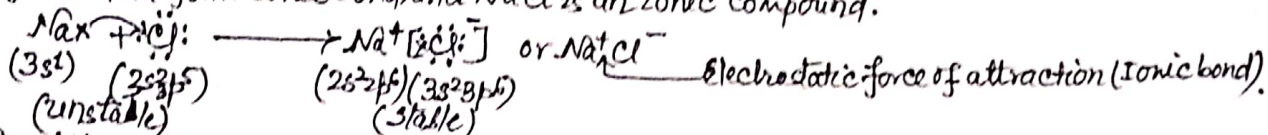


→ Ionic bond:

The chemical bond formed between two elements/atoms by complete transfer of one or more electron(s) from one atom to another is called ionic bond. According to Kassel, when an electro-positive element combines with an electronegative element, one or more electron(s) transferred from the former to the latter, forming cation and anion respectively. As a result of mutual electrostatic attraction between two oppositely charged ions, an ionic bond is formed.

e.g. Na & Cl form ionic bond, and NaCl is an ionic compound.



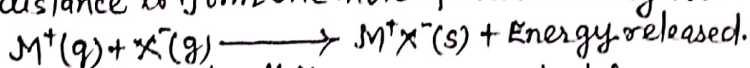
Conditions/Factors for the formation of Ionic bond/Compd. →

- (i) One atom (say A) should have a tendency to loss electron(s) readily, i.e., Ionisation energy of element (A) should be low. Thus, element (A) should be high electropositive such as Gr. 1 & 2 metal.
- (ii) Other atom (say B) should have a tendency to accept the electron readily given out by A, i.e., Electron affinity of B should be large. Thus, atom B should be high electronegative such as Gr. 16 & 17.
- (iii) Higher the value of lattice energy (U) of the resulting ionic compound (A⁺B⁻), the greater is the ease of its formation. The value of U increases if high charges on ions & ionic radii are small.

Characteristics of Ionic Compounds: (i) They are solids, hard and lattice structure.

- (ii) These compounds are polar, soluble in polar solvents, e.g. H₂O (water), liq. NH₃ etc. but insoluble in non-polar solvents, e.g. Carbon tetrachloride (CCl₄), benzene (C₆H₆) etc.
- (iii) They are good conductor of electricity in fused state and solution since they ionise in these states.
- (iv) They possess generally high melting and boiling points.
- (v) They are non-directional, since polar linkage present in them.
- (vi) They react spontaneously in few steps and by simple ionic mechanism.

⇒ Lattice energy: Lattice energy of an ionic crystal can be defined as "the energy released, when the correct number of gaseous cation (M⁺) and anion (X⁻) are brought from an infinite distance to form one mole of the ionic crystal."



It may also be defined as "the energy required to remove ions of 1 mole of a solid ionic crystal from their equilibrium position in the crystal to infinity."



It is denoted by symbol 'U' and expressed in kcal/mole or KJ/mole.

It follows that greater the value of lattice energy, more stable the ionic compd./crystal.

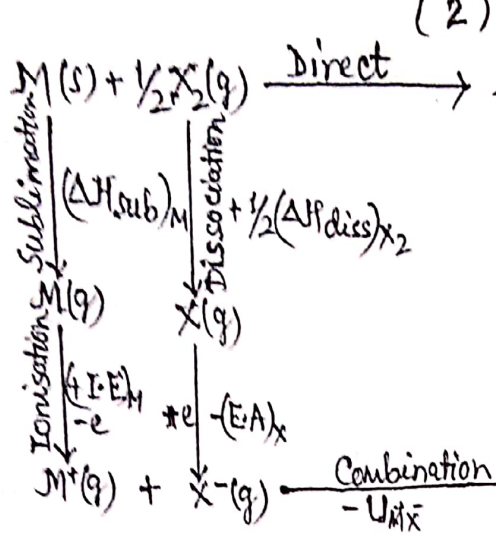
It is theoretically calculated by Born-Landé equation, $U = \frac{NAe^2 z^+ z^-}{r_0} \left(1 - \frac{1}{n}\right)$ - (1)

(where N = Avogadro No. (6.023 × 10²³), e = electronic charge (4.8 × 10⁻¹⁰ e.s.u))

z⁺, z⁻ = Charge on the cation & anion respectively, r₀ = equilibrium distance or inter nuclear distance, A = Madelung constant (z⁺/z⁻), which depends upon geometry of crystal lattice, n = Born constant or Born exponent (≈ 10)

⇒ Experimental determination of Lattice energy / Born-Haber Cycle:

The lattice energy of an ionic crystal (M⁺X⁻) can be experimentally determined by a cyclic process, which was devised by Born-Haber, known as Born-Haber cycle. This is based on assumption that one mole of a crystalline solid (M⁺X⁻) can be formed by direct combination or by alternative process which consists of five steps shown below:



Since the two processes are independent to each other, by Hess's law the heat of formation of M^+X^- ($\Delta H_{\text{form}}^{\text{direct}}$) must be equal to the summation of all other energy terms (indirect process). Thus,

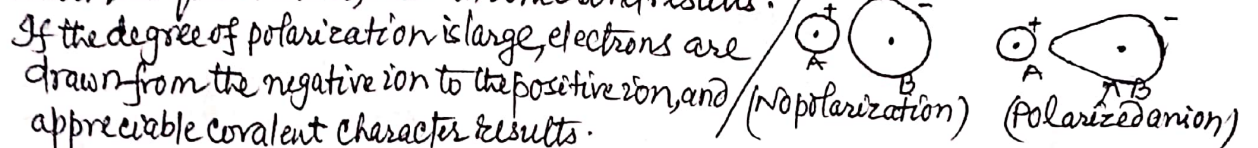
$$(\Delta H_{\text{form}})_{M^+X^-} = (\Delta H_{\text{sub}})_M + \frac{1}{2}(\Delta H_{\text{diss}})_{X_2} + (I.E)_M - (E.A)_X + U_{M^+X^-}$$

Or, $U_{M^+X^-} = (\Delta H_{\text{form}})_{M^+X^-} - (\Delta H_{\text{sub}})_M - \frac{1}{2}(\Delta H_{\text{diss}})_{X_2} - (I.E)_M + (E.A)_X$ (2)

Applications of lattice energy:

- Lattice energy is used (i) to estimate/calculate EA (electron affinity) and heat of formation of ionic compds.
 (ii) in the account of stabilities of metal hydrides, polyhalides, peroxides and super oxides.
 (iii) in the derivation of crystal field stabilization energy (CFSE).
 (iv) in the discussion of the special properties of F_2 in relation to other halogens.

\Rightarrow Fajan's rule or polarizability: If the two ions A^+ & B^- are brought together to their equilibrium distance, the type of bond between them depends upon the effect of one ion on the other. The positive charged ion attracts the electrons on the negative ion and repels the nucleus, thus distorting or polarizing the negative ion. If the polarization is quite small, then an ionic bond results.



The extent of ion distortion depends on both the power of an ion to distort the other, i.e., its polarizing power, and its susceptibility to distortion, i.e., its polarizability. The magnitude of polarization depends upon a number of factors on the increased covalent character is favoured by a number of factors, suggested by Fajan, and are known as Fajan's rule.

- (i) Charge on cation: As the charge on the cation increases, its tendency to polarize the anion increases, which brings more covalent nature in ionic compounds. For example, In $NaCl$, $Mg^{2+}Cl_2$, $Al^{3+}Cl_3$, the polarizing increases thereby covalent character increase, i.e., order of covalent nature: $NaCl < Mg^{2+}Cl_2 < Al^{3+}Cl_3$.
- (ii) Size of the cation: Polarization of an anion increases as the size of cation decreases, i.e., ionic compds having smaller cations show more covalent nature. For example, Covalent character of Gr. 2 halides decreases in order: $BeCl_2 > MgCl_2 > CaCl_2$.
- (iii) Size of anion: The larger the size of the anion, more easily it will be polarized by the cation, i.e., as the size of the anion increases for a given cation, the covalent character increases. For example, Order of covalent character of calcium halides: $CaF_2 < CaCl_2 < CaBr_2 < CaI_2$, since order of size of halide ions: $F^- < Cl^- < Br^- < I^-$. Hence, ionic compound having higher charged, smaller cation or larger anion tends to covalent nature/compound.

\Rightarrow Inert Pair effect: Some of the heavier elements of p-block, i.e., Gr 3, 4, 5 & 6 having 3 to 6 electrons in their valence orbit are expected to show group number oxidation states (+3 to +6) by losing all the valence electrons ($ns^2 np^x$). But quite often they don't lose all those electrons, i.e., np^x electrons only and hence form cations with

Lower oxidation states (+1 to +4) as well. In the formation of lower oxidation states/valencies, the pair of ns electrons does not participate in bonding, i.e., reluctance of ns electrons

"The reluctance of the ns electron pair to take part in bond formation or valency is known as inert pair effect". In this way electrons involved in the inert pair effect are only ns-electrons since s-orbital accommodate only two electrons, the presence of a pair of s electrons results stable structure. For examples Tl, Sn, Pb, As, Sb etc. exhibit variable oxidation states/valencies due to inert pair effect. Tl₈₁: $6s^2 6p^1$ shows oxidation states, 0, state +1 is due to reluctance of $6s^2$ electrons. Sn₅₀: $5s^2 5p^2$, shows oxidation state: +2, +4; As₃₃: $4s^2 4p^3$ shows oxidation states: +3, +5. (Tl, Pb, Bi, Po)

Inert pair effect is more pronounced in last members of respective groups (Gr. 3, 4, 5, 6).

Text Questions

Q.1. Arrange the following with proper explanation:

- LiCl, LiBr & LiI in the decreasing order of their covalent character
- N, P, As, Sb & Bi in the increasing order of stability of O state +5.
- NaCl, MgCl₂ & AlCl₃ in the increasing order of their melting points
- LiCl, NaCl & KCl in increasing solubility in alcohol

Ans. (i) LiI > LiBr > LiCl, since size of anion decrease from I to Cl - (Fajan's rule).

(ii) N < Bi < Sb < As < P, since inert pair effect increase with the increase of atomic mass. N has no d-orbital for unpairing electrons.

(iii) AlCl₃ < MgCl₂ < NaCl, since charge on cation decreases and covalent character or polarizing power increase.

(iv) KCl < NaCl < LiCl, since covalent character increase as size of their cations decrease, so solubility in organic solvent (alcohol) increases.

Q.2. Explain: (i) MgO has higher melting point than NaCl.

(ii) AlCl₃ is largely covalent while AlF₃ is largely ionic

(iii) BeCl₂ shows a high degree of covalency in its reactions whereas BaCl₂ is predominantly ionic

(iv) Sn⁴⁺ is more stable than Pb⁴⁺ but Pb²⁺ is more stable than Sn²⁺.

Ans. (i) Lattice energy of MgO is very high, so it requires more energy to break Mg²⁺O²⁻ linkage in comparison to Na⁺Cl⁻ linkage. Hence, melting point of MgO is higher than NaCl.

(ii) Size of F⁻ is less than Cl⁻, so more polarisation in AlCl₃ than AlF₃. According to Fajan's rule larger the size of anion, higher the covalent nature. Hence, AlCl₃ is largely covalent while AlF₃ is largely ionic.

(iii) Size of Be²⁺ is smaller in comparison to Cl⁻, so distortion occurs and degree of covalency increases. The reverse situation exists in case of BaCl₂ (i.e., size of Ba²⁺ is larger than Cl⁻) Hence, BeCl₂ shows high degree of covalency in its reactions, whereas BaCl₂ ionic nature.

(iv) Inert pair effect is more marked in the heavier elements. Thus, the pair of s-electron is more inert/reluctant in lead (Pb₈₂) than in tin (Sn₅₀). As a result of this there is less tendency for the formation of Pb⁴⁺ ion than for the formation of Sn⁴⁺ ion, i.e., Sn⁴⁺ is more stable than Pb⁴⁺ but Pb²⁺ is more stable than Sn²⁺.

Sn₅₀: $5s^2 5p^2$; Pb₈₂: $6s^2 6p^2$.

→ 0 ← more reluctant/inert to lose forming O state +4.