

IONIC BONDING

Electrovalent or Ionic bond

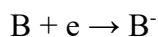
When a bond is formed by complete transfer of electrons from one atom to another so as to complete their octet or duplet and hence acquire the stable nearest noble gas like electronic configuration, then the bond formed is called ionic bond or electrovalent bond.

Formation of ionic bond

Atoms are electrically neutral as they possess equal number of proton and electrons. If an atom loses electron, number of protons exceeds the number of electrons and hence it becomes positively charged cation.



On the other hand, if an atom gains electron, number of electrons exceeds the number of protons and hence it becomes negatively charged anion.



These oppositely charged species attract each other by electrostatic force of attraction and such electrostatic attraction is considered as ionic bond.

Q.1. Explain the formation of the following ionic compounds:

1. Sodium chloride (NaCl)
2. Calcium fluoride (CaF₂)
3. Magnesium oxide (MgO)
4. Magnesium Bromide (MgBr₂)
5. Magnesium fluoride (MgF₂)
6. Calcium Sulphide (CaS)
7. Calcium Oxide (CaO)
8. Sodium Sulphide (Na₂S)

Electrovalency

The number of electrons lost or gained during the formation of an electrovalent linkage (ionic bond) is known as the electrovalency of the corresponding element.

Example : In the formation of NaCl, the electrovalency of sodium is 1 and that of chlorine is 1.

In general, electrovalency can be considered as the magnitude of charge present on the ion.

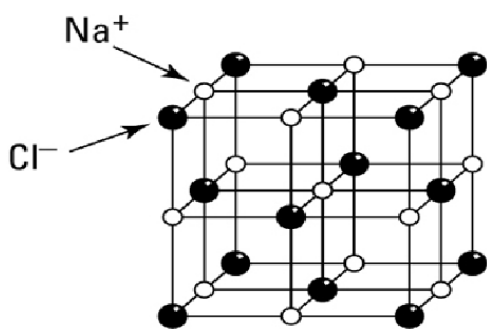
Ionic- Crystal

The electrostatic field of an ion is non directional. Each positive ion attracts several negative ions around it depending upon its size (radius). Similarly, each negative ion attracts several positive ions. This results in the formation of a large, three-dimensional, solid aggregates ,where oppositely charged ions get arranged in regular, continuous, geometrical pattern. This is known as ionic crystal. The 3-D arrangement in a crystal is called the lattice.

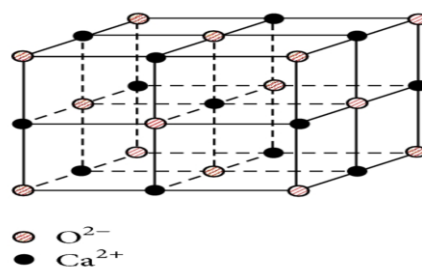
Coordination number

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

Example: In the structure of NaCl crystal,each Na^+ ion is surrounded by six oppositely charged equally spaced Cl^- ions and each chloride ion is also surrounded by six equispaced sodium ion. Hence, in NaCl crystal, the coordination number of sodium ion=6 and the coordination number of chloride ion = 6. Hence NaCl shows 6:6 coordination.



Q.2. The structure of CaO is given below. Calculate the coordination numbers of both Calcium and oxide ion:

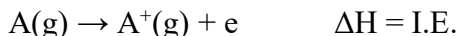


Energy parameters in the formation of ionic bond

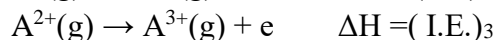
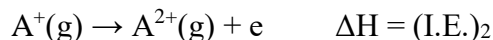
The energy parameters involved in the formation of ionic bond are:

1. Ionization energy(I.E) :

It is defined as the minimum amount of energy required to remove an electron from the outermost shell (most loosely bound electron) of a neutral, isolated, gaseous atom to convert it into a gaseous positive ion.



The successive ionization energies can be defined as:

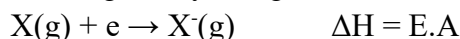


It can be noted that: $(\text{IE})_1 < (\text{IE})_2 < (\text{IE})_3$ because, higher energy will be required to remove electron from a previously positive charged species.

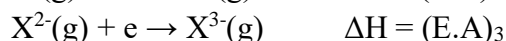
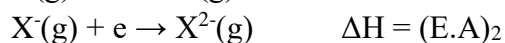
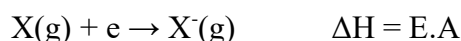
It is clear that, lower the ionization energy, easier will be removal of the electron. This causes easier formation of cation and consequently favors the ionic bond formation. IE of alkali metals are very low, hence they have more tendency to form ionic bond. The IE of alkali earth metals are higher than that for alkali metals, in addition the alkali earth metals attain stable configuration after loss of two electrons. Higher energy will be required for this process ($IE_1 + IE_2$) so alkali metals show comparatively lower tendency (than alkali metals) in forming ionic bond.

2. Electron affinity(E.A):

It is the amount of energy released when an electron is added to the valence shell of a neutral isolated gaseous atom to convert it into gaseous negatively charged anion.



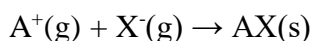
The successive electron affinities can be defined as:



Higher the electron affinity, more is the energy released and the stability of the negative ion produced will be more. This favors the formation of the ionic bond. Halogens have very high EA, hence formation of their negative ion is very common. Therefore halogens are prominent candidates for ionic bonding.

3. Lattice energy :

It is defined as the energy released when the requisite number of cations and anions combine to form one mole of the ionic compound(lattice).



The higher the value of the lattice energy, higher will be stability of compound and greater will be the ease of its formation.

We know, the electrostatic force of attraction is governed by Coulomb's law.

$$F = \frac{1}{k} \frac{q_1 q_2}{r^2}$$

Where, F = electrostatic force of attraction, q_1, q_2 = magnitude of charges, r = distance between the two charges, k = dielectric constant of the medium.

Hence the value of lattice energy will depend upon two factors:

- Charge on the ions: Higher the charge on the ions, higher will be the force of attraction and greater will be the lattice energy.
- Size of the ions: If the size(radius) of the ions is large, inter-nuclear distance will be more and the force of attraction will be less. Hence, lattice energy decreases.

Q.3. Compare the Lattice energy for the following compounds:

1. NaCl, CaCl₂, MgO

2. NaBr, MgBr₂, AlBr₃

Examples:

<i>Compound</i>	<i>Lattice energy(kJ/mol)</i>	<i>Compound</i>	<i>Lattice energy(kJ/mol)</i>
NaCl	758	AgCl	895
NaBr	752	AgI	795
LiF	1033	CaF ₂	2581
LiI	140	CaCl ₂	2254

General characteristics of ionic compounds**1. Physical state :**

These compounds usually exist in solid state (mostly crystalline) due to strong electrostatic force of attraction operating in lattice.

2. High melting and boiling points :

Ionic compounds have high melting and boiling points. This is because ions are tightly held together by strong electrostatic force of attraction and a huge amount of energy is required to break the crystal lattice. In other words, we can say, higher the lattice energy of an ionic compound, greater will be its melting and boiling point.

3. Solubility :

Ionic compounds are soluble in polar solvents with high dielectric constant (e.g. water, methanol etc). This is because the polar solvent interacts with the ions of the crystal and the high dielectric constant of the solvent (ϵ) leads to decrease the electrostatic force of attraction between the ions.

Furthermore, the ions may combine with the solvent to liberate energy known as Solvation energy.

$$\text{Solvation energy} \propto (\text{charge/size})$$

This solvation energy greatly compensates the lattice energy and the ionic compound gets dissolved in the solvent. If the solvent is water, then 'Hydration Energy' term is used instead of solvation energy.

Example : The dielectric constant of D₂O (78.6) is slightly less than that of H₂O (80). Hence ionic solids are less soluble in heavy water (D₂O) than normal water.

4. Electrical conductivity :

Ionic compounds are good conductor of electricity in solution or in their molten state. In solid state the ions are tightly held together by strong electrostatic force of attraction, but in molten state or in solution, the ions become free to move and can conduct electricity.

5. Ionic reactions :

The ionic reactions generally occur in solution and are very fast. Hence the reactions of ionic compounds are also very fast.

Example : $\text{NaCl} + \text{AgNO}_3 = \text{NaNO}_3 + \text{AgCl} \downarrow$ (white precipitate of AgCl is observed)

6. *Isomorphism* :

Many pairs of ionic compounds are known to crystallize simultaneously in the same form and they are called Isomorphous crystals. Such isomorphous compounds can crystallize simultaneously from a solution to produce mixed crystals.

Example : NaNO_3 and CaCO_3 , BaSO_4 and KMnO_4 etc.

Lattice Energy: Determination & Applications

Lattice energy cannot be measured directly. However, it can be calculated by using different mathematical procedures. These are:

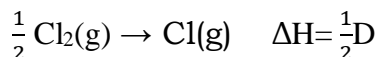
1. Born-Haber Cycle.
2. Born-Landé Equation.
3. Born-Mayer Equation.
4. Kapustinskii equation.

1. Born-Haber Cycle :

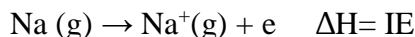
Max Born and Fritz Haber in 1919 put forward a method based on Hess's law for the calculation of lattice energy. This method is called Born-Haber cycle.

Let us consider the formation of NaCl lattice from its constituent gaseous ions. We can imagine that 1 mol NaCl can be prepared from the following steps:

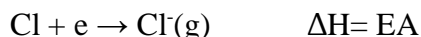
1. Sublimation of crystalline Sodium metal to form gaseous sodium atoms.
$$\text{Na(s)} \rightarrow \text{Na(g)} \quad \Delta H = S$$
2. Half mole of gaseous Cl_2 is dissociated to form 1 mole of gaseous atoms. Hence the change in enthalpy is half of the bond dissociation energy.



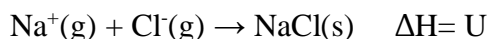
3. The gaseous Na atoms are ionized to form gaseous Na^+ ions.



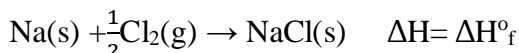
4. The gaseous Cl atoms are converted to gaseous Cl^- ion by addition of electron.



5. The gaseous Na^+ and Cl^- ions combine to form 1 mole of crystalline NaCl lattice.



Again, the standard enthalpy of formation of NaCl is defined as –



Applying Hess's law ,

$$\Delta H^\circ_f = S + \frac{1}{2}D + \text{IE} + \text{EA} + U$$

Where-

S = Enthalpy of Sublimation

D = Bond Dissociation Energy

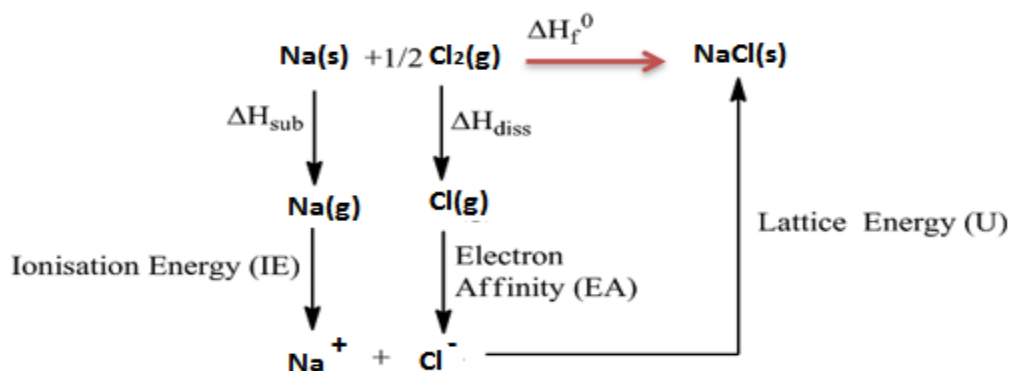
IE = Ionization Energy

EA = Electron Affinity

U = Lattice Energy

ΔH_f° = Standard Enthalpy of Formation

Born Haber Cycle for Sodium Chloride



Q.4. Calculate Electron Affinity of Iodine from the following data :

Lattice energy of KI = 153.0 kcal/mol

Heat of formation of KI = 78.3 kcal/mol

Sublimation energy of K = 21.4 kcal/mol

Ionization potential of K = 100.0 kcal/mol

Dissociation energy of I_2 = 51.0 kcal/mol

Q. 5. Calculate the lattice energy of MgBr_2 using the following data :

Sublimation energy of Mg = 148 kJ/mol

$\text{IE}_1 + \text{IE}_2$ of Mg = 2187 kJ/mol

Vaporization energy of Br_2 = 31 kJ/mol

Dissociation energy of Br_2 = 193 kJ/mol

Heat of formation of MgBr_2 = 524 kJ/mol

Q. CaF does not exist- why ?

Ans. We know that the energy required to produce Ca^+ from Ca (IE_1) is less than the energy required to produce Ca^{2+} from Ca ($\text{IE}_1 + \text{IE}_2$), but the lattice energy caused by Ca^{2+} is very high. This high lattice energy favors the two IEs of Ca. Hence, CaF does not exist and can be considered to undergo following disproportionation reaction where more stable CaF_2 is produced.



Q. Although the 2nd EA of oxygen and sulphur are endothermic, a large number of compounds are available as oxides or sulphides- explain.

Ans. The high lattice energy produced by binegative oxide or sulphide ion(O^{2-} or S^{2-}) overweighs the endothermicity of the 2nd EA.

2. Born-Lande Equation:

The Born Lande equation gives theoretical formula to calculate the lattice energy of an ionic crystal. It considers both the attractive and repulsive forces operating in an ionic crystal and established the following equation-

$$U = - \frac{N_0 A Z_+ Z_- e^2}{r_0} \left(1 - \frac{1}{n}\right)$$

In SI unit, the equation transforms to -

$$U = - \frac{N_0 A Z_+ Z_- e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right)$$

Where,

U= Lattice Energy (in Joules)

N_0 = Avogadro number = $6.023 \times 10^{23} \text{ mol}^{-1}$

A = a constant, known as Madelung constant. It depends upon the geometry of the crystal.

Z_+ & Z_- = magnitude of charges

e = electronic charge= $1.602 \times 10^{-19} \text{ C}$

ϵ_0 = permittivity of free space = $8.854 \times 10^{-12} \text{ C}^2\text{m}^{-1}\text{J}^{-1}$

r_0 = inter-ionic distance (in metre)

n = Born Exponent

Sl no.	Formula of the compound	Madelung constant(A)	Z_+	Z_-
1	NaCl	1.7475	1	1
2	CsCl	1.7627	1	1
3	ZnS	1.6381	2	2
4	CaF ₂	2.5194	2	1

Q.6. NH_4F crystallizes in Wurzite structure (Madelung constant=1.641 and Born exponent=8) in which the closest distance between NH_4^+ and F^- ion is 2.63 \AA . Calculate the lattice energy of NH_4F .

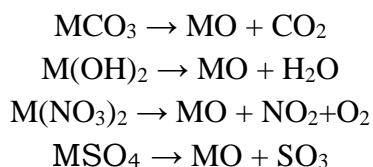
3. Application Of Lattice Energy :

1. Prediction of stability:

Higher the lattice energy, higher will be the electrostatic attraction melting and greater will be the melting and boiling points of ionic compounds.

2. Prediction of thermal stability:

The general equation for thermal dissociation of some typical bivalent carbonates , hydroxides , nitrates , sulphates are given below-



It is seen that in all cases metal oxide is produced as a product. Higher the lattice energy of the product metal oxide, more favored will be the thermal dissociation of the parent compound (carbonates, hydroxides , nitrates , sulphates etc) and lower will be the thermal stability of the parent compound.

It can be mentioned that-lower the thermal stability of parent compound, lower will be its dissociation temperature.

Example : order of thermal stability runs as : $\text{BeCO}_3 < \text{MgCO}_3 < \text{CaCO}_3 < \text{SrCO}_3 < \text{BaCO}_3$

3. Prediction of solubility:

Condition for solubility of an ionic salt in water is : $|\text{Lattice Energy}| \ll |\text{Hydration energy}|$

It has been seen that for a typical MX type of salt :

$$\text{Lattice energy, } U = \frac{K}{r_+ + r_-}$$

$$\text{And hydration energy, } \Delta H_{\text{hyd}} = \frac{k_1}{r_+} + \frac{k_2}{r_-}$$

Where, K, k_1, k_2 are constants and r_+ and r_- represents the radius(size) of cation and anion respectively.

Case-1 : if $r_+ \ll r_-$, then $U = K / r_-$ and $\Delta H_{\text{hyd}} = k_1 / r_+$

In this case, solubility increases with increasing hydration energy of the cation.

Example : $\text{LiClO}_4 > \text{NaClO}_4 > \text{KClO}_4$ (here, the size of ClO_4^- ion is very large)

Case -2 : if $r_+ \gg r_-$, then $U = K / r_+$ and $\Delta H_{\text{hyd}} = k_2 / r_-$

In this case, solubility increases with decreasing lattice energy of the salt.

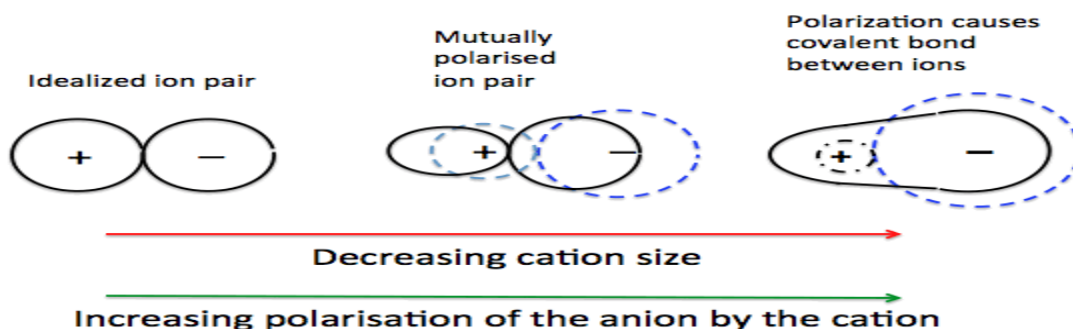
Example : $\text{LiF} < \text{NaF} < \text{KF}$ (here the size of F^- ion is very small)

Polarization: Covalent character in ionic compounds

No chemical bond is 100% ionic or 100% covalent. There is always some covalent character associated in an ionic bond. The extent of covalent nature in an ionic bond is measured by polarization or deformation of ions. The extent of ionic nature in a covalent bond is measured by dipole moment. Here it can be mentioned that incorporation of covalent nature causes many changes in an ionic compound. With increase in covalent character in an ionic compound-

1. The melting and boiling point decreases.
2. The solubility in water or polar solvent decreases.
3. The solubility in non-polar or covalent organic solvents(e.g. kerosene, carbon tetrachloride etc.) increases.
4. The thermal stability decreases.

Cause for polarization :



Fajan's rules :

When a cation approaches an anion, the electron cloud of the anion gets attracted to the cation and gets distorted. This effect is called polarization of the anion. The power of the cation to polarize the anion is called its polarizing power and the tendency of an anion to get polarized is called its polarisability. Greater is the extent of polarization, better will be mutual charge neutralization and higher will be covalent character.

According to Fajan, the extent of polarization (and covalent character) is favoured by:

1. Small size of the cation.
2. Large size of the anion.
3. High magnitude of charge on either cation or anion.
4. Electronic configuration of cation : If two cations have same charge and similar size, then the cation with pseudo-inert electronic configuration (with 18 electron in outermost shell) or with higher number of d-electron will have higher polarizing power.

Example :

1. LiCl is more covalent than KCl (size of $\text{Li}^+ < \text{K}^+$)
2. Order of melting point runs as : $\text{LiF} < \text{LiCl} < \text{LiBr} < \text{LiI}$ (higher polarization, lower melting point)
3. Order of covalent character : $\text{NaCl} < \text{MgCl}_2 < \text{AlCl}_3$
4. CuCl is more covalent than KCl (Cu^+ has $3d^{10}$ configuration, higher polarizing power)
5. The order of solubility in water runs as : $\text{AgF} < \text{AgCl} < \text{AgBr} < \text{AgI}$ (higher polarizability, lower solubility in water)