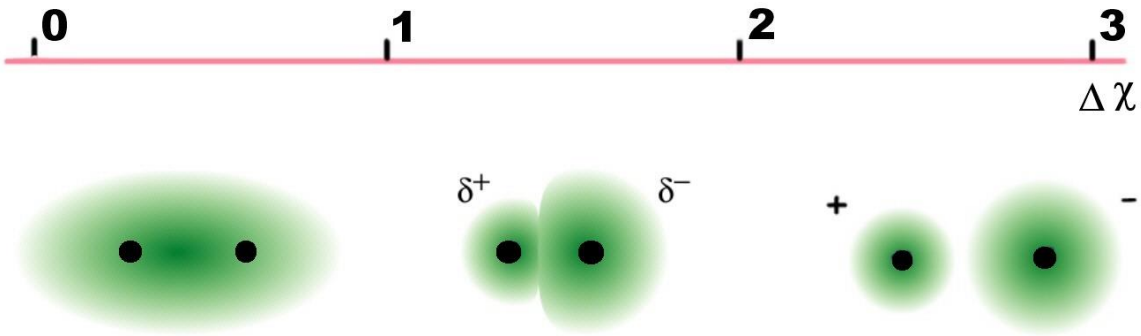
BOND CHARACTER BASED ON ELECTRONEGATIVITY DIFFERENCES

It is possible to predict whether a given bond will be non-polar, polar covalent, or ionic based on the electronegativity difference, since the greater the difference, the more polar the bond.



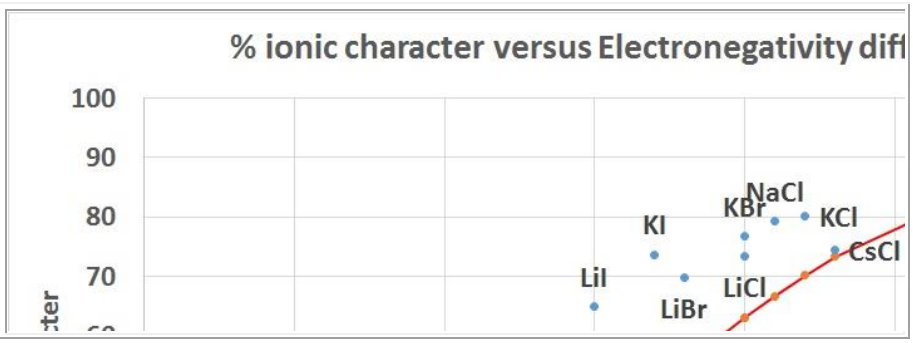
Electronegativity difference, ΔχP	Bond
$\Delta\chi < 0.4$	covalent
$0.4 < \Delta\chi < 1.7$	polar covalent
$\Delta\chi > 1.7$	ionic

Linus Pauling proposed an empirical relationship which relates the percent ionic character in a bond to the electronegativity difference.

percent ionic character= $(1-e^{-(\Delta\chi/2)\wedge 2})* 100$

This is shown as the curve in red below and is compared to the values for some diatomic molecules calculated from observed and calculated dipole moments.

diatomic	Δ χ	%ionic	bond dist /pm	Obs μ /D	Calc μ /D
Cl_2	0.0	0.0	200	0.00	9.60
IBr	0.	5.9	247	0.7	11.



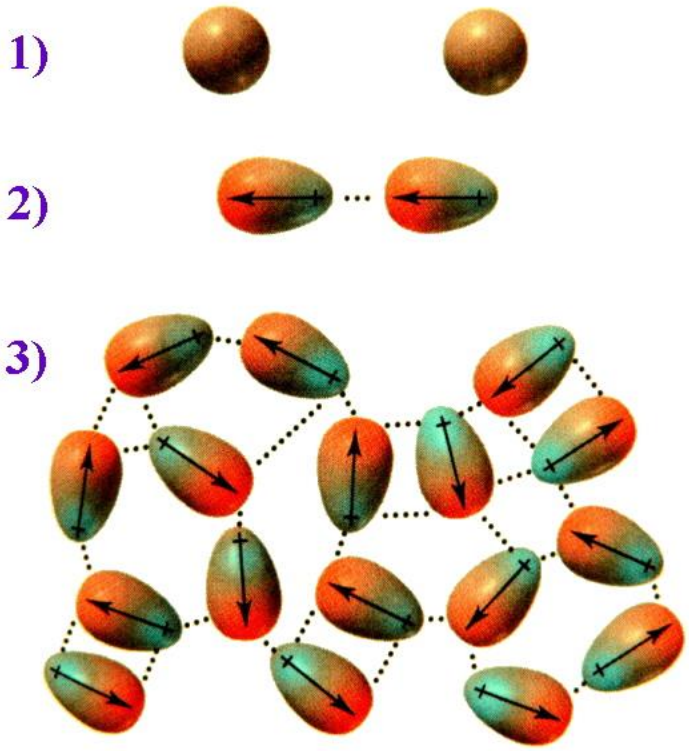
	3			0	86
HI	0.4	5.7	161	0.44	7.73
ICl	0.5	5.4	232	0.60	11.14
HBr	0.7	12.1	141	0.82	6.77
HCl	0.9	17.7	127	1.08	6.10
ClF	1.0	11.2	163	0.88	7.83
BrF	1.2	15.1	178	1.29	8.55
LiI	1.5	65.0	238	7.43	11.43
HF	1.9	41.2	92	1.82	4.42
LiBr	1.8	69.8	217	7.27	10.42
KI	1.7	73.7	305	10.80	14.65
LiCl	2.0	73.5	202	7.13	9.70
KBr	2.0	76.9	282	10.41	13.54
NaCl	2.1	79.4	236	9.00	11.33
KCl	2.2	80.1	267	10.27	12.82
CsCl	2.3	74.6	291	10.42	13.97
LiF	3.0	86.7	152	6.33	7.30
KF	3.2	82.5	217	8.60	10.42
CsF	3.3	64.4	255	7.88	12.25

London dispersion forces

Intermolecular forces are the attractive forces between molecules without which all substances would be gases. The various types of these interactions span large differences in energy and for the halogens and interhalogens are generally quite small. The forces involved in these cases are called London dispersion forces (after Fritz Wolfgang London, 1900-1954). They are derived from momentary oscillations of electron charge in atoms and hence are present between all particles (atoms, ions and molecules).

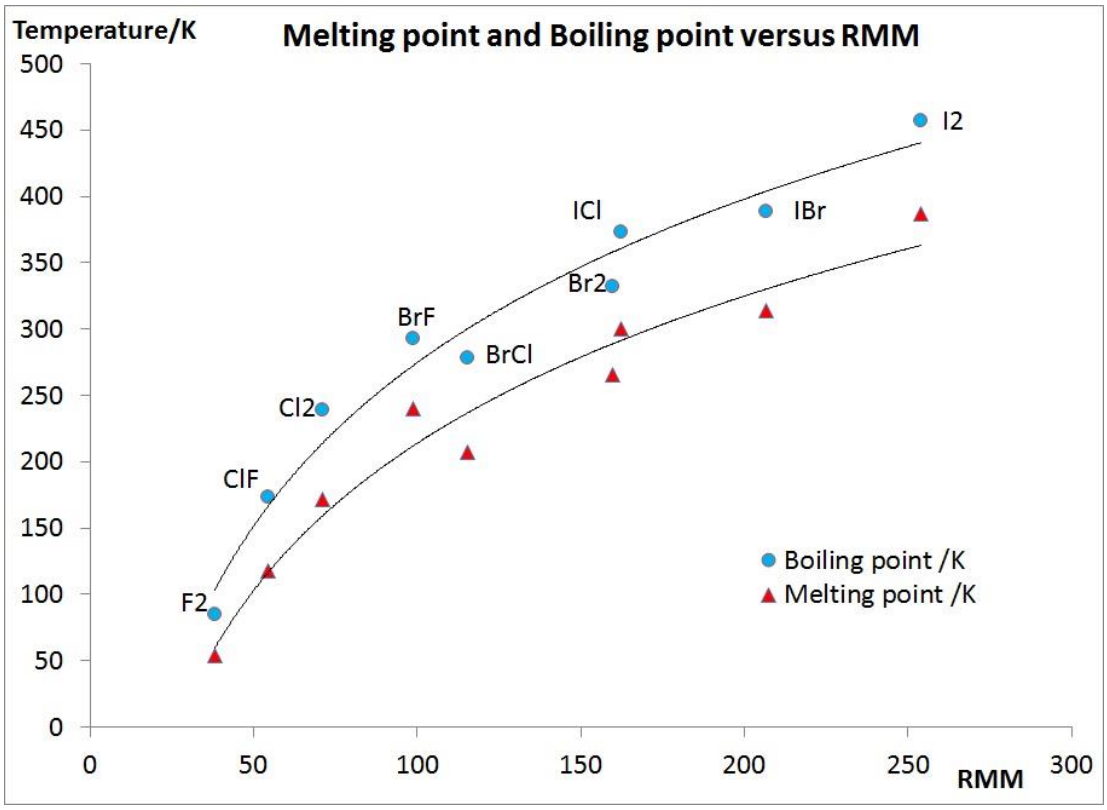
The ease with which the electron cloud of an atom can be distorted to become asymmetric is termed the molecule's **polarizability**. The greater the number of electrons an atom has, the farther the outer electrons will be from the nucleus, and the greater the chance for them to shift positions within the molecule. This means that larger nonpolar molecules tend to have stronger London dispersion forces. This is evident when considering the diatomic elements in Group 17, the Halogens. All of these homo-nuclear diatomic elements are nonpolar, covalently bonded molecules. Descending the group, fluorine and chlorine are gases, bromine is a liquid, and iodine is a solid. For nonpolar molecules, the farther you go down the group, the stronger the London dispersion forces.

To picture how this occurs, compare the situation 1) where the electrons are evenly distributed and then consider 2) an instantaneous dipole that would arise from an uneven distribution of electrons on one side of the nucleus. When two molecules are close together, the instantaneous dipole of one molecule can induce a dipole in the second molecule. This results in synchronised motion of the electrons and an attraction between them. 3) when this effect is multiplied over numerous molecules the overall result is that the attraction keeps these molecules together, and for diiodine is sufficient to make this a solid.



On average the electron cloud for molecules can be considered to be spherical in shape. When two non-polar molecules approach, attractions or repulsions between the electrons and nuclei can lead to distortions in their electron clouds (i.e. dipoles are induced). When more molecules interact these induced dipoles lead to intermolecular attraction.

The changes seen in the variation of MP and BP for the dihalogens and binary interhalogens can be attributed to the increase in the London dispersion forces of attraction between the molecules. In general they increase with increasing atomic number.



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