Polarisation of Ions and fajans's Rules.

When a cation, C^+ of an ionic molecule, C^+A^- approaches closely the anion A^-, electron cloud of the anion withdraw towards itself and symmetrical of the electron cloud of the anion gets distorted. Hence, A^- anion is distorted or deform or polarised by C^+ cation. This phenomenon is called distortion or deformation or polarisation of A^- anion by C^+ cation. The cation C^+ is also deformed by the anion A^- but due to smaller size of the cation, its electrons are strongly held by the anion to the nucleus. Hence the cation is not polarised.

The tendency of a cation to polarise a nearby anion is called its polarising power. It is also known as polarising ability. The tendency of an anion to get distorted or polarised by a cation is called its polarisability.

FACTORS AFFECTING THE MAGNITUDE OF POLARISING POWER OF A CATION AND POLARISABILITY OF AN ANION- FAJAN'S RULES.

The following factors affects the magnitude of polarising power of cation and polarisability of an anion. This factors was given by Fajans and hence are called fajans rules.

1. Charge on cation or Anion; → On increasing the number of +ve charge on the cation, then the polarising power is also increase to polarise given nearby anion.

for example,

Molecules : LiCl $BeCl_2$ BCl_3 CCl_4

Cations (2nd period) : Li^{+} Be^{+2} B^{+3} C^{+4}.

+vely charge on cations : $+1 < +2 < +3 < +4$

Polarising power of cations. : $Li^{+} < Be^{+2} < B^{+3} < C^{+4}$

——— Increasing ⟶

On increasing the -vely charge on the anion, then its polarisability will be more to polarised of cation for example,

Molecules : CH_4 NH_3 H_2O HF
Anion (2nd Period) : C^{4-} N^{-3} O^{-2} F^{-1}
+ve charge on anions : $-4 > -3 > -2 > -1$
Polarisability of anions : $C^{-4} > N^{-3} > O^{-2} > F^{-1}$
——— Decreasing ⟶

Hence, To make a cation to polarise an anion effectively both the +ve charges on the cation and the -ve charges on the anion should be high.

2. Size of the cation and Anion;→ To illustrate these factor, we have to see some examples of cationic molecule and Anionic molecule.

Molecule : $BeCl_2$ $MgCl_2$ $CaCl_2$ $SrCl_2$ $BaCl_2$
cation (Grp- IIA) : Be^{2+} Mg^{2+} Ca^{2+} Sr^{2+} Ba^{2+}
Size of cations (Å) : $0.31 < 0.65 < 0.99$ $1.13 < 1.35$
Polarising power of cations : $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{+2} > Ba^{+2}$
⟶ Decreasing ⟶

Halides : MF MCl MBr MI
Halide ions (Grp- VII A) : F^- Cl^- Br^- I^-
Size of halide ions (Å) : $1.36 < 1.81 < 1.95 < 2.16$
Polarisability of Halide ions : $F^- < Cl^- < Br^- < I^-$
⟶ Increasing ⟶

On above example, we conclude that Smaller is the Size of cation, higher is its polarising power to polarise a given nearby anion, while larger is the size of the anion, then there will be more its polarisability.

4. Electronic configuration of the cation :→ A cation with 18 valence electron shell configuration ($ns^2p^6d^{10}$) has greater polarising power than that with 8 electron valence shell configuration (ns^2p^6). for example, Ag^+ cation ($4s^2p^6d^{10}$) has greater polarising power than K^+ cation ($3s^2p^6$)

PERIODIC TRENDS OF POLARISING POWER OF CATION.

⇒ In going from left to right in period, the size of the cations decreases and +ve charge increases. Both these factor increase the polarising power of the cation, on moving from left to right.

While, On moving down a group, the size of the cation increases and hence polarising power of the cations goes on decreasing.

PERIODIC TRENDS OF POLARISABILITY OF ANIONS

⇒ On going from left to right in a period, both the -ve charges on the anion and their size decreases which both leads the decreases the polarisability ~~of~~ of the anions.

While On moving down a group, the size of anions increases and hence the polarisability of the anions also goes on increasing.

APPLICATIONS OF POLARISATION OF IONS :

FAJAN'S RULES

The process of polarisation produce some amount of covalent character in the ionic bond. The magnitude of covalent character produces due to polarisation effect depends on the amount of polarisation produced in the anion by the cation. Hence

Greater the magnitude of polarising power of a cation or polarisability of an anion, greater the amount of covalent character produces in the ionic bond. The condition which bring about the maximum polarisation of anions by given cation. Theses conditions are called FAJAN'S Rules. These conditions are mentioned below:—

1. Charge either on cation or on anion should be large.
2. Size of the cation should be small.
3. Size of the anion should be large.
4. Cation should have 18 electrons valence shell configuration ($ns^2p^6d^{10}$)