

4. Bonding

Ionic Bonding

Evidence for the existence of ions

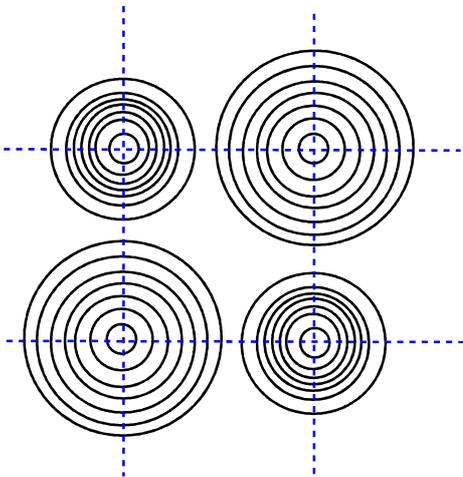
X-ray diffraction: Electron density map of NaCl

These maps show the likelihood of finding electrons in a region

The contours are lines of equal electron density

The maps show that for NaCl

- The ions are arranged in a regular pattern.
- The chloride ions are larger than the sodium ions

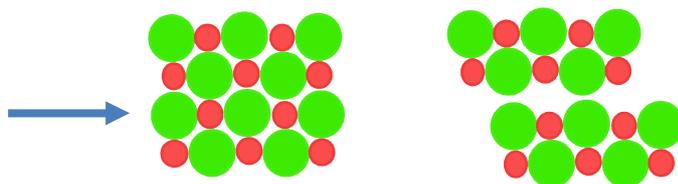


The ions are discrete or separate, because the electron density falls to zero between the ions

The electron density map does not, however, show the edge of the ion and so it is difficult to measure the radius of the ion from an electron density map

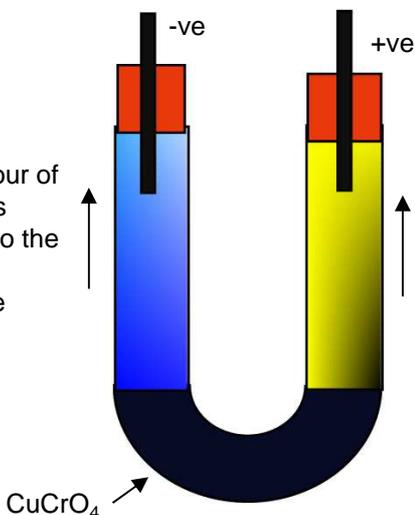
Physical properties of Ionic Compounds

- high melting points (there are strong attractive forces between the ions)
- non conductor of electricity when solid (ions are held together tightly and can not move)
- conductor of electricity when in solution or molten. (ions are free to move)
- brittle / easy to cleave apart



A little force will push the ions along and ions will be next to similar ions. There will be a force of repulsion between like ions, pushing the layers apart

Migration of ions



Blue colour of Cu^{2+} ions migrate to the negative electrode

Yellow colour of CrO_4^{2-} ions migrate to the positive electrode

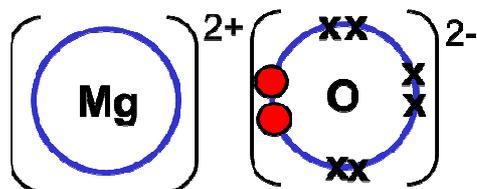
CuCrO_4



A drop of potassium Manganate solution, which is purple, is placed on moist filter paper on a microscope slide and the ends of the slide are connected to a 24 V DC power supply. After ten minutes the purple colour of the MnO_4^- ion has migrated to the positive electrode

Ionic Bonding

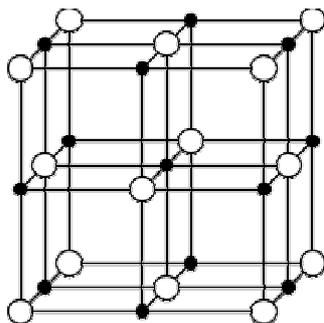
Metal atoms lose electrons to form +ve ions.
Non-metal atoms gain electrons to form -ve ions.



Mg goes from $1s^2 2s^2 2p^6 3s^2$
to $Mg^{2+} 1s^2 2s^2 2p^6$

O goes from $1s^2 2s^2 2p^4$ to
 $O^{2-} 1s^2 2s^2 2p^6$

Ionic crystals have the structure of giant lattices of ions



An ionic bond is the strong **electrostatic force** of attraction between **oppositely charged ions** formed by electron transfer.

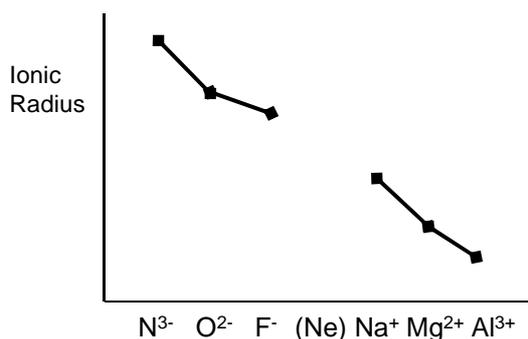
Ionic bonding is stronger and the melting points higher when **the ions are smaller** and/ or have **higher charges**. E.g. MgO has a higher melting point than NaCl as the ions involved (Mg^{2+} & O^{2-} are smaller and have higher charges than those in NaCl, Na^+ & Cl^-)

Ionic Radii

Positive ions are smaller compared to their atoms because it has one less shell of electrons and the ratio of protons to electrons has increased so there is greater net force on remaining electrons holding them more closely.

The negative ions formed from groups five to seven are larger than the corresponding atoms.

The negative ion has more electrons than the corresponding atom but the same number of protons. So the pull of the nucleus is shared over more electrons and the attraction per electron is less, making the ion bigger.



N^{3-} , O^{2-} , F^- and Na^+ , Mg^{2+} , Al^{3+} all have the same electronic structure (of the noble gas Ne)

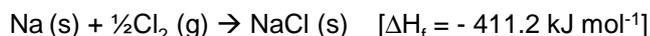
There are increasing numbers of protons from N to F and then Na to Al but the same number of electrons. The effective nuclear attraction per electron therefore increases and ions get smaller

Within a group the size of the ionic radii increases going down the group. This is because as one goes down the group the ions have more shells of electrons.

Definitions of enthalpy changes for stages involved in forming an ionic lattice

Enthalpy change of formation

The standard enthalpy change of formation of a compound is the energy transferred when **1 mole of the compound** is formed from **its elements** under **standard conditions (298K and 100kpa)**, all reactants and products being in their standard states



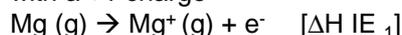
Enthalpy of atomisation

The enthalpy of atomisation of an element is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state



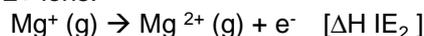
First Ionisation enthalpy

The first ionisation enthalpy is the enthalpy change required to remove 1 mole of electrons from 1 mole of gaseous atoms to form 1 mole of gaseous ions with a +1 charge



Second Ionisation enthalpy

The second ionisation enthalpy is the enthalpy change to remove 1 mole of electrons from one mole of gaseous 1+ ions to produce one mole of gaseous 2+ ions.



First Electron Affinity

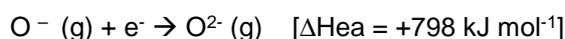
The first electron affinity is the enthalpy change that occurs when 1 mole of gaseous atoms gain 1 mole of electrons to form 1 mole of gaseous ions with a -1 charge



The first electron affinity is exothermic for atoms that normally form negative ions because the ion is more stable than the atom and there is an attraction between the nucleus and the electron

Second Electron Affinity

The second electron affinity is the enthalpy change when one mole of gaseous 1- ions gains one electron per ion to produce gaseous 2- ions.

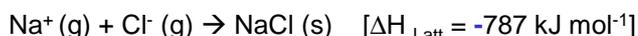


The second electron affinity for oxygen is **endothermic** because it takes energy to overcome the **repulsive force** between the **negative ion and the electron**

First Electron affinity values will become less exothermic as you go down Group 7 from chlorine to iodine because the atoms get bigger and have more shielding so it becomes less easy to attract electrons to the atom to form the negative ion

Enthalpy of lattice formation

The Enthalpy of lattice formation is the standard enthalpy change when **1 mole** of an ionic crystal lattice is formed from its constituent **ions in gaseous form**.



Trends in Lattice Enthalpies

The strength of a enthalpy of lattice formation depends on the following factors

1. The sizes of the ions:

The larger the ions, the less negative the enthalpies of lattice formation (i.e. a weaker lattice). As the ions are larger the charges become further apart and so have a weaker attractive force between them.

2. The charges on the ion:

The bigger the charge of the ion, the greater the attraction between the ions so the stronger the lattice enthalpy (more negative values).

The lattice enthalpies become less negative down any group.
e.g. LiCl, NaCl, KCl, RbCl

e.g group 1 halides (eg NaF KI) have lattice enthalpies of around -700 to -1000

group 2 halides (eg MgCl₂) have lattice enthalpies of around -2000 to -3500

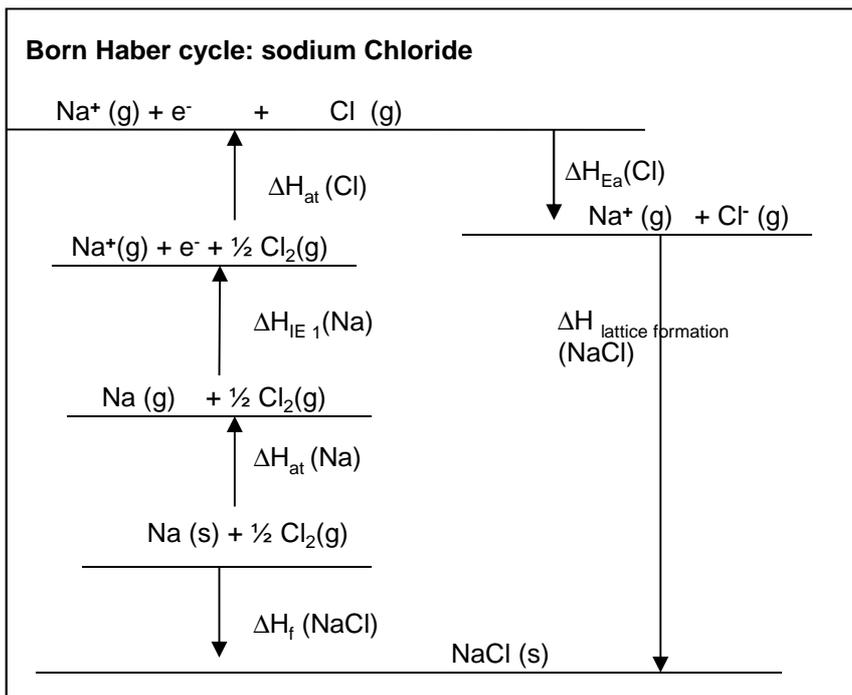
group 2 oxides eg MgO have lattice enthalpies of around -3000 to -4500 kJmol⁻¹

BORN HABER CYCLES

The lattice enthalpy cannot be determined directly. We calculate it indirectly by making use of changes for which data are available and link them together in an enthalpy cycle the Born Haber cycle

Pay attention to state symbols and direction of arrows.

Usually all pieces of data are given except the one that needs to be calculated

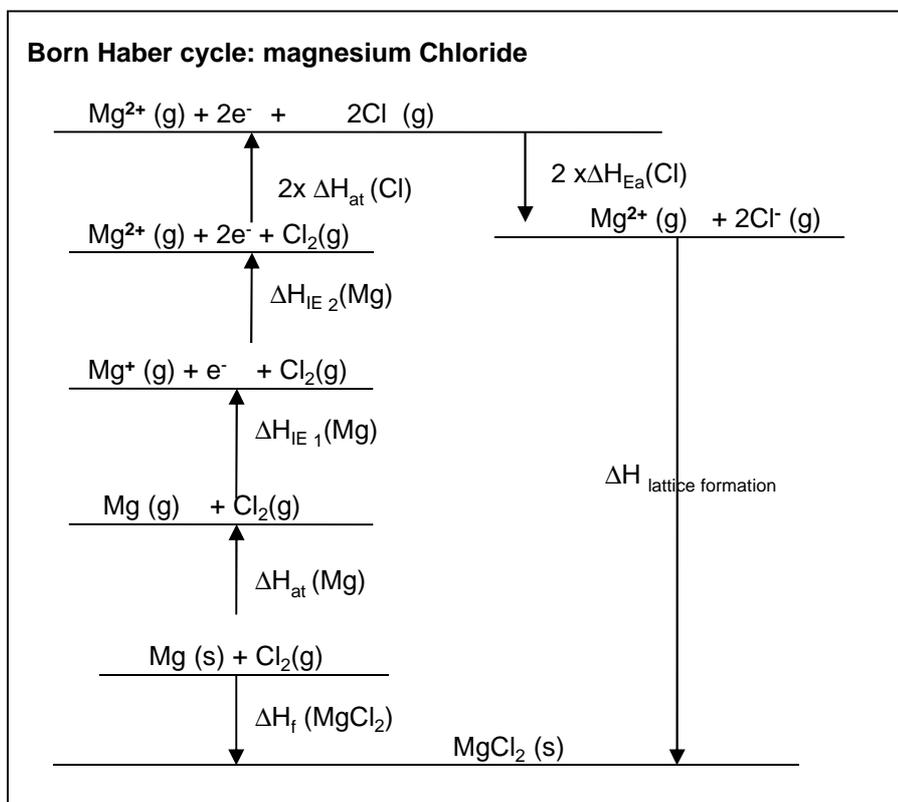


By applying Hess's law the heat of formation equals to the sum of everything else

$$\Delta H_f = \Delta H_{at} \text{Na} + \Delta H_{IE} \text{Na} + \Delta H_{at} \text{Cl} + \Delta H_{Ea} \text{Cl} + \Delta H_{latt \text{ formation}}$$

Rearrange to give $\Delta H_{latt \text{ formation}} = \Delta H_{formation} - (\Delta H_{atm} \text{Na} + \Delta H_{IE} \text{Na} + \Delta H_{atm} \text{Cl} + \Delta H_{Ea} \text{Cl})$

$$\Delta H_{lattice \text{ formation}} = -411 - (+107 + 496 + 122 + -349) = -787 \text{ kJmol}^{-1}$$



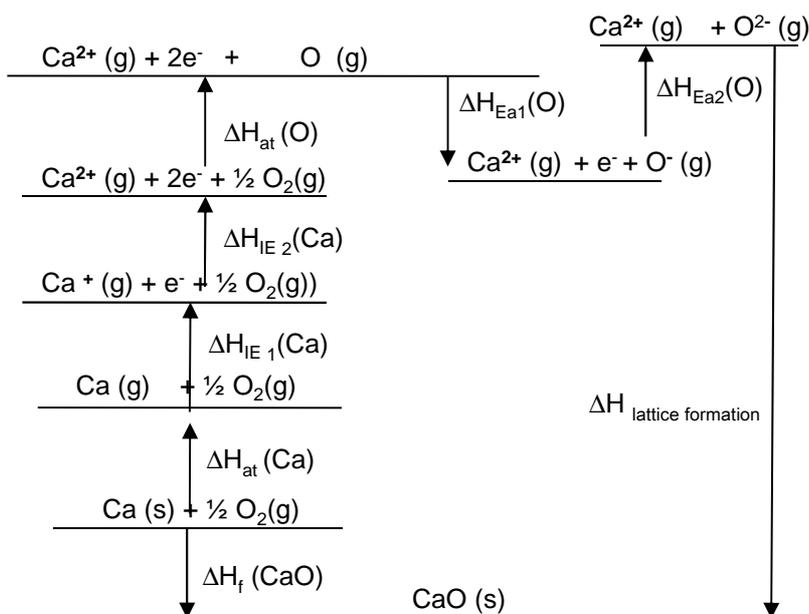
The data for the $\Delta H_{at}(\text{Cl})$ could also be given as the bond energy for $\text{E}(\text{Cl}-\text{Cl})$ bond.

Remember :

$$\text{E}(\text{Cl}-\text{Cl}) = 2 \times \Delta H_{at}(\text{Cl})$$

Note in this example the first and second ionisation energies of magnesium are needed as Mg is a +2 ion

Born Haber cycle: calcium oxide



Notice the second electron affinity for oxygen is **endothermic** because it takes energy to overcome the **repulsive force** between the **negative ion and the electron**

Perfect Ionic Model

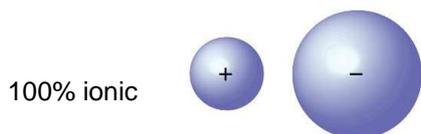
Theoretical lattice enthalpies assume a **perfect ionic model** where the **ions are 100% ionic** and **spherical** and the **attractions are purely electrostatic**.

Differences between theoretical and Born Haber (experimental) lattice enthalpies

The Born Haber lattice enthalpy is the real experimental value.

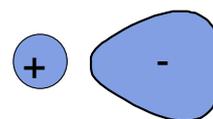
When a compound shows covalent character, the theoretical and the Born Haber lattice enthalpies differ. The more the covalent character the bigger the difference between the values.

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



When 100% ionic the ions are spherical. The theoretical and the Born Haber lattice enthalpies will be the same

Ionic with covalent character



The charge cloud is distorted. The theoretical and the experimental Born Haber lattice enthalpies will differ

The polarising power of a cation increases when

- the positive ion is small
- the positive ion has multiple charges

The polarizability of an anion depends on its size. The bigger the ion the more easily it is distorted

When a compound has some covalent character- it tends towards giant covalent so the lattice is stronger than if it was 100% ionic. Therefore the Born Haber value would be larger than the theoretical value.

Why does Calcium chloride have the formula CaCl_2 and not CaCl or CaCl_3 ?

It is useful to draw out the born haber cycles for each potential case.

We need to calculate an enthalpy of formation for each case.

The one with the **most exothermic enthalpy of formation** will be the one that forms as it will be the most thermodynamically stable

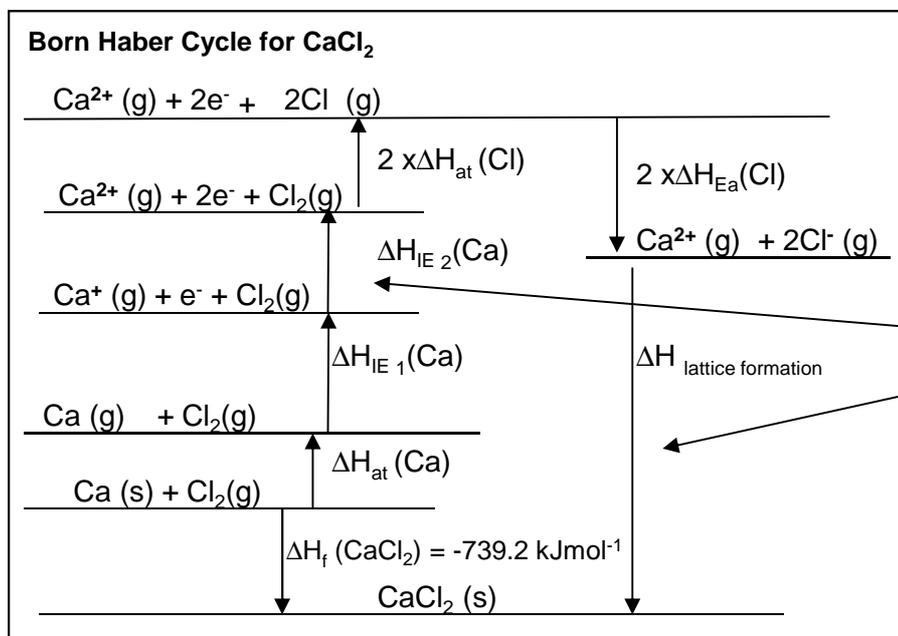
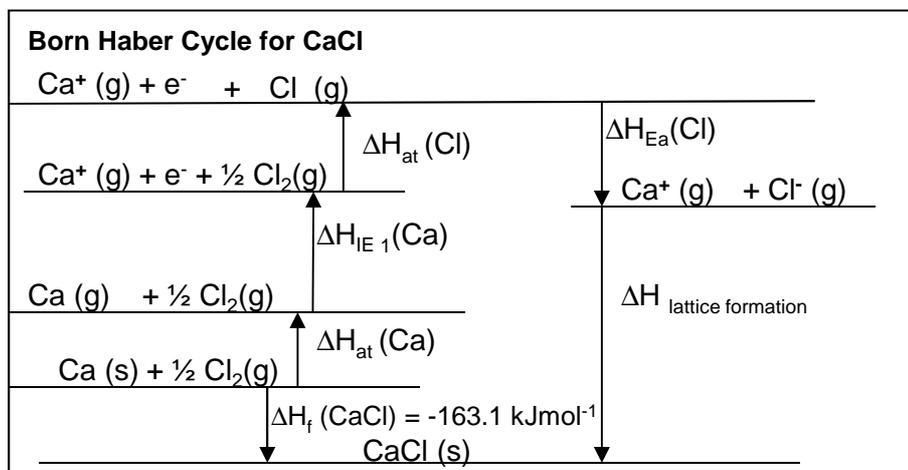
Theoretical lattice enthalpies have been calculated for each case

Theoretical lattice enthalpies
 $\Delta H_{\text{latt}} \text{CaCl} = -719 \text{ kJ mol}^{-1}$
 $\Delta H_{\text{latt}} \text{CaCl}_2 = -2218 \text{ kJ mol}^{-1}$
 $\Delta H_{\text{latt}} \text{CaCl}_3 = -4650 \text{ kJ mol}^{-1}$

These get larger as the positive charge on the calcium ion becomes bigger.

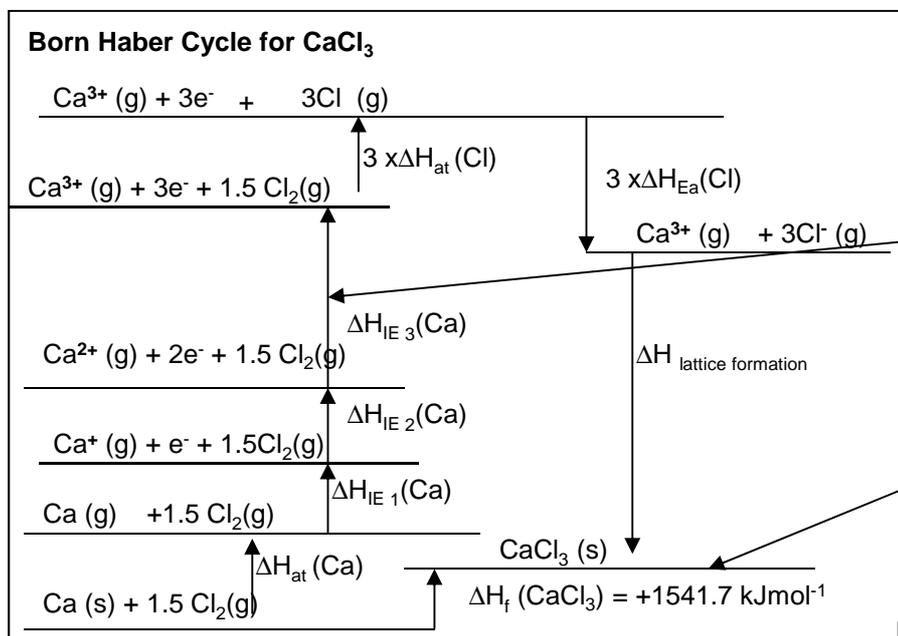
The enthalpy of formation is largely a balance of the ionisation energy and lattice enthalpy.

$\Delta H_f (\text{CaCl})$ is $-163.1 \text{ kJ mol}^{-1}$. This is exothermic.



The increased ionisation enthalpy to form Ca^{2+} is more than compensated for by the stronger lattice enthalpy of formation

The enthalpy of formation is therefore more exothermic. This is the most stable form



The big increase in ionisation enthalpy to remove the 3rd electron is not compensated for by the stronger lattice enthalpy of formation

The enthalpy of formation is therefore endothermic. This is the least stable form

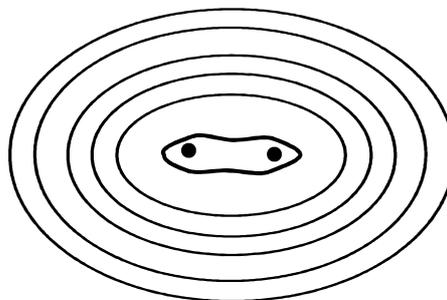
Covalent Bonding

A covalent bond strong and is caused by the electrostatic attraction between the bonding pair of electrons and nuclei.

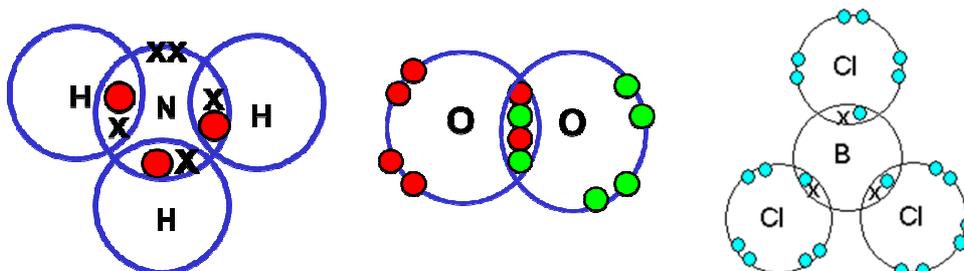
The strength of covalent bond can be demonstrated by the high melting points of giant atomic structures like diamond and graphite. They have high melting points because they contain many strong covalent bonds in a macromolecular structure. It takes a lot of energy to break the many strong bonds.

The X-ray diffractions for the hydrogen molecule show high concentration of negative charge between H nuclei. This negative charge is strongly attracted by both nuclei so attractive interactions exceed repulsive ones

In a covalent compound there is significant electron density between the atoms



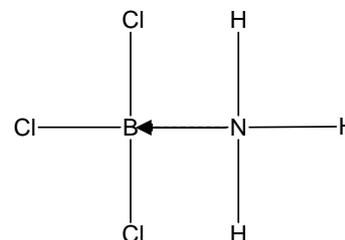
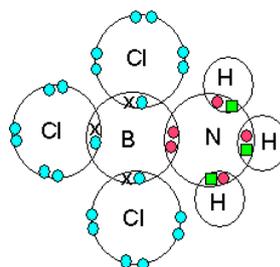
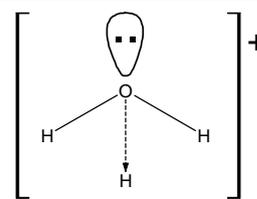
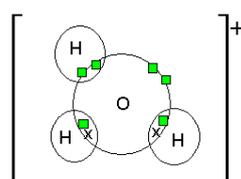
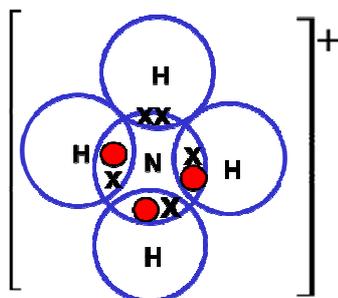
Electron Configuration Diagrams



Dative Covalent bonding

A **Dative covalent bond** forms when the **shared pair of electrons** in the covalent bond come from **only one of the bonding atoms**. A **dative covalent bond** is also called co-ordinate bonding.

Common examples you should be able to draw that contain dative covalent bond (e.g. NH_4^+ , H_3O^+ , NH_3BF_3)



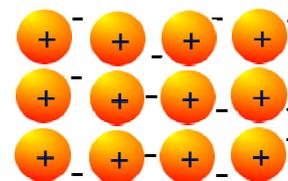
The dative covalent bond acts like an ordinary covalent bond when thinking about shape so in NH_4^+ the shape is tetrahedral

The direction of the arrow goes from the atom that is providing the lone pair to the atom that is deficient

Metallic bonding

Metals consist of giant lattices of metal ions in a sea of delocalised electrons

Definition: A **metallic bond** is the **electrostatic force** of attraction between the **positive metal ions** and the **delocalised electrons**



sodium

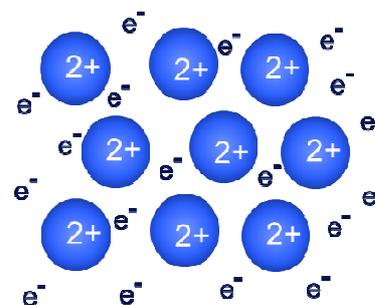
The three main factors that affect the strength of a **metallic bond** are:

1. Number of protons/ Strength of nuclear attraction.
The more protons the stronger the bond
2. Number of delocalised electrons per atom (the outer shell electrons are delocalised)
The more delocalised electrons the stronger the bond
3. Size of ion.
The smaller the ion, the stronger the bond.

Metals have high melting points because the strong electrostatic forces between positive ions and sea of delocalised electrons require a lot of energy to break

Example

Mg has stronger metallic bonding than Na and hence a higher melting point. The Metallic bonding gets stronger because in Mg there are more electrons in the outer shell that are released to the sea of electrons. The Mg ion is also smaller and has one more proton. There is therefore a stronger electrostatic attraction between the **positive metal ions and the **delocalised electrons** and **higher** energy is needed to break bonds.**

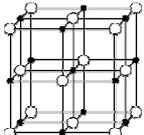
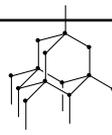
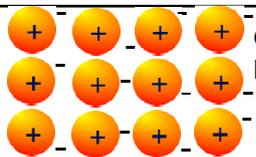


magnesium

Metals can conduct electricity well because the delocalised electrons can move through the structure

Metals are malleable because the positive ions in the lattice are all identical. So the planes of ions can slide easily over one another. The attractive forces in the lattice are the same whichever ions are adjacent

Bonding and Structure

Bonding	Structure	Examples
Ionic : electrostatic force of attraction between oppositely charged ions	 <p>Giant Ionic Lattice</p>	Sodium chloride Magnesium oxide
Covalent : shared pair of electrons	<p>Simple molecular: With intermolecular forces (van der Waals, permanent dipoles, hydrogen bonds) between molecules</p>	Iodine Ice Carbon dioxide Water Methane
Covalent : shared pair of electrons	<p>Macromolecular: giant molecular structures.</p> 	Diamond Graphite Silicon dioxide Silicon
Metallic: electrostatic force of attraction between the metal positive ions and the delocalised electrons	 <p>Giant metallic lattice</p>	Magnesium, Sodium (all metals)

Only use the words **molecules** and **intermolecular forces** when talking about simple molecular substances

Property	Ionic	Molecular (simple)	Macromolecular	Metallic
boiling and melting points	high- because of giant lattice of ions with strong electrostatic forces between oppositely charged ions.	low- because of weak intermolecular forces between molecules (specify type e.g van der waals/hydrogen bond)	high- because of many strong covalent bonds in macromolecular structure. Take a lot of energy to break the many strong bonds	high- strong electrostatic forces between positive ions and sea of delocalised electrons
Solubility in water	Generally good	generally poor	insoluble	insoluble
conductivity when solid	poor: ions can't move/ fixed in lattice	poor: no ions to conduct and electrons are localised (fixed in place)	diamond and sand: poor, because electrons can't move (localised) graphite: good as free delocalised electrons between layers	good: delocalised electrons can move through structure
conductivity when molten	good: ions can move	poor: no ions	poor	(good)
general description	crystalline solids	mostly gases and liquids	solids	shiny metal Malleable as the positive ions in the lattice are all identical. So the planes of ions can slide easily over one another -attractive forces in the lattice are the same whichever ions are adjacent