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Chapter 4 Chemical Bonding

Fajan's Rule

- None of the hetero-atomic bond of nature is completely ionic (electrovalent) or completely covalent in nature.
- In general, ionic compounds acquire covalent character and covalent compounds acquire ionic character. For example,

Na^+Cl^-	$H \overset{\delta^+}{\rightarrow} Cl^{\delta^-}$
Ionic compound with covalent character	Covalent compound with ionic character

- Fajan's rule is useful in deciding the extent of covalent character in ionic compounds.

Terminology-

(1) Polarising power of cation- The power of cation to polarise anion.

(2) Polarisability of anion- The ease to which an anion gets polarised.

(3) Ionic Potential- The ratio of the charge on cation and its ionic radius. It decides polarising power of cation. The greater the ionic potential of cation, more is its polarising power.

Cation Polarisation of Anion by Cation

Fig.- Fajan's rule

(1) Small size of Cation
(2) High Charge density on Cation (More No. of Charge on Cation) → More Polarising Power of Cation
(3) Large size of Anion
(4) More No. of Charge on Anion → More Polarisability of Anion

→ More Polarisation of Anion by Cation → More Covalent Character in compound

- The ion having pseudo inert gas configuration i.e. 18 electrons in their outermost shell such as Cu^+\{[Ar],$3d^{10}$\}, Ag^+ \{[Kr],$4d^{10}$\}, Au^+ \{[Xe],$5d^{10}$\} etc. have more polarising power due to insufficient screening effect of the electrons of relatively more diffused d-orbitals as compared to those having real inert gas configuration i.e. 8 electrons in their outermost shell such as Na^+\{[Ne]\}, Mg^{2+}\{[Ne]\}, Ca^{2+}\{[Ar]\} etc. and therefore, their compounds have relatively more covalent character.

Examples-

(1) Order of covalent character in LiCl, NaCl, KCl –

$$LiCl > NaCl > KCl$$

Here, all the compounds have same anion i.e. chloride ion. Hence, extent of covalent character in different compounds will be decided by relative polarising power or ionic potential of their cations, which follows following order-

$$Li^+ > Na^+ > K^+$$

(2) Order of covalent character in LiCl, $BeCl_2$, BCl_3 –

$$LiCl < BeCl_2 < BCl_3$$

Here also, all the compounds have same anion i.e. chloride ion. Hence, extent of covalent character in different compounds will be decided by relative polarising power or ionic potential of their cations, which follows following order-

$$Li^+ < Be^{2+} < B^{3+}$$

(3) Order of covalent character in NaCl, $MgCl_2$, $AlCl_3$ –

$$NaCl < MgCl_2 < AlCl_3$$

Here also, all the compounds have same anion i.e. chloride ion. Hence, extent of covalent character in different compounds will be decided by relative polarising power or ionic potential of their cations, which follows following order-

$$Na^+ < Mg^{2+} < Al^{3+}$$

(4) Order of covalent character in LiF, Li_2O, Li_3N-

$$LiF < Li_2O < Li_3N$$

Here also, all the compounds have same cation i.e. Li^+ ion. Hence, extent of covalent character in different compounds will be decided by relative polarisability of their anions, which follows following order-

$$F^- < O^{2-} < N^{3-}$$

(5) Order of covalent character in Li_2O, Na_2O, Cu_2O

$$Na_2O < Li_2O < Cu_2O$$

Here also, all the compounds have same anion i.e. oxide ion. Hence, extent of covalent character in different compounds will be decided by relative polarising power or ionic potential of their cations, which follows following order-

$$Na^+ < Li^+ < Cu^+$$

- Here, Cu^+ {[Ar],$3d^{10}$}ion having pseudo inert gas configuration i.e. 18 electrons in their outermost shell has the highest polarising power amongst three ions and therefore, its compound has the highest covalent character.
- Amongst, Li^+ and Na^+ ions, Li^+ ion having the smaller ionic size has more polarising power and therefore, its compound has more covalent character.