Bonding

By: Mahmoud Taha

Special thanks to Ms Williams and Ms Matrella for their constant support and inspiration

Please note that these guides are a collation of my personal notes, teachers' notes, chemistry books, and websites such as chemguide, chemsheets, chemwiki and wikipedia.

Ions and Ionic Bonds

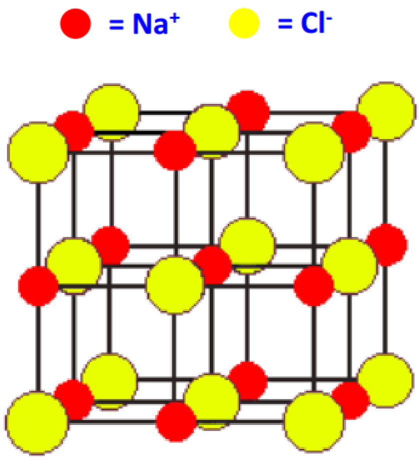
An **ionic bond** is formed when one or more electrons are transferred from a metal to non-metal atom. Ionic compounds are made of ions.

An **ion** is an electrically charged particle formed from an atom by gaining or losing one or more electrons.

A **giant ionic lattice** is the regular arrangement of alternating +ive and -ive ions in an ionic crystals. These are held together by the strong electrostatic attraction between the oppositely charged ions. Hence they often have high mp and bp. They also have the following properties:

- Hard
- Brittle
- Usually soluble in water but not in organic solvents such as ethanol
- Conduct electricity when **molten** or **in solution not when solid.** This is because in solid state, the ions aren't free to move, while if liquid or dissolved the ions are free to move.

Example of ionic compound:



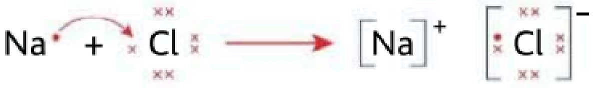
NaCl Sodium Chloride

Each sodium ion is surrounded by six chloride ions. Each chloride ion is surrounded by six sodium ions. Hence it is a 6:6 coordination.

It has a very high mp = 801°C

Dot and Cross Diagrams

If an exam question asks for the dot and cross diagram with only outer shell electrons, you would draw something like this. You only draw the second half of the diagram which contains the ions. The first part is there to clarify whose electrons goes where.



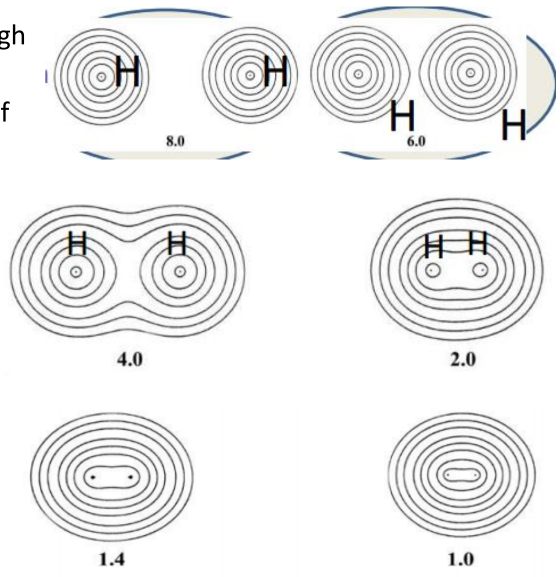
Evidence for Ions Existence

1- Physical Properties

Here we can mention the electrical conductivity of the ions when molten or dissolved.
We can also talk about the main difference between metals and ionic substance. Ionic substances are brittle. On the other hand metals are ductile and malleable. The ionic lattice model -with no free electrons- is responsible for that. When a force is applied to the lattice, the ions in one layer shift relative to the other layers. This results in ions of the same charge being next to each other and a repulsive forces would force the two layers apart, which shatter the ionic substance.

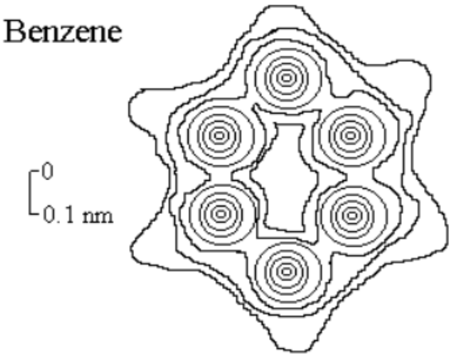
2- Electron Density Maps

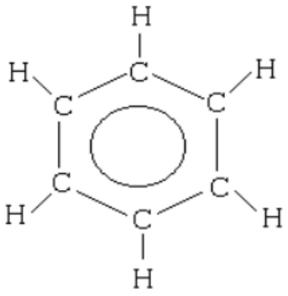
Electron density maps are maps which show how electrons are distributed in a chemical substance. A high electron density means there is a high probability of finding the electrons The diagrams show a sequence of electron density maps which illustrate the distribution of two hydrogen atoms in a hydrogen molecule .
The number below each map indicates the distance between both nuclei. In the last three maps (2.0, 1.4 and 1.0) electrons from both atoms are being shared as they can move around both nuclei.

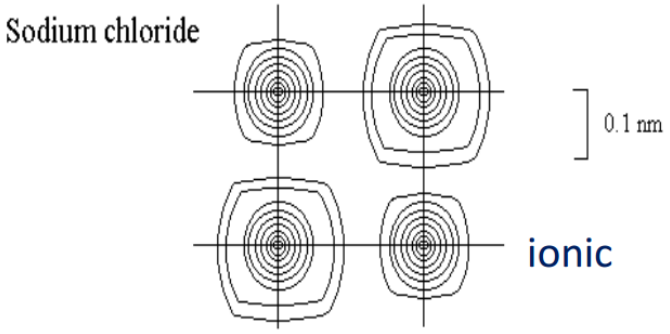


Below is an example of another covalent compound electron density map as well as an ionic one.

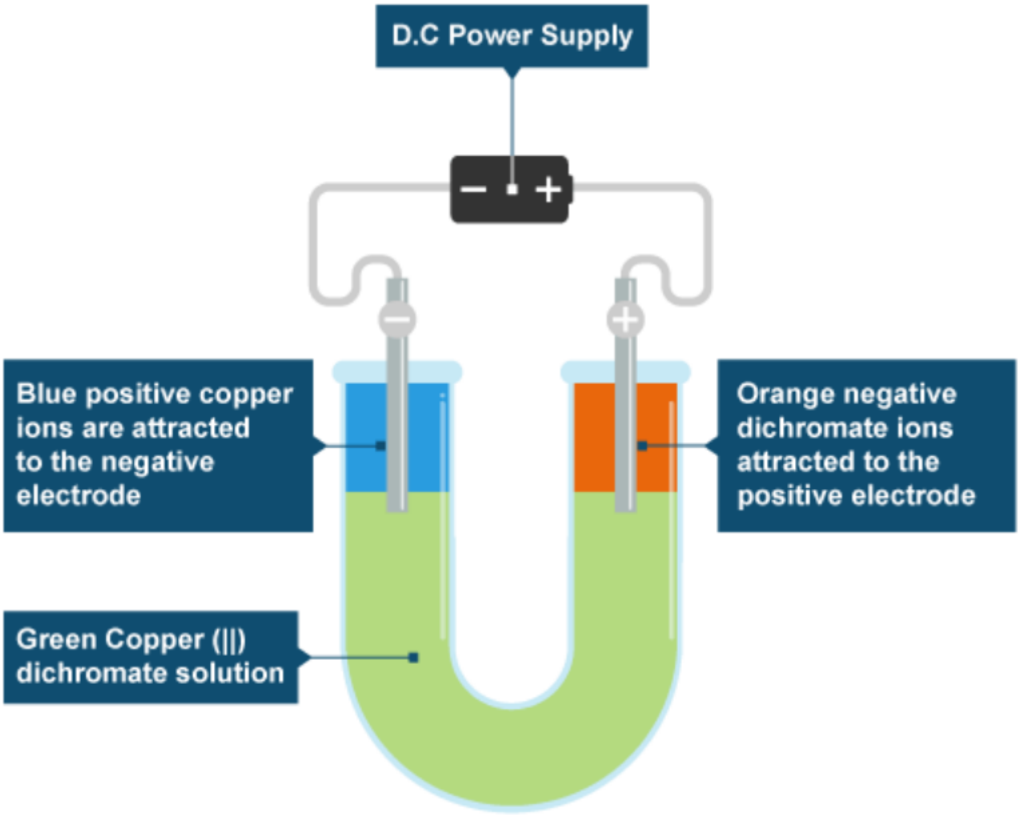
Measurements taken from the electron density maps allow different ions to be identified and also allows chemists to calculate their distance apart in the lattice.







3- Migration of ions

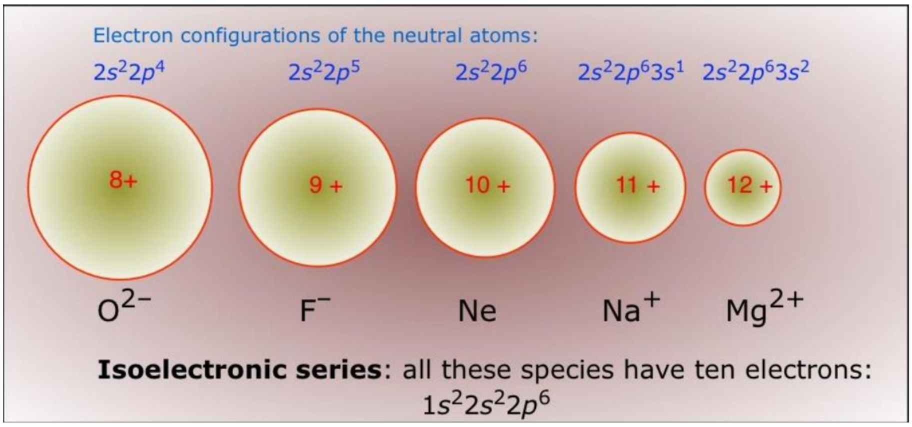


Isoelectronic Ions and Octet Rule

Isoelectronic ions have the same electrons arrangement. For example both Na^+ and Ne have the electron configuration of : $1s^2\ 2s^2\ 2p^6$.

Normally when atoms react, they tend to follow the **octet rul**e. This basically states that when elements react, they do so in order to gain an outer shell of 8 electron. Obviously there are exceptions such as the H^+ ion.

Why do isoelectronic ions have different ionic radii?

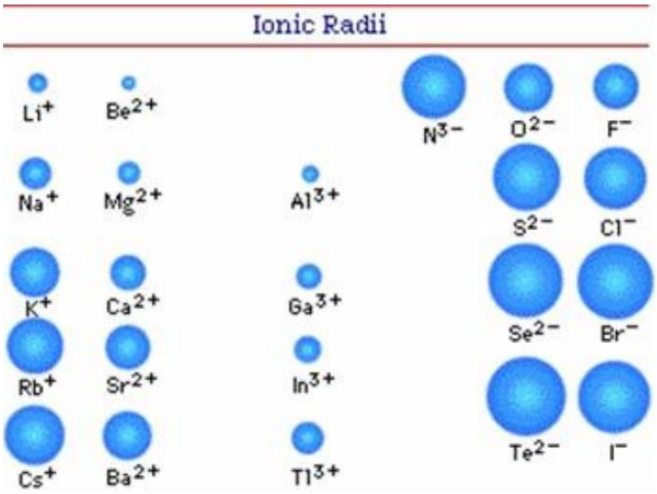


When fewer protons are in the nucleus, the attraction between the electrons and nucleus is weaker. The electrons will consequently be farther away from the nucleus. The farther away electrons are, the larger the radius of the ion. O^{2-} is the ion with the fewest amount of protons, and therefore has the largest radius. O^{2-} is also considered to have the lowest charge density of all the ions displayed above. From here, I can then talk about electronegativity, but first lets briefly look at ionic radii trends.

Ionic Radii Trend

Down a group

As illustrated by the diagram, as we go down a group of either positive or negative ions, the ionic radii increase. This is because overall, there are more electron shells.



Across a period

If we were to compare the ionic radii across a period, we would find that the trend is variable.

+ive ions

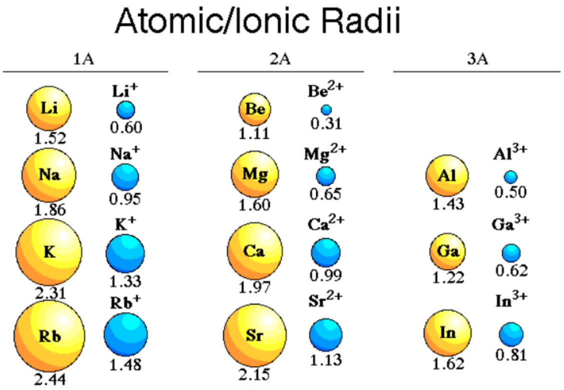
In each case, the ions have exactly the same electronic structure - they are said to be isoelectronic. However, the number of protons in the nucleus of the ions is increasing. That will tend to pull the electrons more and more towards the centre of the ion - causing the ionic radii to fall.

-ive ions

The difference is much less significant across the period with negative ions, the extra proton as you go from left to right doesn't make a huge difference. The difference is clearst between N^{3-} and O^{2-}.

Atoms vs Ions

Ions with less outermost electrons than in its atoms = small ionic radius compared to atomic radius.
Ions with more outermost electrons than in its atoms = bigger ionic radius compared to atomic radius.



Electronegativity

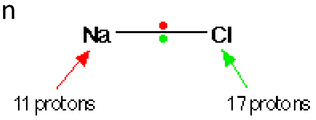
Quite a lot of the following is from:
http://www.chemguide.co.uk/atoms/bonding/electroneg.html
I used it as I couldn't have explained electronegativity any better

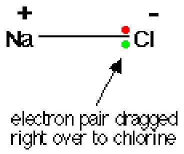
Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. The Pauling scale is the most commonly used. Fluorine (the most electronegative element) is assigned a value of 4.0, and values range down to caesium and francium which are the least electronegative at 0.7.

Across a Period

Consider sodium at the beginning of period 3 and chlorine at the end (ignoring the noble gas, argon). Think of sodium chloride as if it were covalently bonded.

Both sodium and chlorine have their bonding electrons in the 3rd electron shell. The electron pair is screened from both nuclei by the 1s, 2s and 2p electrons, but the chlorine nucleus has 6 more protons in it. It is no wonder the electron pair gets dragged so far towards the chlorine that ions are formed.





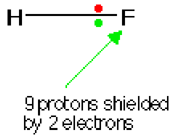
Electronegativity increases across a period because the number of charges on the nucleus increases. That attracts the bonding pair of electrons more strongly.

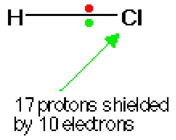
Down a group

Think of hydrogen fluoride and hydrogen chloride.

The bonding pair is shielded from the fluorine's nucleus only by the $1s^2$ electrons. In the chlorine case it is shielded by all the $1s^2$ $2s^2$ $2p^6$ electrons.

In each case there is a net pull from the centre of the fluorine or chlorine of +7. But fluorine has the bonding pair in the 2nd electron shell rather than the 3rd electron shell as it is in chlorine. If it is closer to the nucleus, the attraction is greater.

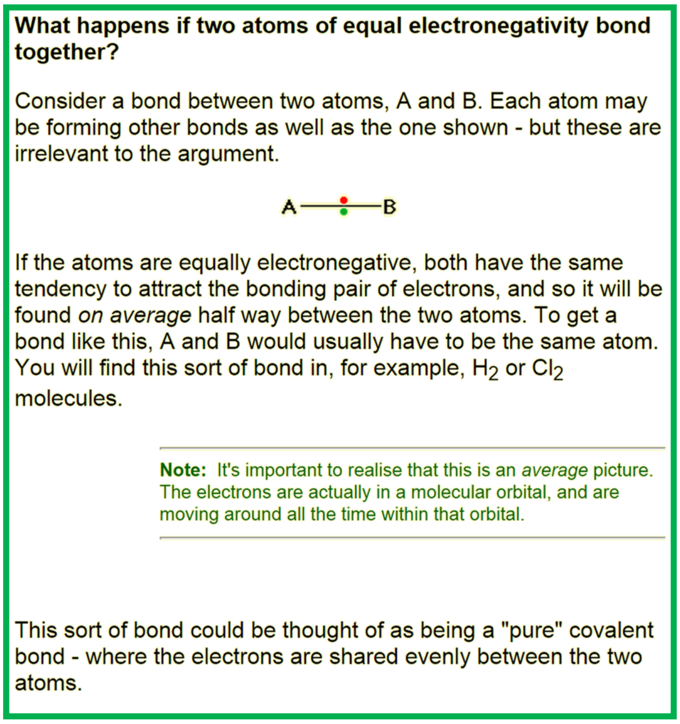




As you go down a group, electronegativity decreases because the bonding pair of electrons is increasingly distant from the attraction of the nucleus.

Why all this?

I went through electronegativity in order to explain the next section. It is quite long so just bear with me :P



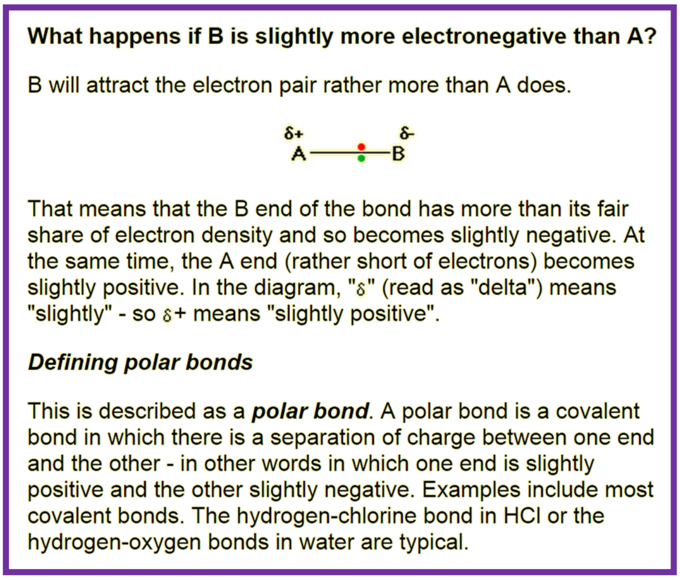
What happens if two atoms of equal electronegativity bond together?

Consider a bond between two atoms, A and B. Each atom may be forming other bonds as well as the one shown - but these are irrelevant to the argument.

If the atoms are equally electronegative, both have the same tendency to attract the bonding pair of electrons, and so it will be found *on average* half way between the two atoms. To get a bond like this, A and B would usually have to be the same atom. You will find this sort of bond in, for example, H_2 or Cl_2 molecules.

Note: It's important to realise that this is an *average* picture. The electrons are actually in a molecular orbital, and are moving around all the time within that orbital.

This sort of bond could be thought of as being a "pure" covalent bond - where the electrons are shared evenly between the two atoms.



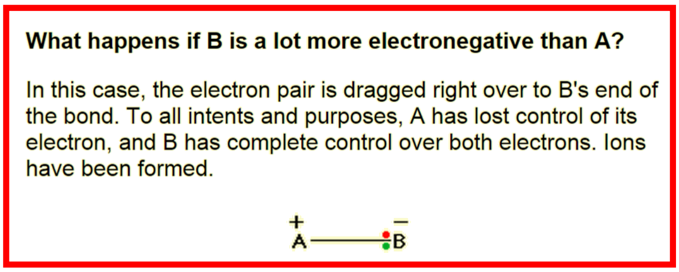
What happens if B is slightly more electronegative than A?

B will attract the electron pair rather more than A does.

That means that the B end of the bond has more than its fair share of electron density and so becomes slightly negative. At the same time, the A end (rather short of electrons) becomes slightly positive. In the diagram, "δ" (read as "delta") means "slightly" - so δ+ means "slightly positive".

Defining polar bonds

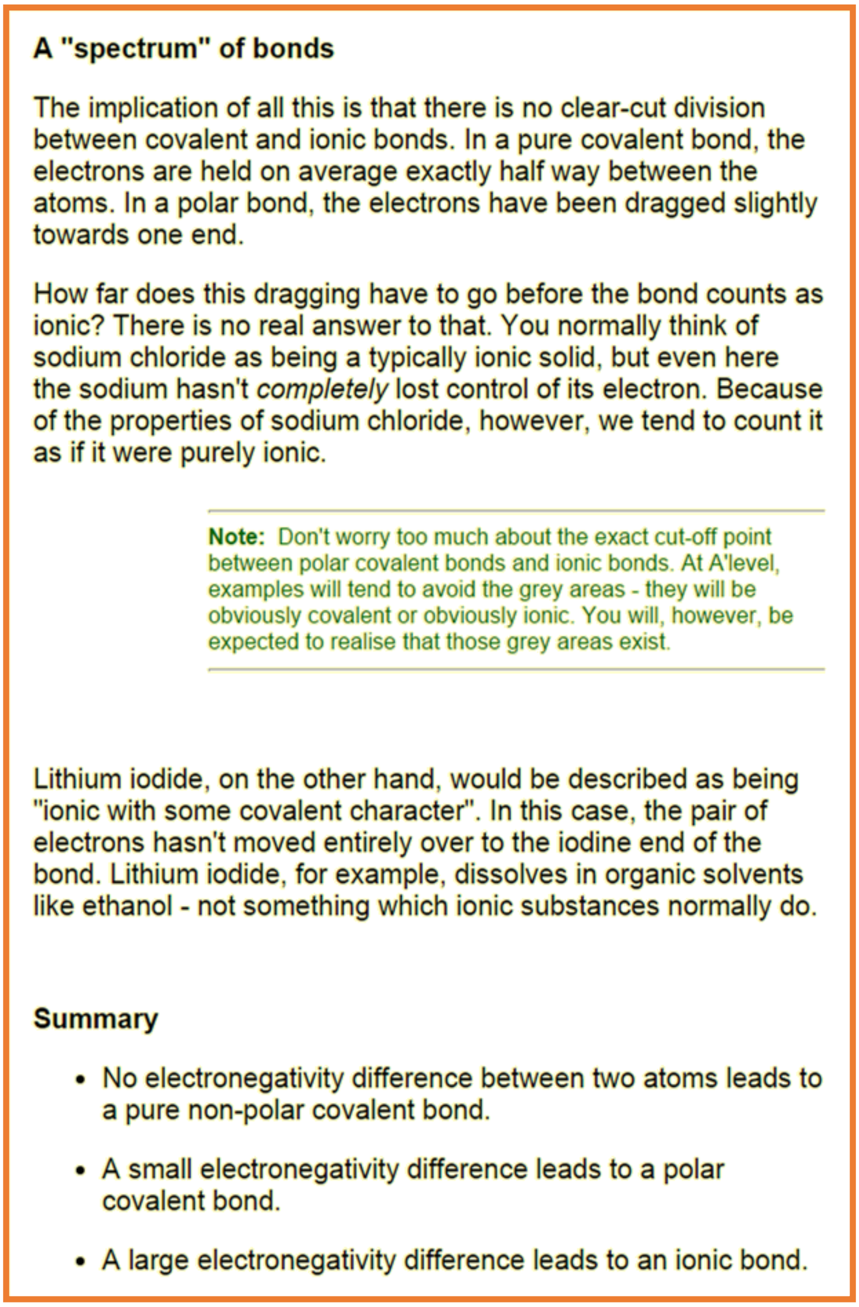
This is described as a ***polar bond***. A polar bond is a covalent bond in which there is a separation of charge between one end and the other - in other words in which one end is slightly positive and the other slightly negative. Examples include most covalent bonds. The hydrogen-chlorine bond in HCl or the hydrogen-oxygen bonds in water are typical.



What happens if B is a lot more electronegative than A?

In this case, the electron pair is dragged right over to B's end of the bond. To all intents and purposes, A has lost control of its electron, and B has complete control over both electrons. Ions have been formed.

Summary



A "spectrum" of bonds

The implication of all this is that there is no clear-cut division between covalent and ionic bonds. In a pure covalent bond, the electrons are held on average exactly half way between the atoms. In a polar bond, the electrons have been dragged slightly towards one end.

How far does this dragging have to go before the bond counts as ionic? There is no real answer to that. You normally think of sodium chloride as being a typically ionic solid, but even here the sodium hasn't *completely* lost control of its electron. Because of the properties of sodium chloride, however, we tend to count it as if it were purely ionic.

Note: Don't worry too much about the exact cut-off point between polar covalent bonds and ionic bonds. At A'level, examples will tend to avoid the grey areas - they will be obviously covalent or obviously ionic. You will, however, be expected to realise that those grey areas exist.

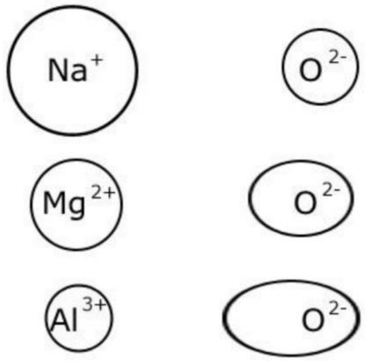
Lithium iodide, on the other hand, would be described as being "ionic with some covalent character". In this case, the pair of electrons hasn't moved entirely over to the iodine end of the bond. Lithium iodide, for example, dissolves in organic solvents like ethanol - not something which ionic substances normally do.

Summary

- No electronegativity difference between two atoms leads to a pure non-polar covalent bond.
- A small electronegativity difference leads to a polar covalent bond.
- A large electronegativity difference leads to an ionic bond.

Polarisation

Polarisation is how much distortion the cation causes in the shape of the anion electron cloud. As the cation gets smaller and more charged, it has a higher charge density and its polarising power increases. As the anion gets larger, its polarisability increases (gets polarised more easily) because the electrons are less tightly held by ions with a large ionic radius.



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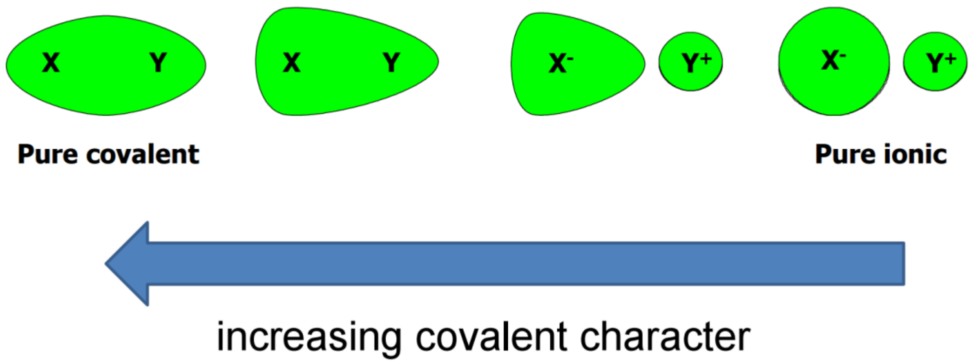
Notice how the Na^+ caused the least distortion in the O^{2-} electron cloud. On the other hand the Al^{3+} caused the most distortion in the O^{2-} electron cloud.

Ionic or Covalent



The more polarising the positive ion, the more the negative ion is distorted in shape and the more covalent character. The smaller the positive ion, and the higher its charge, the more polarising it is. Larger negative ions are polarised more easily.

Lattice Enthalpy

This is the energy change that occurs when 1 mole of a solid lattice is formed from its constituent gaseous ions (at 298K and 1 atm). It could also be defined as the enthalpy of formation of 1 mole of a solid ionic compound from gaseous ions under standard conditions.

Lattice enthalpy vs bond energy
They aren't the same

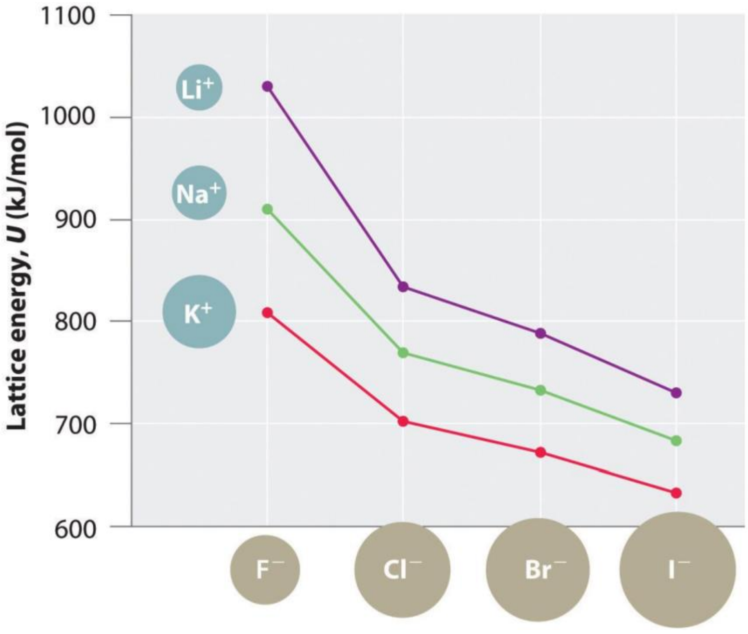
Lattice Enthalpy (LE)	Bond Energy
Energy given off when 1 mole of an ionic solid is formed from its gaseous ions under standard conditions	Energy needed to break one mole of covalent bonds in the gas phase
Only deal with ionic solids.	Only deals with covalent molecules
Negative enthalpy change	Positive enthalpy change

Also note that lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the lattice enthalpy, the stronger the forces.

What does the value of LE depend on?

The lattice energy depends upon the **electrostatic attraction** between the ions. Therefore it is proportional to the **product** of the **charges** (LE $\propto z$), i.e. more charge more attraction

It is therefore **inversely proportional** to the **distance** between them (LE $\propto 1/r$), i.e. closer = less distance = more attraction. The effect of the cation and anion size can be seen using this graph:

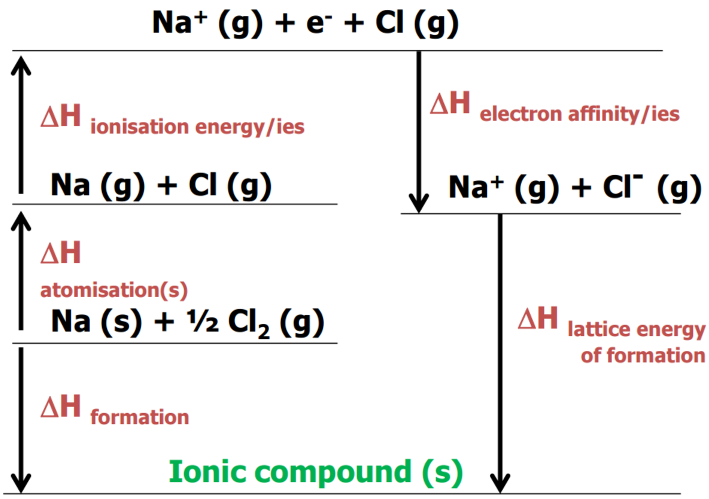


Born Haber Cycles

Similar to Hess's Law cycles, a Born Haber cycle is a special type of enthalpy level diagram. The Born-Haber cycle is specific application of Hess' Law which relates to Ionic compounds. You use Born Haber cycles to calculate lattice enthalpy of an ionic compound.

A key component in Born Haber is electron affinity. Electron affinities are the negative ion equivalent of ionisation energies . 1st electron affinity is the energy released when 1 mole of gaseous atoms each acquire an electron to form 1 mole of gaseous 1^- ions. This is usually an exothermic process. 2nd electron affinities are invariably endothermic. This is because you are forcing a negatively charged electron into an already negative ion.

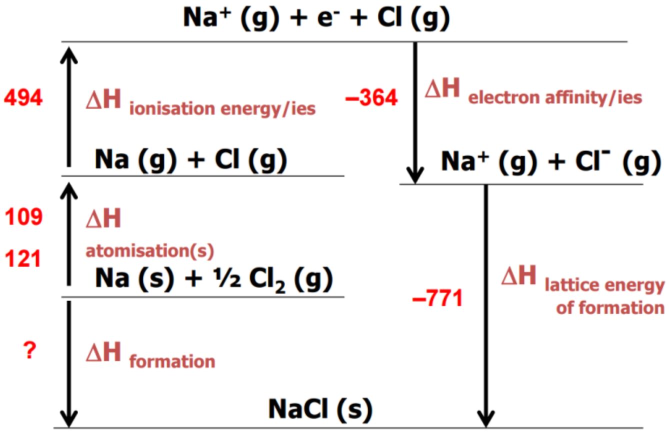
The Born Haber cycle for $NaCl_{(s)}$ can be draw like this:



The 'ies' is used if we have more than one ionisation energy or more than one electron affinity as the case is in MgO. We have to consider 2 ionisation energies for Mg (the first and second one) and 2 electron affinities for Oxygen.

As with Hess' Law, if we go in the opposite direction of the arrow we flip the sign of that enthalpy. For example to calculate the enthalpy of formation of $NaCl_{(s)}$, we do the following:

The values to be used in the calculation will be given to you in the exam, don't worry.



$$= 109 + 121 + 494 - 364 - 771 = \underline{-411\ \text{kJmol}^{-1}}$$

Theoretical LE vs Born-Haber LE

Some Born Haber lattice energies don’t match calculated theoretical values for ionic compounds. This is because the compound has some covalent character caused by polarisation of ions.

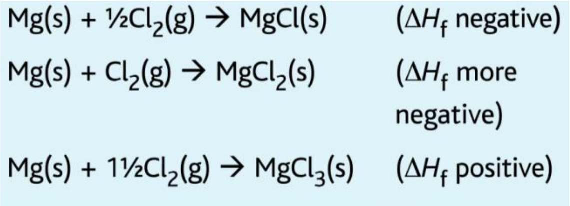
For example, the difference between Theoretical and Born-Haber values in NaF is 6 kJ mol^{-1} while in NaI the difference is 18 kJ mol^{-1} , why? Because as we mentioned earlier, larger anions = more polarisation. Hence the larger difference in NaI means it has a greater covalent character than NaF.

The theoretical lattice energy of sodium iodide matches well with its experimental (Born Haber) value but this is not true for magnesium iodide, why? Experimental and theoretical lattice energies match well when there is a high degree of ionic character. NaBr has more ionic character because Na^+ is a bigger ion with smaller charge than Mg^{2+}, hence Mg^{2+} has a higher charge density.

Stability

Why can't we have $NaCl_2$ rather than NaCl ?
The ionisation energy of the second electron of sodium is nearly 10 times greater than that of the first! The estimated ΔH_f for $NaCl_2$ = +2186 kJ mol^{-1}. The ΔH_f for NaCl = - 411 kJ mol^{-1}. So NaCl is energetically favourable because its formation is exothermic. (or another way to say it…) $NaCl_2$ is energetically unfavourable because its formation is significantly endothermic, it is unstable.

Another question is why $MgCl_2$ is more stable than MgCl? Well because by calculation, the ΔH_f for $MgCl_2$ is more exothermic, i.e. more negative as this picture from the book suggests:



$Mg(s) + ½Cl_2(g) \rightarrow MgCl(s)$ (ΔH_f negative)

$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$ (ΔH_f more negative)

$Mg(s) + 1½Cl_2(g) \rightarrow MgCl_3(s)$ (ΔH_f positive)

Covalent Bonding

The electrostatic attraction between the positive nuclei and the negative electron pairs shared between those nuclei.

Both of electron density maps and physical properties serve as evidence for the existence of covalent bonding.

Physical properties of simple covalent compounds:

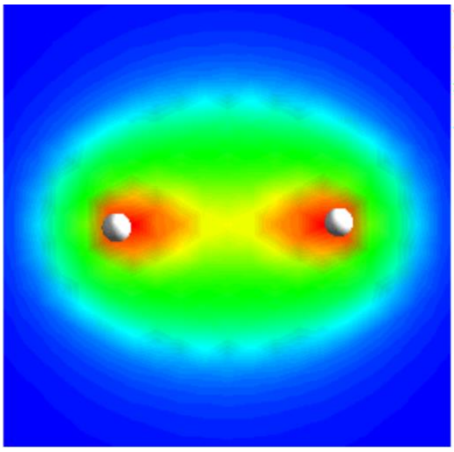
1- All covalent substances are non-conducting because no mobile ions or electrons present **(except graphite!!)**.

2- Simple covalent molecules are :
(a) Gases e.g. nitrogen
(b) Liquids e.g. water
(c) Low melting point solids e.g. iodine

(a, b and c) ALL have LOW melting & boiling points
Strong covalent bonds **within** the molecules DO NOT BREAK during melting or boiling
Weaker intermolecular forces (imf) between molecules DO BREAK during melting or boiling. These weaker imf take less energy to break and give the simple covalent compounds their low mp and bp.

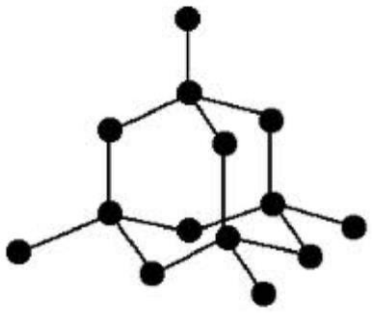
Electron density maps of simple molecules

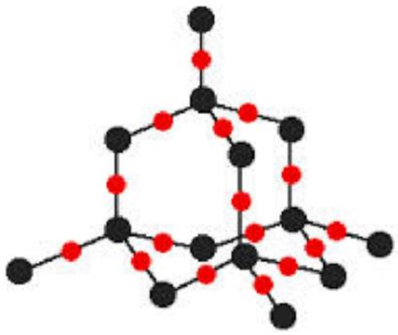
Since we mentioned electron density, we can also talk about bond length and refresh on bond enthalpy. Distance between two nuclei = bond length, while the energy released when the atoms form bond = bond enthalpy. You can research more about electron densities if you want to learn more about it.



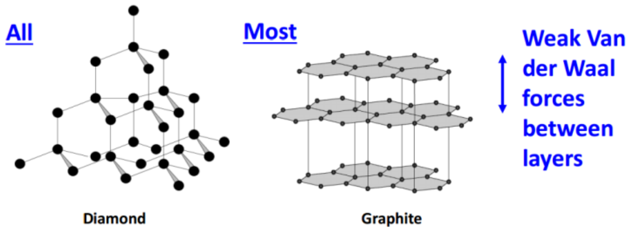
Evidence for covalent bonding in giant structures

These giant atomic crystals contain atoms held together by strong covalent bonds. The structure on the left is diamond and the one on the right is silicon dioxide.



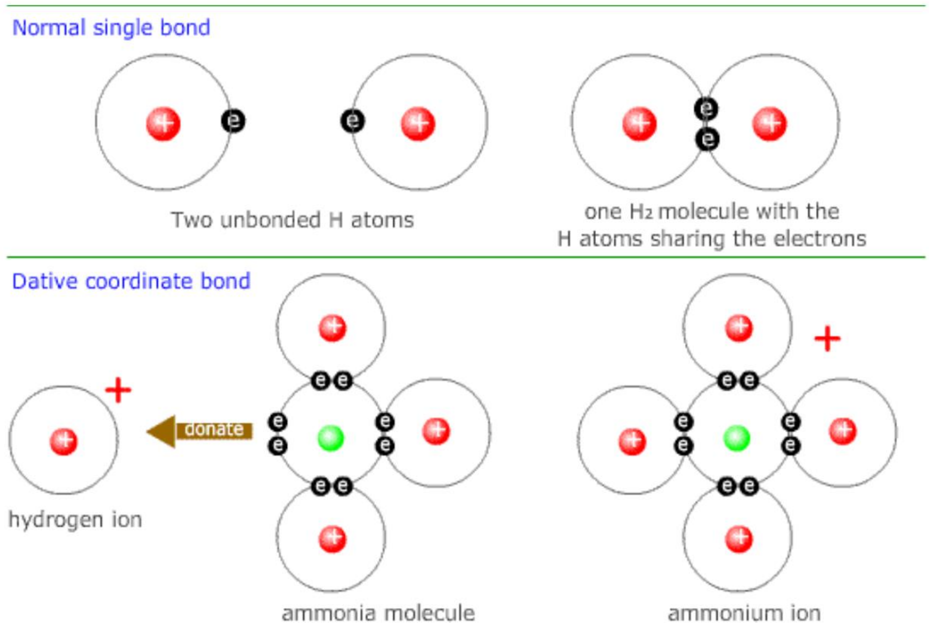


GIANT covalent structures are ALL high melting point solids because a lot of energy is needed to break the STRONG covalent bonds. Strong covalent bonds can exist throughout most, or all of, the structure.



Why do the elements covalently bond?
In HCl, each atom will share ONE electron from the other Hydrogen Chloride attain noble gas configuration.

Dative Covalent Bonding



Metallic Bonding

You don't need to know much about this, it can be summarized in this table.

	Monatomic	Simple Molecular	Giant Covalent	Ionic	Metallic
Substances	Group 8 (Noble Gases)	Elements: H_2, N_2, F_2, Cl_2, Br_2, I_2, S_8, P_4 Compounds: Non-metal with non-metal	Elements: Si, diamond, graphite Compounds: SiO_2	Compounds: metal with non-metal	Elements: metals
What the structure is?	Individual atoms with very weak forces between them	Individual molecules with weak forces between them (atoms joined molecules are joined by covalent bonds)	Lattice structure in which all atoms are joined to others by covalent bonds	Lattice structure of positively and negatively charged ions (ions are held together by attraction between the + and - ions (this +/- attraction is known as an ionic bond, though it is just an electrostatic attractive force)	Lattice structure of metal ions with outer shell electrons free to move through the structure
The formula	Just the symbol e.g. Ar	e.g. H_2O **each molecule contains** 1 O and 2 H **atoms**	e.g. SiO_2 **ratio** of Si:O **atoms** is 1:2 **through** the **structure**	e.g. $MgCl_2$ **ratio** of Mg^{2+}:Cl^- **ions** is 1:2 **through** the **structure**	Just the symbol e.g. Fe
Melting and Boiling Points and Why?	Very Low Very weak forces between atoms	Low Weak forces **between molecules, these ones break to boil to melt (NOT THE ONES WITHIN THE MOLECULES,** the ones in the molecules	Very high Need to break many string covalent bonds	High Strong electrostatic attraction between positive and negative ions	High Strong electrostatic attraction between positive and negative electrons

		are very strong)			
Conductivity	DO NOT CONDUCT No charged particles that can move - atoms are neutral	DO NOT CONDUCT No charged particles that can move - molecules are neutral	DO NOT CONDUCT No charged particles that can move - electrons are NOT delocalised Except graphite, delocalised electrons can move between layers of atoms	CONDUCT (molten / dissolved) Ions can move DO NOT CONDUCT (as solids) Ions cannot move	CONDUCT Outer shell electrons are delocalised
Solubility in water	Insoluble	Insoluble (usually)	Insoluble	Soluble (usually)	Insoluble (but some react with water)