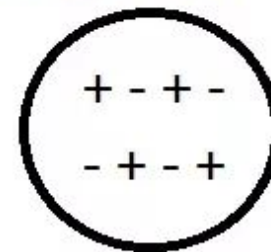


Polarizability and Fajans' Rule

Polarizability

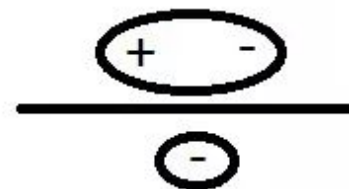
- Polarizability usually refers to the tendency of matter, when subjected to an electric field, to acquire an electric dipole moment which is proportional to that applied field.
- Magnetic polarizability likewise refers to the tendency for a magnetic dipole moment to appear in proportion to an external magnetic field.
- Electric and magnetic polarizabilities determine the dynamical response of a bound system (such as a molecule or crystal) to external fields, and provide insight into a molecule's internal structure.
- "Polarizability" should not be confused with the intrinsic magnetic or electric dipole moment of an atom, molecule, or bulk substance; these do not depend on the presence of an external field.

Neutral Molecule

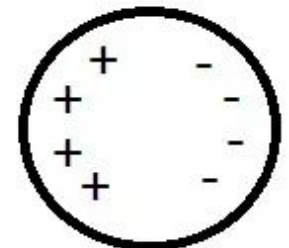


upon introducing
an ion or a dipole:

dipole

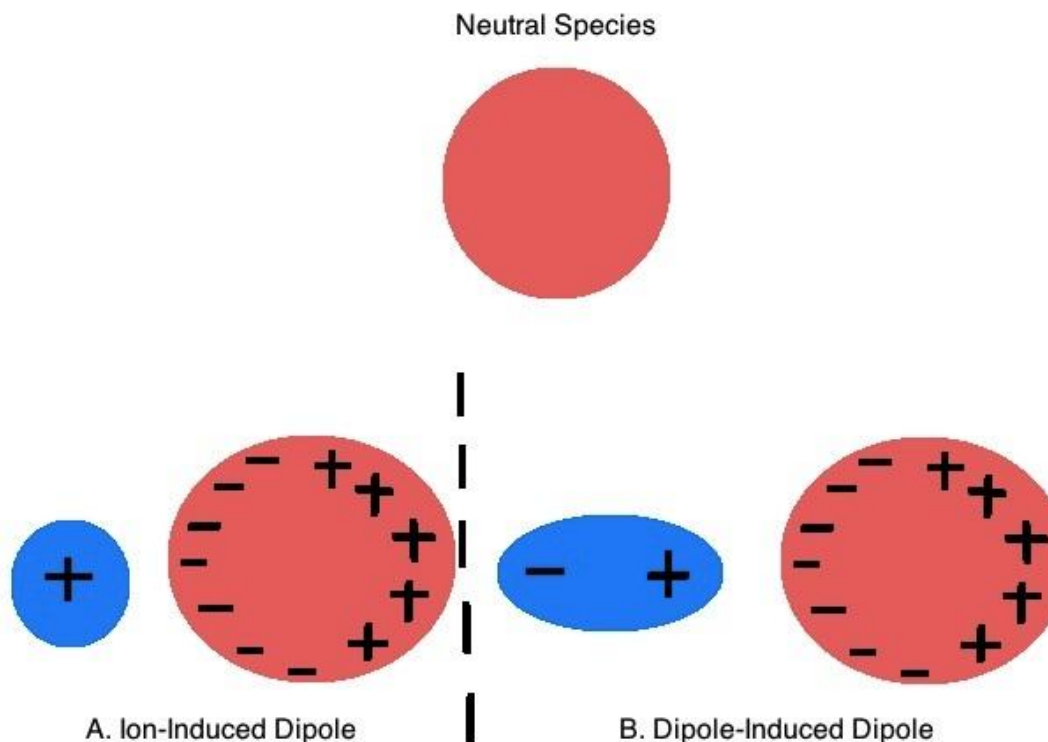
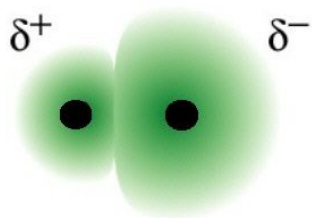


ion



Polarizability

- Neutral nonpolar species have spherically symmetric arrangements of electrons in their electron clouds. When in the presence of an electric field, their electron clouds can be distorted.
- The created distortion of the electron cloud causes the originally nonpolar molecule or atom to acquire a dipole moment. This induced dipole moment is related to the polarizability of the molecule or atom.
- Such distortion due to polarizability within a chemical bond increases covalent character.



Fajans' Rule

- Fajans' rules, (formulated by Kazimierz Fajans) are used to predict whether a chemical bond will be covalent or ionic, and depend on the charge on the cation and the relative sizes of the cation and anion.
- Polarization will be increased by:
 - high charge and small size of the cation
 - **ionic potential** (ionic potential is a measure of the charge to radius ratio = polarizing power)
 - High charge and large size of the anion
 - The polarizability of an anion is related to the deformability of its electron cloud (i.e. its "softness")

Polarizing power is more for smaller cations



Large cations have less Polarizing power

Smaller anions are less polarizable

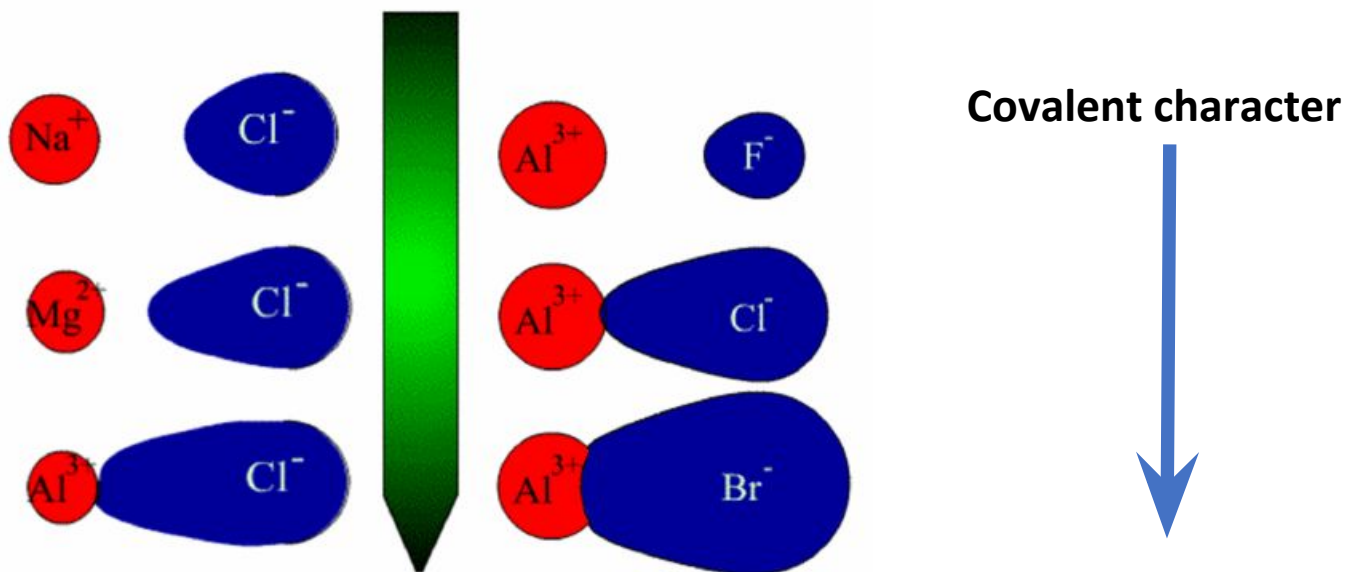


Larger anions are more polarizable



Fajans' Rule

- **Small cation:** the high polarizing power stems from the greater concentration of positive charge on a small area. This explains why LiBr is more covalent than KBr (Li^+ 90 pm, K^+ 152 pm).
 - **Large anion:** the high polarizability stems from the larger size where the outer electrons are more loosely held and can be more easily distorted by the cation. This explains why for the common halides, iodides, are the most covalent in nature (I^- 206 pm).
 - **Large charges:** as the charge on an ion increases, the electrostatic attractions of the cation for the outer electrons of the anion increases, resulting in the degree of covalent bond formation increasing.
-
- **When the cation is the same, larger the size of the anion, higher would be the covalent character.** $\text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI}$
 - **When the anion is the same, the smaller is the size of the cation, the higher is the covalency.** $\text{CsF} < \text{RbF} < \text{KF} < \text{NaF} < \text{LiF}$



Q. Maximum covalent character is associated with the compound:

- A) NaI B) MgI_2 C) AlCl_3 **D) AlI_3**

Among cations, Al^{3+} has smaller size and greater charge hence it has greater polarizing power. Among anions, iodide (I^-) is larger and hence can be polarized easily. Hence the combination of these two ions i.e. Al^{3+} and I^- results in more covalent nature.

Q. Amongst LiCl , RbCl , BeCl_2 and MgCl_2 the compounds with the greatest and the least ionic character, respectively, are:

- A) LiCl and RbCl
B) RbCl and BeCl_2
 C) RbCl and MgCl_2
 D) MgCl_2 and BeCl_2

Fajans' Rule

- When the cations have octet configuration or inert gas configuration (ns^2np^6) in their outer shells, the effective nuclear charge is properly shielded by the inner s and p electrons. Hence their polarizing power is less than expected. Therefore the ionic compound with these cations has less covalent character.
- Whereas, the nuclear attraction is not properly shielded when there are electrons in the d-sub-level. Therefore the cations with pseudo-octet configuration i.e. $ns^2np^6nd^{10}$ possess high polarizing power. Therefore the main group metal compounds are more ionic while the transition metal compounds are more covalent.
- For example, CaCl_2 is more ionic due to the inert gas configuration ($3s^23p^6$) in the Ca^{2+} ion. While the ZnCl_2 is more covalent due to pseudo-inert gas configuration in the Zn^{2+} ion ($3s^23p^63d^{10}$).

Q. Even though the crystal radii of both K^+ and Ag^+ are almost same, the melting point of AgCl is only 455°C , while that of KCl is 776°C . The best explanation is:

- A) AgCl has more ionic character than KCl due to greater polarizing power of potassium ion.
- B) KCl has more ionic character than AgCl due to greater polarizing power of potassium ion.
- C) AgCl has more covalent character than KCl due to greater polarizing power of silver ion.**
- D) KCl has more covalent character than AgCl due to greater polarizing power of silver ion.

Thank You!