S-14: Polarizability, Explanation based on Fajan's rule

Dt. 17/11/2021

Distortion or polarization

When a cation approaches an anion closely, then

- the net positive charge on cation tends to attract the electron cloud of the anion towards itself
- Also, it tends to repel the positively charged nucleus of the anion

- The net effect is that the electron cloud of the anion no longer remains symmetrical, but elongated towards cation. This is called **distortion, deformation or polarization** of the anion by the cation.

- The anion is said to be polarized.

- The ability of a cation to polarize a nearby anion is called its polarization power.

Polarizability

The unevenly distribution of charge over an anion and distortion of electro density in the presence of a cation is referred to as polarization.

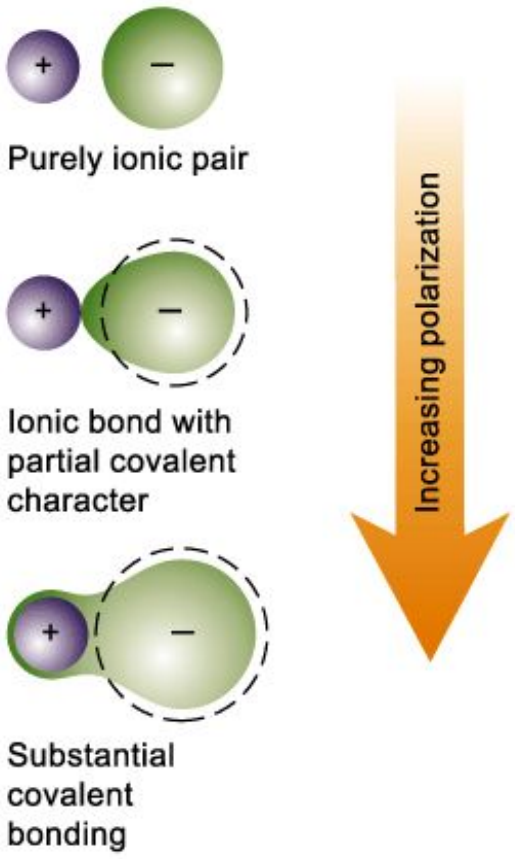
Factors affecting the polarization of anion

i) Polarizing power of cation

The polarizing power of cation depends on its **size and charge**

- **Smaller the size of cation, higher is the polarizing power of cation**
- **Higher the charge on cation, higher is the polarizing power of cation**

Covalent nature α polarizing power



(ii) Polarizability of anion

The ease with which an anion undergoes polarization

The polarization of anion depends on its **size and charge**

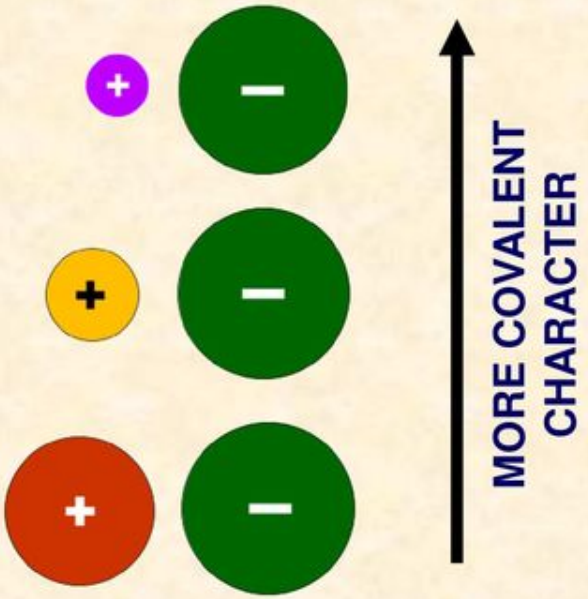
- Larger the size of anion, higher is the polarizability of anion
- Higher the charge on anion, higher is the polarizability of anion

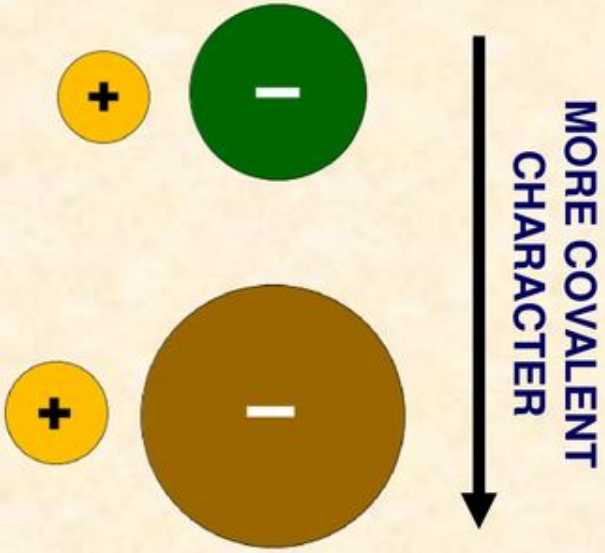
- Size ↑ polarizability ↑ covalent nature ↑
- Charge ↑ polarizability ↑ covalent nature ↑

FAJAN'S RULES

A COMPOUND IS MORE LIKELY TO HAVE SOME COVALENT CHARACTER IF...

- THE CATION IS SMALL AND/OR HAS A HIGH CHARGE - HIGHLY POLARISING
- THE ANION IS LARGE AND/OR HAS A HIGH CHARGE - HIGHLY POLARISABLE





Fajan's rules

Rule-1: Smaller the cation or larger the anion, greater is the covalent nature

Ex: Covalent character of Metal halides

Cation size: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

Covalent nature: LiX> NaX> KX > RbX > CsX

Anion size: $F^- < Cl^- < Br^- < I^-$

Covalent nature: MF < MCl < MBr < MI

Fajan's rules

Rule-2: Greater the charge on either cation or anion, greater is the covalent nature

Charge on the cation:

$Na^{+} < Mg^{2+} < Al^{3+} < Si4+$

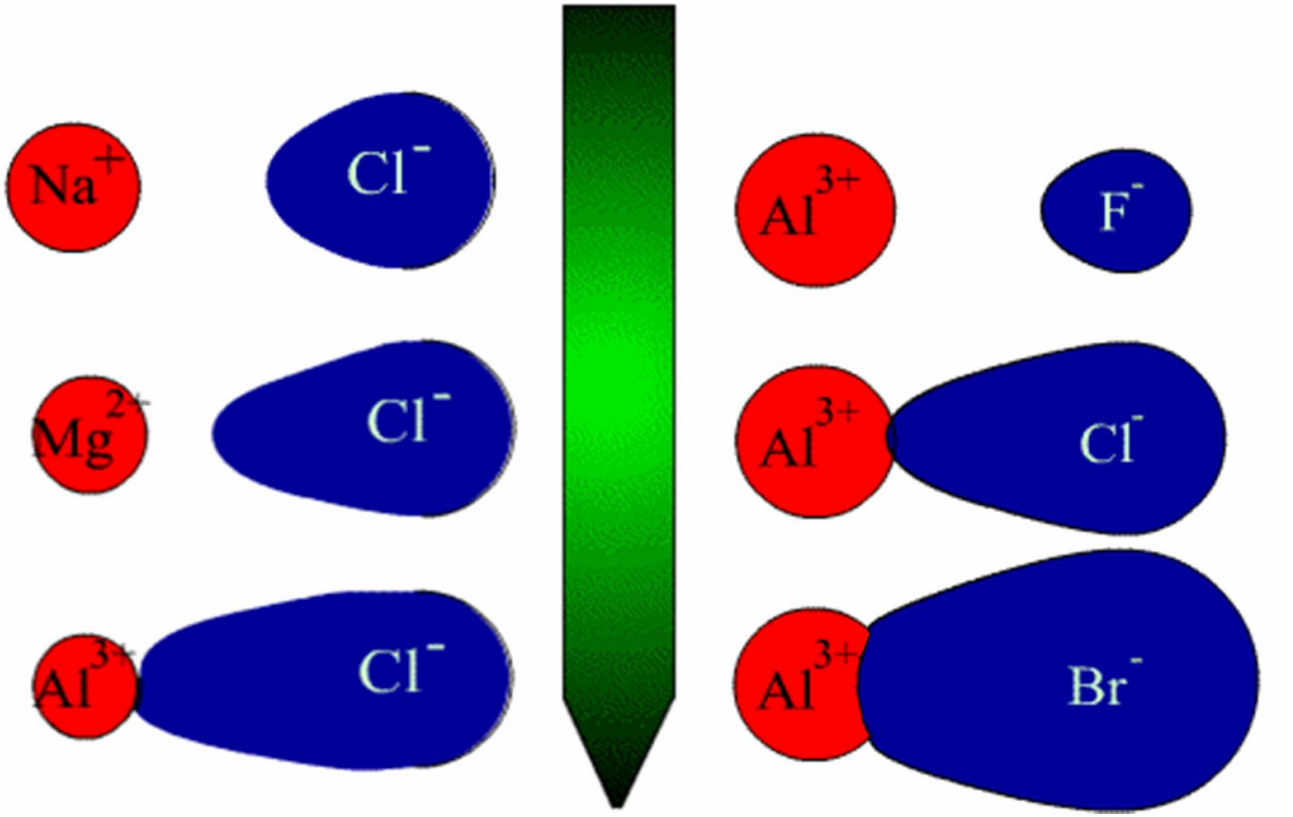
Covalent nature:

$NaCl < MgCl_2 < AlCl_3 < SiCl_4$

Charge : $Al^{3+} > Mg^{2+} > Na^{+}$

$\frac{\text{Charge}}{\text{Size}}$: $Al^{3+} > Mg^{2+} > Na^{+}$

Polarizing power : $Al^{3+} > Mg^{2+} > Na^{+}$



Fajan's rules

Rule-3:

Cation with octet configuration: Less covalent or greater ionic nature

$ns^2\ np^6$: Effective nuclear charge is properly shielded by inner s and p- electrons
Thus, less polarizing power and hence compounds are less covalent

Cation with pseudo-octet configuration: Greater covalent nature

$(n-1)d^{10}\ ns^2$: Effective nuclear charge is not properly shielded by inner d-electrons

Hence more polarizing power and compounds are more covalent

Fajans' rules – A summary

Ionic	Covalent
Low charge on ions	High charge on ions
Large cation	Small cation
Small anion	Large anion
Noble gas configuration	Valence shell electron configuration with incomplete d/f subshell

FAJAN'S RULES

PROOF

Chlorides can be used to demonstrate changes in bond type as the positive charge density increases due to higher charge (across Period 3) or larger size (down Group 1)

		'charge'	ionic rad.		m.pt./°C	solubility	bonding
Period 3	NaCl	1+	0.095nm	GREATER POSITIVE CHARGE DENSITY ↓	808	soluble	ionic
	$MgCl_2$	2+	0.065nm		714	soluble	ionic
	$AlCl_3$	3+	0.050nm		180	hydrolysed	covalent
	$SiCl_4$	4+	0.041nm		-70	hydrolysed	covalent
Group 1	LiCl	1+	0.060nm	GREATER POSITIVE CHARGE DENSITY ↑		soluble	cov. character
	NaCl	1+	0.095nm			soluble	ionic
	KCl	1+	0.133nm			soluble	ionic
	RbCl	1+	0.148nm			soluble	ionic