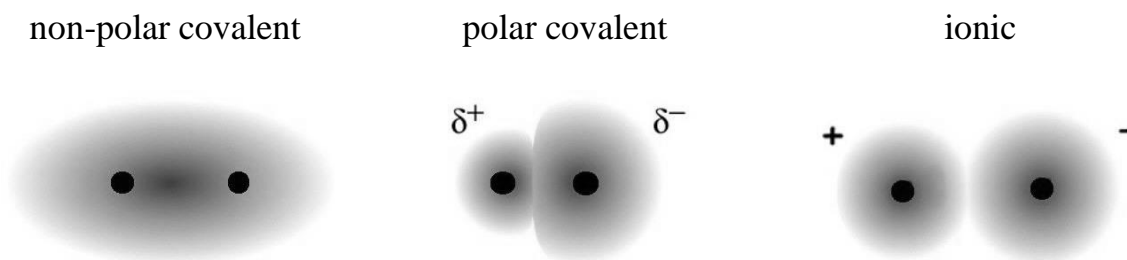


# Fajan's rule

## Fajans' Rules

This rules formulated by Kazimierz Fajans in 1923, can be used to predict whether a chemical bond is expected to be predominantly ionic or covalent, and depend on the relative charges and sizes of the cation and anion. **If two oppositely charged ions are brought together, the nature of the bond between them depends upon the effect of one ion on the other.**



Fajan's rules for predicting whether a bond is predominantly Covalent or Ionic	
Covalent	Ionic
Small cation (< ~100 pm)	Large cation (> ~100 pm)
Large anion	Small anion
High charges	Low charges

Although the bond in a compound like  $X^+Y^-$  may be considered to be 100% ionic, it will always have some degree of covalent character. When two oppositely charged ions ( $X^+$  and  $Y^-$ ) approach each other, the cation **attracts** electrons in the outermost shell of the anion but **repels** the positively charged nucleus. This results in a distortion, deformation or polarization of the anion. If the degree of polarization is quite small, an ionic bond is formed, while if the degree of polarization is large, a covalent bond results.

The ability of a cation to distort an anion is known as its **polarization power** and the tendency of the anion to become polarized by the cation is known as its **polarizability**.

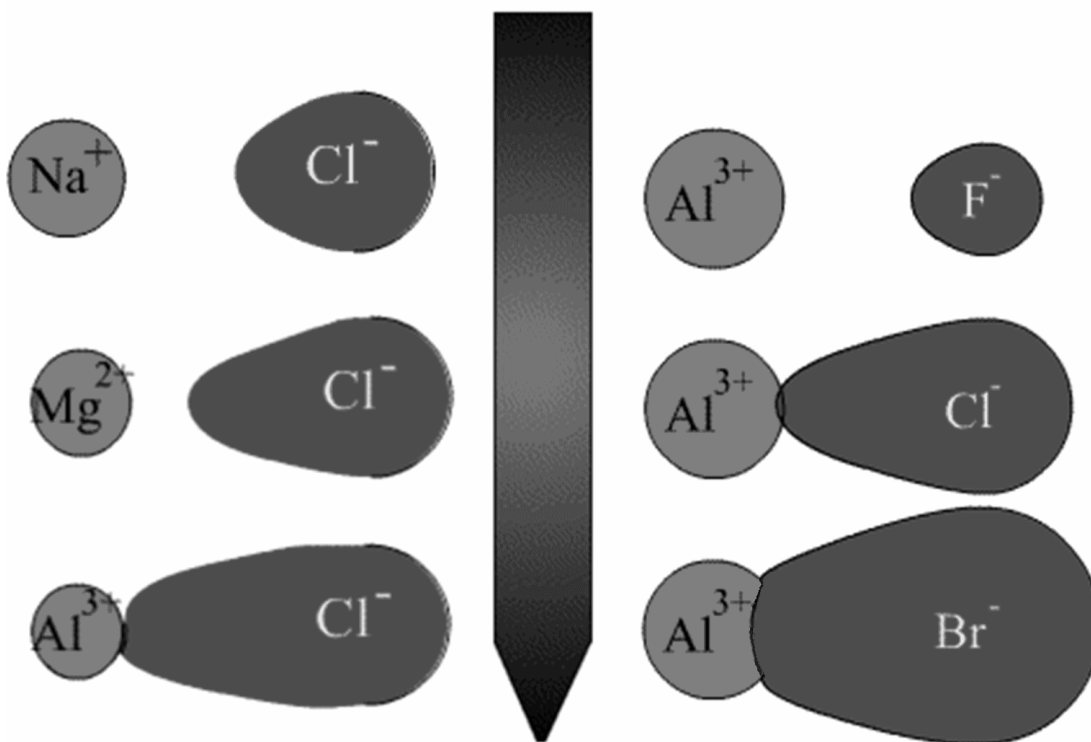
**The polarizing power and polarizability that enhances the formation of covalent bonds is favoured by the following factors:**

**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<sup>+</sup> 90 pm cf. K<sup>+</sup> 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<sup>-</sup> 206 pm).

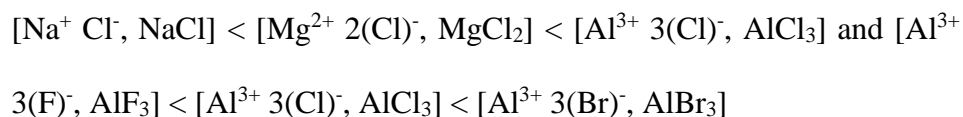
**Large charges:** as the charge on an ion increases, the electrostatic attractions of the cation for the outer electrons of the anion increases, resulting in the degree of covalent bond formation increasing.

**Points to remember:** Large cations are to be found on the bottom left of the periodic table and small anions on the top right. The greater the positive charge, the smaller the cation becomes and the *ionic potential* is a measure of the charge to radius ratio.



On the left, the cation charge increases (size decreases) and on the right, the anion size increases, both variations leading to an increase in the covalency.

Thus covalency increases in the order:



**Electronic configuration of the cation:** for two cations of the same size and charge, the one with a pseudo noble-gas configuration (with 18 electrons in the outer-most shell) will be more polarizing than that with a noble gas configuration (with 8 electrons in the outermost shell). Thus zinc (II) chloride (  $\text{Zn(II)} 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$  and  $\text{Cl}^-$

$1s^2 2s^2 2p^6 3s^2 3p^6$  ) is more covalent than magnesium chloride (  $\text{Mg(II)} 1s^2 2s^2 2p^6$  ) despite the  $\text{Zn}^{2+}$  ion (74 pm) and  $\text{Mg}^{2+}$  ion (72 pm) having similar sizes and charges.

From an MO perspective, the orbital overlap disperses the charge on each ion and so weakens the

electrovalent forces throughout the solid, this can be used to explain the trend seen for the melting points of lithium halides.

LiF = 870 °C, LiCl = 613 °C, LiBr = 547 °C, LiI = 446 °C

It is found that the **greater the possibility of polarization, the lower is the melting point and heat of sublimation and the greater is the solubility in non-polar solvents.**

**Example 1:** The melting point of KCl is higher than that of AgCl though the crystal radii of  $\text{Ag}^+$  and  $\text{K}^+$  ions are almost the same.

➤ When the melting points of two compounds are compared, the one having the lower melting point is assumed to have the smaller degree of ionic character. In this case, both are chlorides, so the anion remains the same. The deciding factor must be the cation. (If the anions were different, then the answer could be affected by the variation of the anion.) Here the significant difference between the cations is in their electronic configurations.  $\text{K}^+ = [\text{Ar}]$  and  $\text{Ag}^+ = [\text{Kr}] 4d^{10}$ . This means a comparison needs to be made between a noble gas core and pseudo noble gas core, which as noted above holds that the pseudo noble gas would be the more polarizing.

## Percentage of ionic character and charge distribution

Based on Fajan's rules, it is expected that every ionic compound will have at least some amount of covalent character. The percentage of ionic character in a compound can be estimated from dipole moments.

The bond dipole moment uses the idea of electric dipole moment to measure the polarity of a chemical bond within a molecule. It occurs whenever there is a separation of positive and negative charges. The bond dipole  $\mu$  is given by:

$$\mu = \delta d$$

A bond dipole is modeled as  $+\delta - \delta^-$  with a distance  $d$  between the partial charges. It is a vector, parallel to the bond axis and by convention points from minus to plus (note that many texts appear to ignore the convention and point from plus to minus). The SI unit for an electric dipole moment is the coulomb-meter, (C m). This is thought to produce values too large to be practical on the molecular scale so bond dipole moments are commonly measured in Debye, represented by the symbol, D.