Electronegativity and intermediate bonding

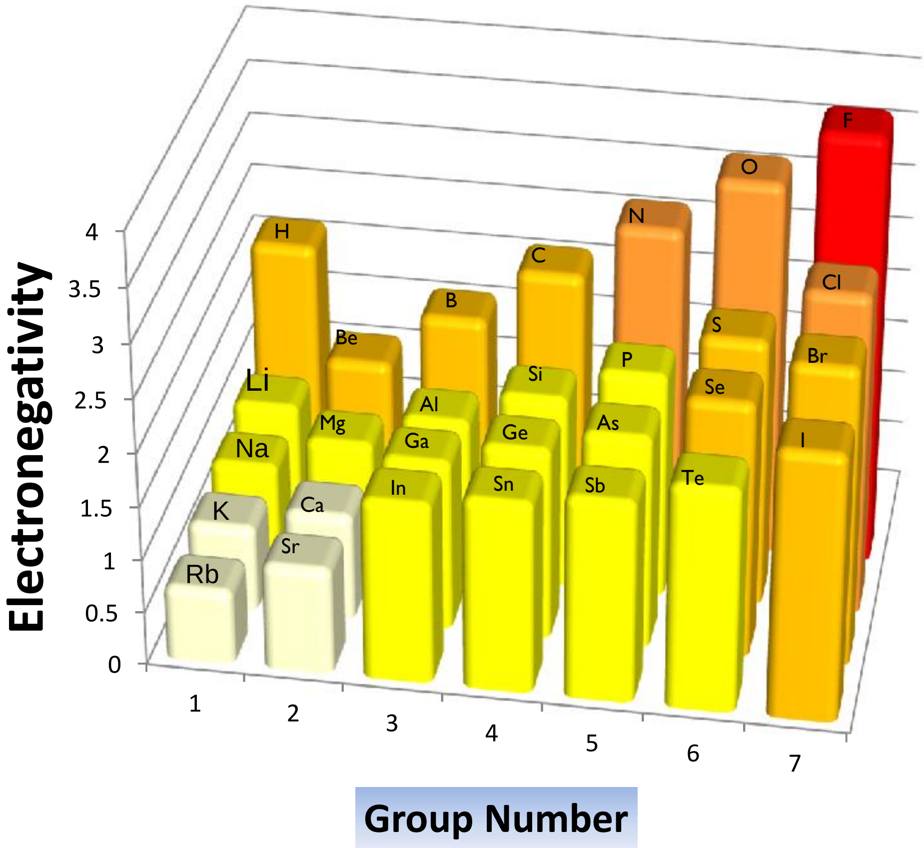
Definition

Electronegativity is the relative tendency of an **atom in a <u>covalent bond</u>** in a molecule **to <u>attract electrons</u>** in a covalent bond **to itself**.

F, O, N and Cl are the most electronegative atoms

Electronegativity is measured on the **Pauling scale** (ranges from 0 to 4)

The **most** electronegative element is **fluorine** and it is given a value of 4.0



Factors affecting electronegativity
Electronegativity increases across a period as the **number of protons increases** and the atomic radius decreases because the **electrons in the same shell** are pulled in more.

Electronegativity decreases down a group because the **distance** between the nucleus and the outer electrons **increases and the shielding** of inner shell electrons increases.

INCREASING ELECTRONEGATIVITY

DECREASING ELECTRONEGATIVITY

						H 2.1										
Li 1.0	Be 1.5											B 2	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.7	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2	At 2.2
Fr 0.7	Ra 0.9	Ac 1.1														

Intermediate bonding

Ionic and covalent bonding are the extremes of a continuum of bonding type. Differences in electronegativity between elements can determine where a compound lies on this scale

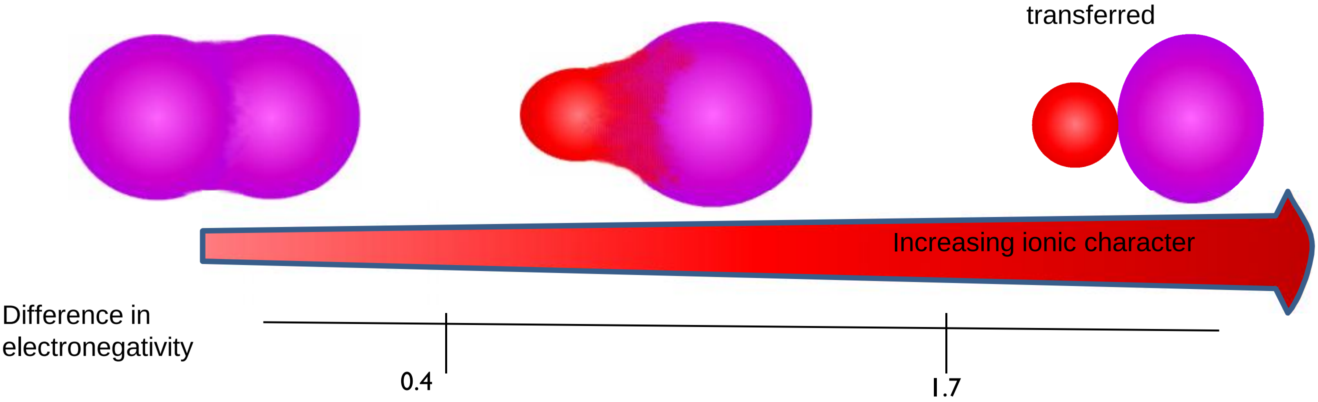
A compound containing elements of similar electronegativity and hence a **small electronegativity difference** will be purely **covalent**

A compound containing elements of very different electronegativity and hence a very **large electronegativity difference** (> 1.7) will be **ionic**

Non polar Covalent bond
Electrons shared equally

Polar Covalent bond
Electrons shared unequally

Ionic bond
Electrons are transferred

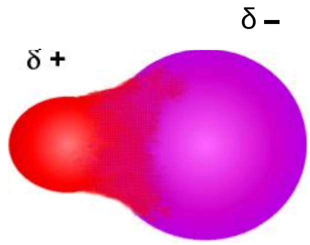


Formation of a permanent dipole – (polar covalent) bond

A **polar covalent bond** forms when the elements in the bond have **different electronegativities (**of around 0.3 to 1.7)

When a bond is a **polar covalent bond,** the bond has an **unequal distribution** of **electrons** in the bond and produces a **charge separation**, **(dipole)** δ+ δ- ends.

δ indicates a **slight deviation** from being neutral



Covalent with ionic character (polar covalent)

The element with the larger electronegativity in a polar compound will be the δ- end

$\overset{\delta+}{H} - \overset{\delta-}{Cl}$

Polar and Non Polar molecules

Symmetric molecules

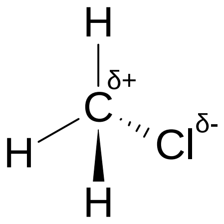
A symmetric molecule (all bonds identical and no lone pairs) will not be polar even if individual bonds within the molecular are polar.

The individual dipoles on the bonds 'cancel out' due to the symmetrical shape of the molecule.
There is no net dipole moment: the molecule is non-polar.

O = C = O

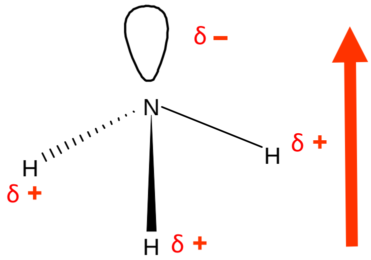
CO_2 is a symmetrical molecule and is a non-polar molecule

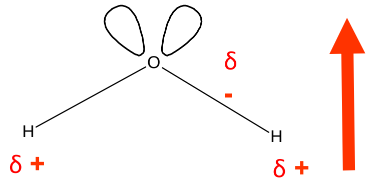
e.g. CCl_4 will be non-polar whereas CH_3Cl will be polar



Non-symmetrical molecule

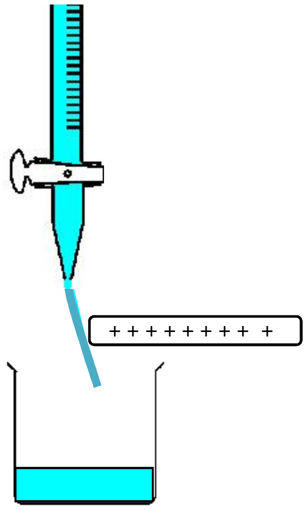
A non-symmetrical molecule (different bonds *OR* the same bonds *and* having lone pairs) will be polar if individual bond(s) are themselves polar.





Experiment effect of charged rod on polar/non-polar liquids

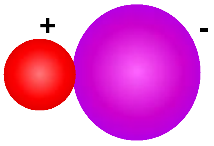
In this experiment, a charged rod (formed by rubbing a plastic rod) is brought close to a jet of liquid flowing from a burette.



If the liquid is polar, the jet of liquid will be attracted to the electrostatic force of the rod. The dipoles in the polar molecules will all align and the negative end δ- will be attracted to the positive rod (or vice versa). The stronger the dipole the more the deflection of the jet.

Non-polar liquids will not be deflected and attracted to the charged rod. Hexane will not be deflected by a charged rod.

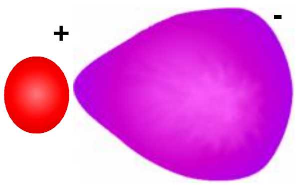
Pure ionic



When 100 % ionic the ions are spherical.

Another point in the continuum between ionic and covalent is ionic with covalent character. It is possible to explain this with difference in electronegativity but more commonly Fajan's rules are used to explain the change from purely ionic to ionic with covalent character.

Ionic with covalent character



When the negative ion becomes distorted and non spherical, it is more covalent and is called polarised. The metal cation that causes the polarisation is called more polarising if it polarises the negative ion.

Fajan's Rules

The extent of polarisation of the negative ion by the positive ion can be explained by Fajan's rules.

There is a tendency towards covalent character when

- the positive ion is small
- the positive ion has multiple charges
- the negative ion is large
- the negative ion has multiple negative charges.

Example

$AlCl_3$ shows quite large covalent character because Al has a +3 charge and is quite small, so is highly polarising.

Example

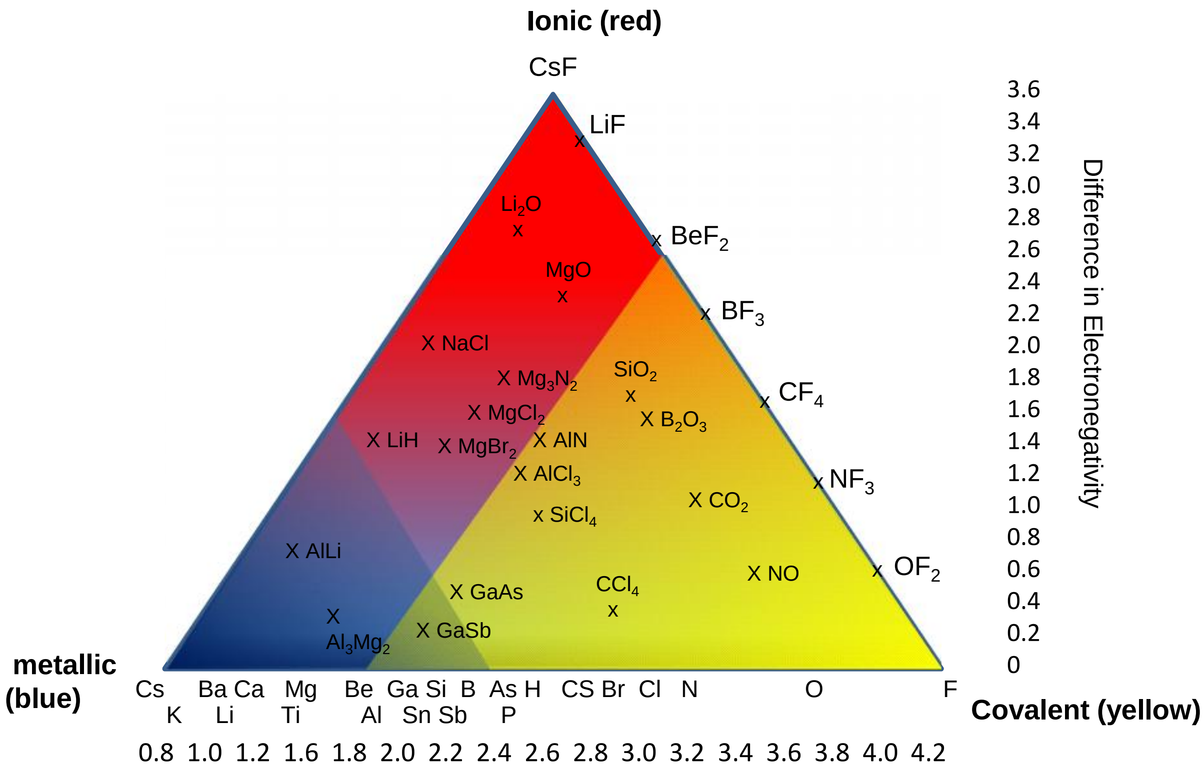
Consider the halides of magnesium.

$MgCl_2$, $MgBr_2$, MgI_2.

As the anions become larger they are more easily polarised, so they show more covalent character.

Van Arkel diagrams

Van Arkel diagrams illustrate on one diagram the type of bonding for all binary compounds. It extends the continuum to include metallic bonding as well as ionic and covalent.
It shows their bonding type in terms of the difference in electronegativity (which is plotted on the y-axis) and the average electronegativity of their constituent elements (which is plotted on the x-axis).



Intermediate bonding Questions

1) Define electronegativity

2) Give 3 factors that affect electronegativity

Table of Electronegativities

H 2.1						
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0

3) a) State and explain the trend in electronegativity down a group

b) State and explain the trend in electronegativity across a period

4) Draw diagrams to show the shape of the electron charge clouds in an ion, in a purely covalent molecule and a polar covalent molecule. Explain using the ideas of electronegative difference how each case can occur.

5) Deduce using the ideas of electronegativity difference whether the following compounds have ionic bonding, covalent bonding or intermediate polar covalent bonding. Predict for each one whether you would expect the melting point to be high or low

a) sulfur dioxide

b) sodium oxide

c) lithium fluoride

d) nitrogen monoxide

e) hydrogen chloride

f) F_2O

g) phosphine (PH_3)

h) magnesium chloride

I) nitrogen trichloride

J) boron hydride

6) Explain why the chlorides NaCl, $MgCl_2$, $AlCl_3$ and $SiCl_4$ have lower melting points as you move across the period from Na to Si.

7) a) Describe what a polar covalent bond is and explain how one forms.

b) Find out and draw the displayed structures of the following compounds and draw on the relevant bonds the correct dipoles

(i) H_2O

(ii) NH_3

(iii) HF

(iv) CH_3Cl

(v) ethanol CH_3CH_2OH

(vi) SO_2

(vii) CH_3CH_2Br

(viii) IF

8) The polarity of a carbon-hydrogen bond can be shown as $\overset{\delta^+}{C}\text{-}\overset{\delta^-}{H}$

(i) What does the symbol δ+, above the hydrogen atom, signify?

(ii) Why is there a charge separation on the C-H bond

(iii)Explain briefly, in terms of its shape, why a CH_4 molecule has no overall polarity.

9) Find out and draw the displayed structures of the following compounds. Identify which of the following compounds have no overall polarity and for the ones that are polar draw on the dipole

i) CH_3Br

ii) CCl_4

iii) BF_3

iv) NF_3

v) CO_2

vi) $BeCl_2$

vii) methanal

viii) Cl_2O

ix) SO_3