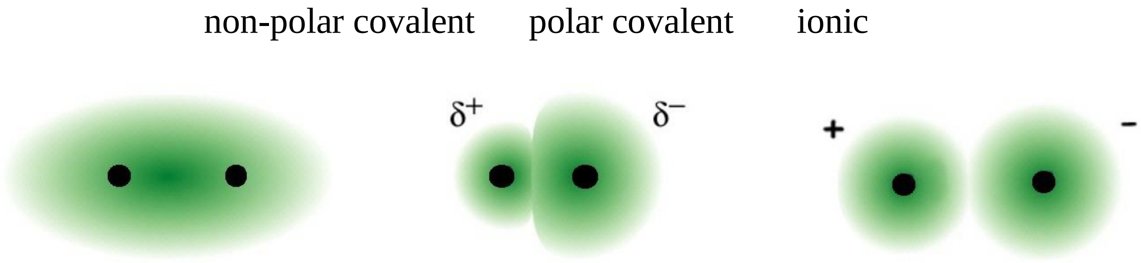
POLARIZABILITY

Having now revised the basics of trends across and down the Periodic Table, we can use the concepts of Effective Nuclear Charge and Electronegativity to discuss the factors that contribute to the types of bonds formed between elements.

Fajans' Rules

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 $\mathbf{X}^+\mathbf{Y}^-$ 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**.

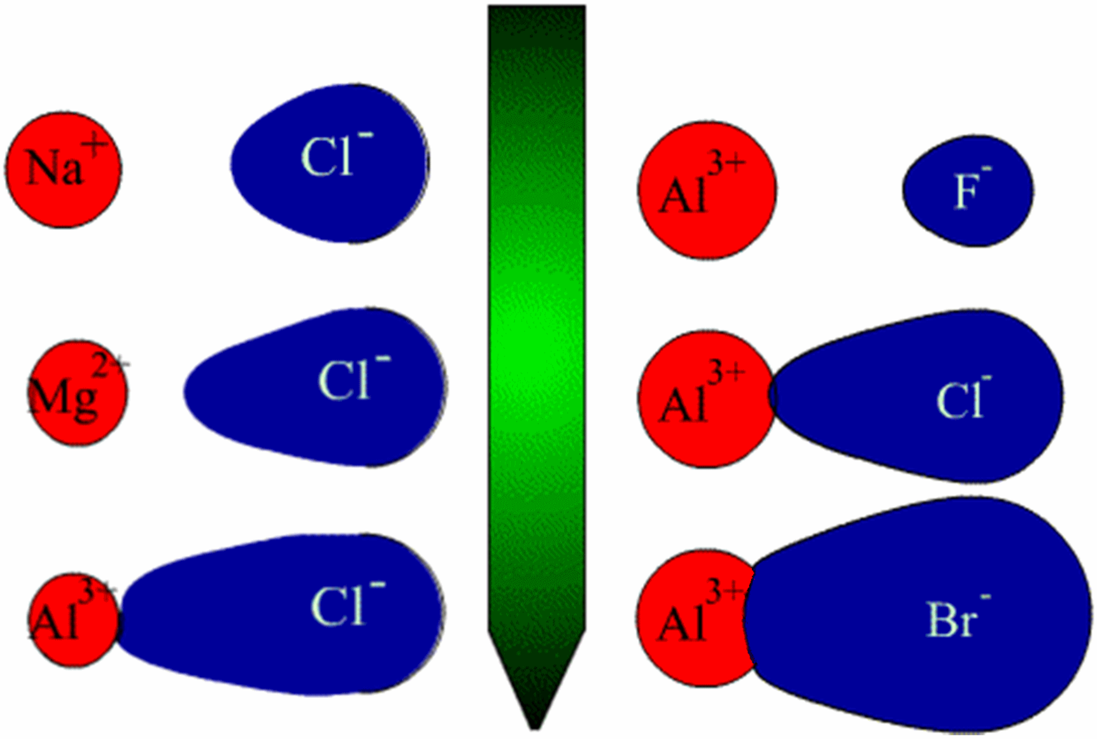
The polarizing power and polarizability that enhances the formation of covalent bonds is favoured by the following factors:

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^+ 90 pm cf. 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.

Reminder. 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:
[Na$^+$ Cl$^-$, NaCl] < [Mg^{2+} 2(Cl)$^-$, MgCl$_2$] < [Al^{3+} 3(Cl)$^-$, AlCl$_3$] and
[Al^{3+} 3(F)$^-$, AlF$_3$] < [Al^{3+} 3(Cl)$^-$, AlCl$_3$] < [Al^{3+} 3(Br)$^-$, AlBr$_3$]

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 (Zn(II) 1s^2 2s^2 2p^6 **3s^2 3p^6 3d**^{10} and Cl$^-$ 1s^2 2s^2 2p^6 3s^2 3p^6) is more covalent than magnesium chloride (Mg(II) 1s^2 **2s^2 2p^6**) despite the Zn^{2+} ion (74 pm) and 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: The melting point of KCl is higher than that of AgCl though the crystal radii of Ag$^+$ and K$^+$ ions are almost the same.

Solution: 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. K$^+$= [Ar] and Ag$^+$ =[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 μ is given by:

$\mu = \delta\ d$

A bond dipole is modeled as $+\delta$ - δ- 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.

Historically the Debye was defined in terms of the dipole moment resulting from two equal charges of opposite sign and separated by 1 Ångstrom (10^{-10} m) as 4.801 D. This value arises from $(1.602 \times 10^{-19} * 1 \times 10^{-10}) / 3.336 \times 10^{-30}$
where D = 3.336×10^{-30} C m (or 1 C m = 2.9979×10^{29} D).

Typical dipole moments for simple diatomic molecules are in the range of 0 to 11 D (see Table below).

The % ionic character = $\mu_{observed}$ / $\mu_{calculated}$ (assuming 100% ionic bond) * 100 %

Example: From the Table below the observed dipole moment of KBr is given as 10.41 D, (3.473×10^{-29} coulomb metre), which being close to the upper level of 11 indicates that it is a highly polar molecule. The interatomic distance between K^+ and Br^- is 282 pm. From this it is possible to calculate a theoretical dipole moment for the KBr molecule, assuming opposite charges of one fundamental unit located at each nucleus, and hence the percentage ionic character of KBr.

Solution: Dipole moment $\mu = q * e * d$ coulomb metre
q = 1 for complete separation of unit charge
e = 1.602×10^{-19} C
d = 2.82×10^{-10} m for KBr (282 pm)

Hence calculated $\mu_{KBr} = 1 * 1.602 \times 10^{-19} * 2.82 \times 10^{-10} = 4.518 \times 10^{-29}$ Cm (13.54 D)

The observed $\mu_{KBr} = 3.473 \times 10^{-29}$ Cm (10.41 D)

the % ionic character of KBr = $3.473 \times 10^{-29} / 4.518 \times 10^{-29}$ or 10.41 / 13.54 = 76.87% and the % covalent character is therefore about 23% (100 - 77).

Given the observed dipole moment is 10.41 D (3.473 x 10^{-29}) it is possible to estimate the charge distribution from the same equation by now solving for q:

Dipole moment $\mu = q * e * d$ Coulomb metre
but since q is no longer 1 we can substitute in values for μ and d to obtain an estimate for it.

$q = \mu /(e * d) = 3.473 \times 10^{-29} / (1.602 \times 10^{-19} * 2.82 \times 10^{-10})$

thus $q = 3.473 \times 10^{-29} / (4.518 \times 10^{-29}) = 0.77$ and the $\delta-$ and $\delta+$ are -0.8 and +0.8 respectively.

Example. For HI, calculate the % of ionic character given a bond length = 161 pm and an observed dipole moment 0.44 D.

Solution: To calculate μ considering it as a 100% ionic bond

$\mu = 1 * 1.602 \times 10^{-19} * 1.61 \times 10^{-10} / (3.336 \times 10^{-30}) = 7.73$ D

the % ionic character = 0.44/7.73 * 100 = 5.7%

The calculated % ionic character is only 5.7% and the % covalent character is (100 - 5.7) = 94.3%. The ionic character arises from the polarizability and polarizing effects of H and I. Similarly, knowing the bond length and observed dipole moment of HCl, the % ionic character can be found to be 18%. Thus it can be seen that while HI is essentially covalent, HCl has significant ionic character.

Note that by this simplistic definition, to achieve 100 % covalent character a compound must have an observed dipole moment of zero. Whilst not strictly true for heteronuclear molecules it does provide a simple qualitative method for predicting the bond character.

Source :

http://wwwchem.uwimona.edu.jm:1104/courses/CHEM1902/IC10K_MG_Fajans.html