E-Content Study Material

B. Sc. Chemistry (H)

1st Year

Paper I B

Inorganic Chemistry

Chapter III: Chemical Bonding

Topic: Polarizing Power and Polarisability of ions (Fajan's Rule)

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Polarizing Power and Polarisability of ions (Fajan's Rule)

Covalent Character of Ionic Bonds (Fajan's Rules)

It is a common experience that many times an ionic bond has some covalent character and a covalent bond has some ionic character. The formation of a bond intermediate between an ionic and a covalent bond occurs through a phenomenon known as polarization of ions. When oppositely charged ions approach each other, the attraction between the positive charge of cation and negative charge of anion and also the simultaneous repulsion between their nuclei and between their electrons results in the distortion, deformation or polarization of the electron charge cloud of the anion. The electron charge cloud of the anion no longer remains spherical but gets distorted, i,e. polarised towards the cation, as shown in Fig.

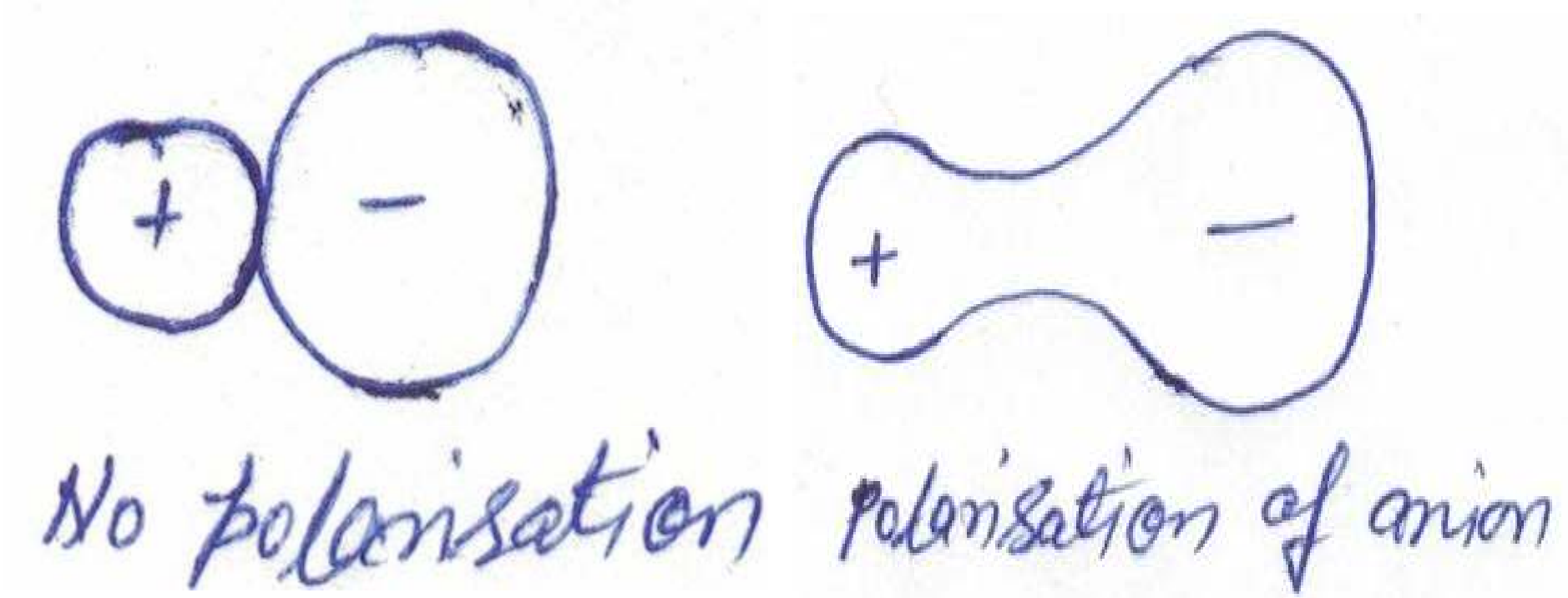

Fig. Polarisation of electron charge cloud of an anion by a cation.

The effect is called polarization of the anion. The power of the cation to polarise the anion is called its polarizing power and the tendency of the anion to get polarized is called its polarisability. The electron charge cloud of the cation also gets distorted, i.e, polarised by the anion through a similar process but the polarization of the cation is far less pronounced because of its small size. The polarisation of ions results in a high electron charge concentration between the two nuclei. This results in the formation of a bond which is intermediate between an ionic and a covalent bond. This type of bond is called polar covalent bond. A polar covalent bond is more stable than a pure covalent bond. The higher the degree of ionic polarisation, the greater is the stability of the polar covalent bond. The extent of polarization depends, evidently, on the polarising power of the cation and the polarisability of the anion.

The rules regarding polarisation are known as Fajan's rules. These are given below.

1. The cation with smaller size have higher polarising power, i.e, they cause polarization of electron charge cloud of an anion to a greater extent. Such cations have positive charge concentrated over a small surface area, i.e. they have a high charge density and thus distort the electron charge cloud of the anion highly efficiently. The cations with large size have low polarising power. This explains why LiCl is more covalent than KCl.

2. The anions with large size have high polarisability, i.e. their electron charge cloud can be deformed easily. The grip of the nucleus on the orbital electrons in large anions will be weak and hence such anions will get polarised by a cation relatively easily. This explains why covalent character of lithium halides is in the order

$$LiI > LiBr > LiCl > LiF$$

Their melting points are in the order

$$LiI < LiBr < LiCl < LiF$$

$$(446\ ^0C) \quad (547\ ^0C) \quad (613\ ^0C) \quad (870\ ^0C)$$

3. For effective polarisation, there should be a high charge on the cation or the anion or both. The electrostatic forces which cause polarisation, would increase with increase in the charge on the ions. Hence covalent character increases. That is why the covalent character of the chlorides is in the order,

$$Na^{+}Cl^{-} < Mg^{2+}Cl_2 < Al^{3+}Cl_3$$

Similarly, greater the charge on the anion more easily it gets polarized.

4. Cations with pseudo inert gas configuration, $ns^2p^6d^{10}$ or with inert pair configuration, $d^{10}(n+1)s^2$ have high polarizing power while cations with noble gas configuration ns^2p^6 have low polarizing power. This is due to greater effective nuclear charge in the former cases and smaller effective nuclear charge in the latter cases. This explains why Cu^+Cl^- is more covalent than Na^+Cl^-.

Effects of Polarisation.

1. Bromides and iodides have higher lattice energies (and hence higher stabilities) than expected from theoretical calculations. The extra stability is due to polarization of the anions resulting in the formation of a polar covalent bond which is more stable than a pure ionic bond.
2. The solubility of ionic compounds in polar solvents decreases with increase in the degree of polarization, i.e. with increase in the degree of covalent bonding.
3. The hardness of ionic compounds decreases with increase in the degree of polarization, i.e. with increase in the covalent character.