:} \longrightarrow \underset{(2, 8)}{Na^+} \quad \underset{(2, 8, 8)}{:\overset{..}{\underset{..}{Cl}}:^-}$$

(2) Formation of calcium fluoride. Calcium (atomic No = 20, electronic configuration = 2, 8, 8, 2) loses two electrons to attain the stable noble gas configuration of argon. As a result, it is converted into calcium ion. On the other hand, fluorine (atomic No. = 9, electronic configuration = 2, 7) can gain one electron to acquire the stable configuration of neon. As a result, it is converted into fluoride ion.

Here, calcium atom loses two electrons and forms calcium ion with two units of positive charge and the two electrons are transferred to two fluorine atoms, which are converted into fluoride ions, each with one unit negative charge. These oppositely charged ions are then held together by strong electrostatic forces of attraction.
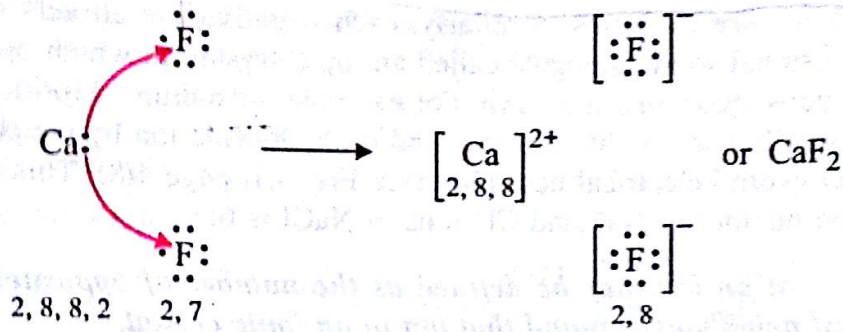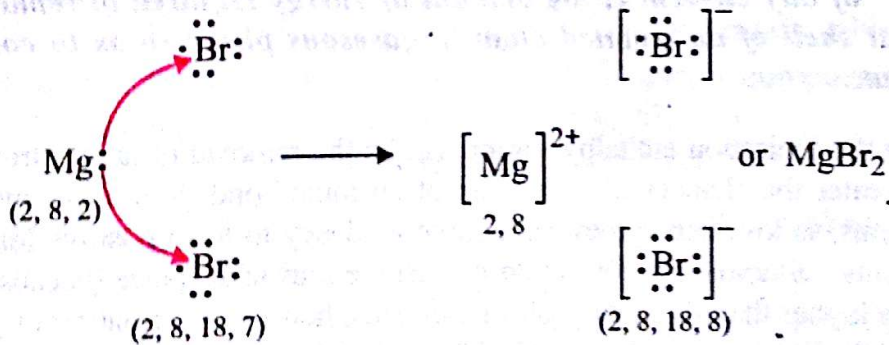

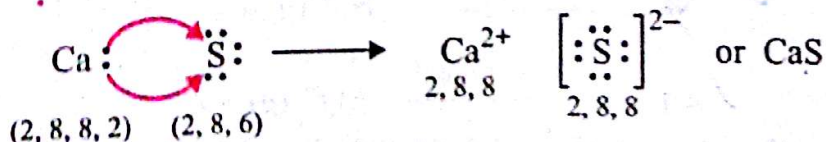**Some More Examples of Formation of Ionic Bonds :**

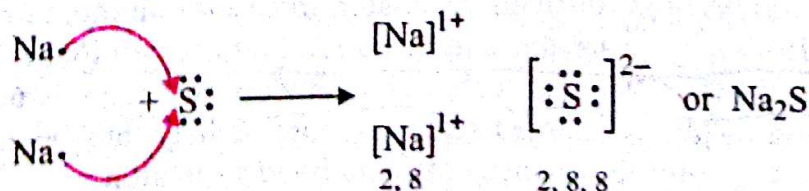**(1) Formation of magnesium oxide from magnesium and oxygen.**
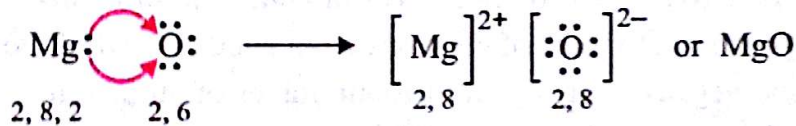
(2) Formation of magnesium bromide from magnesium and bromine.

(3) Formation of calcium sulphide.

(4) Formation of sodium sulphide.

When the structures of atoms or ions are written in such a way that the electrons present in the outermost shell (valence shell) are represented by dots (•) around the symbol of the element, as in the examples above, these structures are called **Lewis dot structures.**

The number of electrons lost or gained during the formation of an electrovalent linkage is termed as the electrovalency of the element.

For example, sodium and calcium lose 1 and 2 electrons respectively and so their valencies are 1 and 2. Similarly, chlorine and oxygen gain 1 and 2 electrons respectively, so they possess an electrovalency of 1 and 2. In other words, valency is equal to the charge on the ion.

The electrostatic field of an ion is non-directional. Each positive ion attracts several negative ions around it depending upon its size or radius. Similarly, each negative ion attracts several positive ions, resulting into a three dimensional solid aggregate called an ionic crystal, in which oppositely charged ions alternate in regular, continuous, geometrical pattern. For example, in sodium chloride crystal, each sodium ion is surrounded by six equally spaced chloride ions and each chloride ion by six equally spaced sodium ions, so that there exists an overall electrical neutrality (see Fig. 4.1, page 4/8). This is called coordination number. Thus, coordination number of Na^+ and Cl^- ions in NaCl is 6.

Coordination number of an ion may be defined as the number of oppositely charged ions present as the nearest neighbours around that ion in an ionic crystal.

4.6. Factors Governing the Formation of Ionic Bonds

The formation of ionic bond involves

(i) the formation of a positive ion by loss of electrons from one kind of atoms.

(ii) the formation of a negative ion by gain of electrons from another kind of atom.

(iii) holding the positive and negative ions by electrostatic forces of attraction.

The formation of ionic bond depends upon the following factors :

(i) Ionisation Enthalpy (Ionization Energy).

Ionisation enthalpy of any element is the amount of energy required to remove an electron from the outermost shell of an isolated atom in gaseous phase so as to convert it into a gaseous positive ion.

It is clear that lesser the ionisation enthalpy, easier will be the removal of an electron, *i.e.*, formation of a positive ion and hence greater the chances of formation of an ionic bond. Ionisation enthalpy (I.E.) of alkali metals (*i.e.*, group I elements) is low, hence they have more tendency to form positive ions. In case of alkaline earths (*i.e.*, group 2 elements), although the formation of positive ions takes place (because ionisation energy is not high) but the I.E.'s are higher than those of group I elements, hence the formation of positive ions is not as easy as in case of alkali metals. For example, in case of sodium, the I.E. is 495 kJ/mole while in case of magnesium, it is 743 kJ/mole. So the formation of positive ion of sodium is easier than that of magnesium.
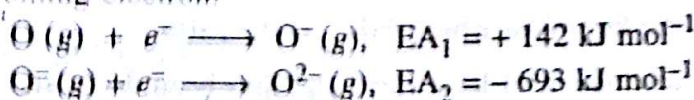
$$Na\ (g) \xrightarrow{\ 495\,kJ\,mol^{-1}\ } Na^+\ (g) + e^-$$

$$Mg\ (g) \xrightarrow{\ 743\,kJ\,mol^{-1}\ } Mg^+\ (g) + e^-$$
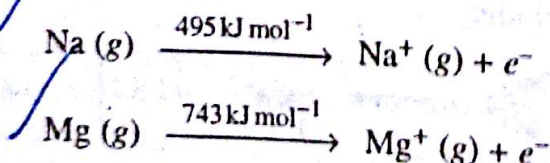
The energy required for the removal of second electron from Mg^+ ion (second ionization enthalpy) is very high (because after the removal of the first electron, the effective nuclear charge increases). Hence, the formation of divalent Mg^{2+} ion becomes difficult. Similarly, in case of aluminium, the formation of triply charged Al^{3+} ion requires 3158 kJ/mol^{-1} (as the sum of its 1st, 2nd and 3rd ionisation enthalpies). Thus, it is not generally possible to form this ion since such a huge amount of energy is not available in chemical reaction. Hence, the formation of highly charged species is rare. It may thus be concluded that lower the values of ionisation enthalpies, greater the chances of ionic bond formation.

(ii) Electron Gain Enthalpy (Electron Affinity)

Electron affinity or Electron gain enthalpy of an element is the enthalpy change that takes place when an extra electron is added to an isolated atom in the gaseous phase to form a gaseous negative ion.

Higher is the electron affinity, more is the energy released and stabler will be the negative ion produced. Consequently, the probability of formation of ionic bond will be enhanced. Halogens possess high electron affinity. So the formation of their negative ions is very common, e.g., in case of chlorine, electron affinity is +348 kJ/mole, i.e., $Cl(g) + e^- \longrightarrow Cl^- + 348$ kJ/mole   or   E.A. = + 348 kJ mol^{-1}

Hence, the halogens can form negative ions easily. On the other hand, elements of group 16 form divalent negative ions (by gaining two electrons) but not so easily. This is because the second electron affinity in case of these elements is negative, i.e., energy is required to form divalent ions. Let us discuss the case of oxygen. First, oxygen will add up one electron to form monovalent ion which is accompanied by release of certain amount of energy. But in the process of addition of second electron to the monovalent oxygen ion, energy is required to overcome the force of repulsion exerted by the negatively charged monovalent ion to the incoming electron.

$$O(g) + e^- \longrightarrow O^-(g), \quad EA_1 = + 142 \text{ kJ mol}^{-1}$$
$$O^-(g) + e^- \longrightarrow O^{2-}(g), \quad EA_2 = - 693 \text{ kJ mol}^{-1}$$

[handwritten: $E_{gE} = 551$ kJ/mol]

So electron affinity for the overall process will be given by EA = + 142 – 693 = – 551 kJ mol^{-1}.

The negative sign indicates that energy is required to form divalent oxide ion. Similarly, in case of formation of trivalent negative ions, the amount of energy required will be much higher. Hence, monovalent species are most common, divalent are rare and trivalent are rarer.

> **Note Carefully** that the term used in the above discussion is Electron Affinity (A_e). However, now a days, the term Electron Gain Enthalpy ($\Delta_{eg} H$) is used in place of Electron Affinity (as discussed in unit 3). The two are taken as equal in magnitude (as $\Delta_{eg} H$ is only slightly higher than A_e) but opposite in sign. $\Delta_{eg} H$ has same sign as required according to thermodynamics, i.e., if energy is released, it is given a –ve sign. A_e has signs contrary to thermodynamic conventions.

It may be concluded from the above discussion that ionic bonds are generally formed between the atoms of the elements placed on the left and on the right side of the periodic table.

(iii) Lattice Enthalpy (Lattice Energy).
In the formation of ionic compounds, the positively charged ions combine with negatively charged ions to form the compound.

$$A^+(g) + B^-(g) \longrightarrow A^+B^-(s)$$
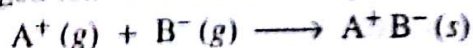
The energy released when the requisite number of gaseous positive and negative ions combine to form one mole of the ionic compound is called lattice enthalpy.

The higher the value of lattice enthalpy of the resulting ionic compound, the greater will be the stability of the compound and hence greater will be the ease of its formation.

We know that the force of attraction between the oppositely charged ions is directly proportional to the magnitude of the charges (q_1, q_2) and inversely proportional to the square of the distance (d) between them,

i.e.,
$$\text{Force of attraction} \propto \frac{q_1 \times q_2}{d^2}$$

Hence, the value of lattice enthalpy depends upon the following two factors :

(a) **Charge on the ions.** The higher the charge on the ions, greater is the force of attraction and hence larger is the amount of energy released.

For example, lattice enthalpies of some ionic compounds are in the order :

NaCl	<	CaCl$_2$	<	MgO
(– 758)		(– 2254)		(– 3932) kJ mol^{-1}
(Uni-univalent)		(Bi-univalent)		(Bi-bivalent)
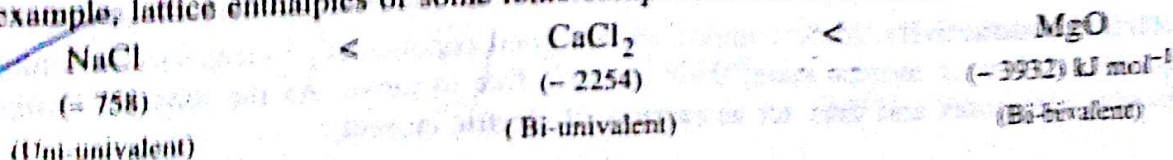
(b) Size of the ions. As highly charged species are rare, the other factor, *i.e.,* the internuclear distance between the ions becomes more important. If the size of the ions is large, internuclear distance will be more and force of attraction will be less while in case of small ions, internuclear distance is less and so force of attraction is greater.

For example, lattice enthalpies of some ionic compounds are in the order :

NaCl > NaBr,	LiF > LiI,	AgCl > AgI	CaF$_2$ > CaCl$_2$,	BeO < MgO
(– 758) (– 752)	(– 1033) (– 140)	(– 895) (– 795)	(– 2581) (– 2254)	(– 3125) (– 3932)
$(r_{Br^-} > r_{Cl^-})$	$(r_{I^-} \gg r_{F^-})$	$(r_{I^-} > r_{Cl^-})$	$(r_{F^-} < r_{Cl^-})$	

(as BeO has greater covalent character. Refer to Art. 4.21)

Net effect. If Lattice enthalpy + Electron gain enthalpy > Ionization enthalpy, the net effect will be the release of energy and hence an ionic bond is formed.

Most of the ionic compounds are formed between cations from metals (because of low ionization enthalpy) and anions from non-metals (because of high negative electron gain enthalpy). However, a very common exception is ammonium ion (NH_4^+), *i.e.,* a cation made from two non-metallic elements. A large number of ionic compounds are known in which NH_4^+ is the cation.

Born-Haber cycle for calculation of lattice enthalpy has been discussed in unit 6.

4.7. General Characteristics of Ionic Compounds

The ionic compounds possess the following characteristics :

1. Physical State. These compounds usually exist in the solid state.

2. Crystal Structure. X-ray analysis of the ionic compounds shows that they exist as ions and not as molecules. These ions are arranged in a regular pattern in the three dimensional space to form a lattice.

The pattern of arrangement, however, depends upon the size and charges of the ions. For example, in case of sodium chloride, each sodium ion is surrounded by six chloride ions and each chloride by six sodium ions, thus giving rise to a three dimensional octahedral crystal strucutre (Fig. 4.1). The formula of an ionic compound merely indicates the relative number of ions present.

3. High melting and boiling points. Ionic compounds possess high melting and boiling points. This is because ions are tightly held together by strong electrostatic forces of attraction and hence a large amount of energy is required to break the crystal lattice.

4. Solubility. Electrovalent compounds are soluble in solvents like water which are polar in nature and have high dielectric constant. It is due to reason that the polar solvent interacts with the ions of the crystals and further the high dielectric constant of the solvent (*i.e.,* capacity of the solvent to weaken the forces of attraction) cuts off the force of attraction between these ions. Furthermore, the ions may combine with the solvent to liberate energy called *hydration enthalpy* which is sufficient to overcome the attractive forces between the ions.

Non-polar solvents like carbon tetrachloride, benzene etc. having low dielectric constants are not capable of dissolving ionic solids. Hence, ionic solids are soluble in polar solvents and insoluble in non-polar solvents.

5. Electrical conductivity. Ionic compounds are good conductors of electricity in solution or in the molten state. In solution or molten state, their ions are free to move. As the ions are charged, they are attracted towards electrodes and thus act as carriers of electric current.

FIGURE 4.1

Cl⁻
Na⁺

Representing Na⁺ ion surrounded octahedrally by 6 Cl⁻ ions
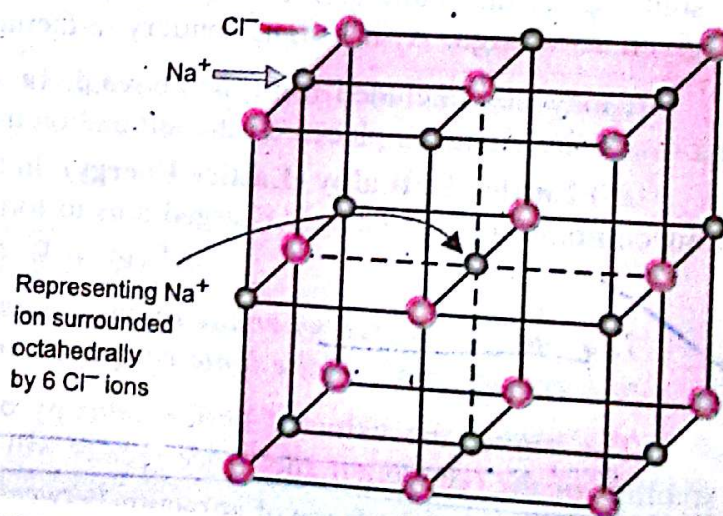
Crystal structure of NaCl

6. **Ionic reactions.** The reactions of the ionic compounds are, in fact, the reactions between the ions produced in solution. As the oppositely charged ions combine quickly , these reactions are, therefore, quite fast. [e.g. $Na^+ Cl^- (aq) + Ag^+ NO_3^- (aq) \longrightarrow AgCl (s) + NaNO_3 (aq)$].

SUPPLEMENT YOUR KNOWLEDGE

1. The dielectric constant of D_2O (80·5) is slightly less than that of H_2O (82). The dielectric constants of some solvents are given below :

Solvent	Water	Methyl alc.	Ethyl alc.	Acetone	Ether
Dielectric const.	82	35	27	21	4·1

2. **Variable electrovalency.** In case of transistion metals, certain atoms can lose different numbr of electrons to acquire a stable configuration. Hence, they show **variable electrovalency.** For example, Fe forms Fe^{2+} and Fe^{3+} ions and Cu forms Cu^+ and Cu^{2+} ions. As already discussed in unit 2, the more stable ion is the one which has more stable core, i.e., the configuration obtained after the loss of valence electrons. For example, Fe^{3+} salts are more stable than Fe^{2+} salts

$_{26}Fe = 2, 8, 14, 2$

$Fe^{2+} = 2, 8, 14 = [Ne]^{10} 3 s^2 3 p^6 3 d^6$ (unstable core)

$Fe^{3+} = 2, 8, 13 = [Ne]^{10} 3 s^2 3 p^6 3 d^5$ (stable core)·

Cu^{2+} salts are more stable than Cu^+ salts.

$_{29}Cu = 2, 8, 18, 1$

$Cu^+ = 2, 8, 18 = [Ne]^{10} 3 s^2 3 p^6 3 d^{10}$ (stable core)

$Cu^{2+} = 2, 8, 17 = [Ne]^{10} 3 s^2 3 p^6 3 d^9$ (more stable core)

Greater stability of Cu^{2+} than Cu^+ is due to the fact that the nuclear charge of Cu is not sufficient enough to hold 18 electrons of Cu^+ ion present in the outermost shell.

Similarly, in case of heavier p-block elements like Sn and Pb with the valence shell configuration $ns^2 np^2$, all the four electrons may be lost giving a valency of +4 or only p-electrons may be lost giving a valency of +2 The s-electrons remain attracted by the nucleus due to poor screening effect of the intervening d and f electrons and do not take part in bonding. The effect is called **inert pair effect.**