

4.10. Polarisation of Ions

When two oppositely charged ions approach each other, the cation tends to attract the electrons of the anions and repels the positively charged nuclei of the anion. The combined effect of these two forces is that the anion is distorted or **polarised**. This is known as **polarising effect**. The ability of a cation to polarise anion is called **polarisation ability** or polarisation power [Fig. 4.12].

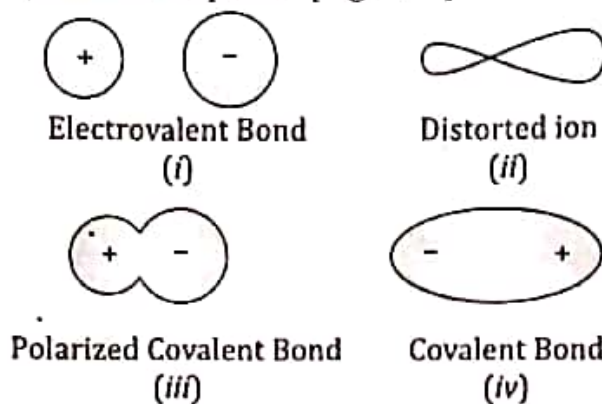


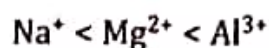
Fig. 4.12. Transition between Ionic and Covalent Bonds.

The anion also has a similar effect on the cation. As the size of the cation is generally smaller than the anion, the cation is polarised by the anion to a lesser extent. We say, therefore, that a cation has a strong polarisation power and the anion has more polarisability.

» Factors Affecting Polarisation of Ions - Fajan's Rules.

The factors which affect the polarisation of ions have been given by **Fajan's Rules**. These rules are :

(i) High Charge on the Cation and Anion : The polarising power of a cation to polarise an anion increases with the increase in its positive charge because larger the charge on the cation, greater is the force of attraction between cation and anion. Thus, more is polarisation. For example in NaCl, MgCl₂ and AlCl₃ the polarising power of cations increases in the order

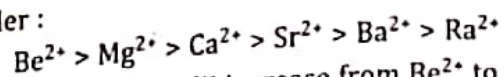


Since the positive charges on these cations also increase in the same order.

Similarly polarisability of anion also increases with the increase in its negative charge because it will be more attracted towards cation *e.g.*, oxide of a metal is more covalent than its fluoride.

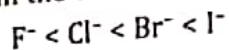
(ii) Small Cation : In small cation the positive charge is concentrated over a small surface and hence a smaller cation has greater polarising effect on the anion. Thus, the polarising power of the cations of IIA sub group elements is

in the order :



because their cationic radii increase from Be^{2+} to Ra^{2+} .

(iii) Large Anion : The polarisability of an anion increases with the increase in its size because in larger anion, the influence of the nucleus on the outer electrons decreases due to shielding effect by inner electrons. Thus the polarisability of the halide ions is in the order :



Hence CaI_2 is more covalent than CaF_2 .

(iv) Cations with Non-inert gas Configuration : A cation with 18 electrons in its outermost shell polarises an anion more effectively than a cation with 8 electrons in its outermost shell. It is because ten d-electrons of $ns^2p^6d^{10}$ shell shield the nuclear charge of the cation less effectively than s and p electrons of ns^2p^6 shell. For example AgCl is more covalent than NaCl because Ag^+ ion has 18 electrons in its outermost shell while Na^+ ion has 8 electrons in its outermost shell. Size of Ag^+ and Na^+ ions is almost the same.

The polarising power of a cation is directly proportional to its charge (z) and inversely proportional to its radius (r). It is represented by ϕ (phi) and is called **ionic potential** or **charge density**. i.e.,

$$\text{Polarising power of cation} = \frac{\text{Charge on cation (z)}}{\text{Radius of cation (r)}}$$

or
$$\phi = \frac{z}{r}$$

Applications of the Concept of Polarisation : Following are the important applications of the concept of polarisation of ions :

(1) Covalent Character in Ionic Compound : From equation (4.7) it appears that a cation with high ionic potential (ϕ) will produce greater polarisation and hence greater is the degree of covalent character in its ionic compounds.

(2) The tendency of a cation to form complexes : A cation with high ionic potential has greater tendency to form complexes.

(3) Nature of Oxides : Larger the value of ionic potential for a cation, greater is its polarising power and greater will be covalent character of the metal-oxygen bond.

Cartlidge has suggested that the oxide of a metal is basic when $\sqrt{\phi} < 2.2$, amphoteric when $\sqrt{\phi} = 2.2 - 3.2$ and acidic when $\sqrt{\phi} > 3.2$.

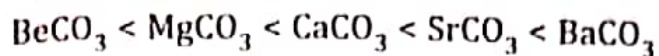
Thus, as the value of $\sqrt{\phi}$ increases, the acidic character of the oxide also increases due to the increase in the covalent character of metal-oxygen bond.

(4) Stability of Compounds : Let us consider MCO_3 type carbonate. The greater the value of ϕ for the cation, greater will be its polarising power and greater will be the covalent character of the metal-oxygen bond. Thus, the metal carbonate gets decomposed into CO_2 and the oxide of the

metal. Greater the value of ϕ for a cation, the lesser is the stability of the carbonate.



For IIA sub-group cations, the value of ϕ decreases from Be^{2+} to Ba^{2+} and hence the thermal stability of their carbonates increases in the order :



The thermal stability of MSO_4 , $M(OH)_2$ etc. can also be explained on the above basis.



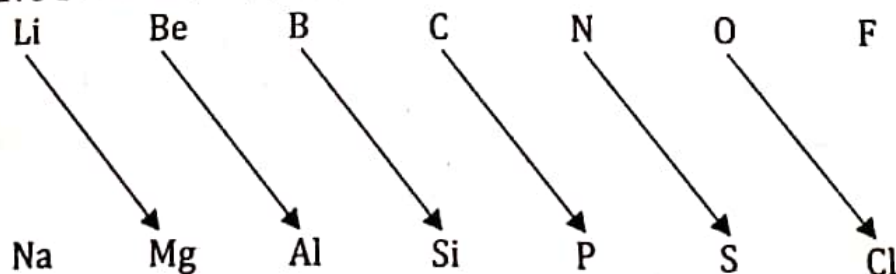
(5) Nature of Halides : It has been observed that if the value of $\sqrt{\phi}$ for cation in halide is less than 2.2, the halide will be ionic and good conductor of electricity. On the other hand, if $\sqrt{\phi}$ is more than 2.2, the halide will be covalent and non-conductor of electricity.

(6) Solubility of Salts : The solubility of the salts decreases with the increase of polarisation e.g. S^{2-} ion is more polarised by cation than O^{2-} ion since S^{2-} ion is bigger than O^{2-} ion. Hence sulphides are less soluble than the oxides of the same metal.

(7) Melting Points : Since covalent character increases with increase in polarisation and this decreases the melting points of the compounds.

(8) Tendency of Cation for Solvation : The larger the value of ϕ for a cation, greater is its tendency for solvation e.g. Li has highest tendency for solvation due to maximum value of ϕ . The degree of solvation decreases from Li^+ to Cs^+ .

(9) Diagonal Relationship : The diagonal relationships have been shown below :



Diagonally related elements form ions with the same case. These elements have almost similar properties.

(10) Strength of Hydracids : The acidic character increases as we go down the group. For example H_2S is stronger acid than H_2O due to the larger size of S^{2-} ion. Similarly the acidic character of halogen acids increases in the following order :

