

BONDING

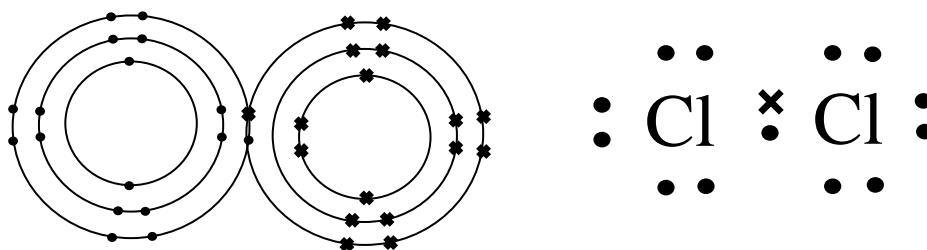
In the process of bonding electrons move to a lower energy level to form a more stable structure. This can be done by transferring electron(s) to another atom or by pairing with an electron from another atom.

Covalent bonding

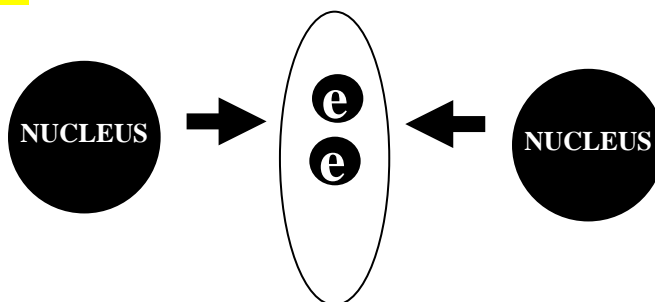
Two non-metal atoms can form a stable octet structure by sharing electrons.

Many simple covalent compounds obey the **octet rule**: the atoms form sufficient covalent bonds to make their outer shells up to eight electrons.

Example; chlorine



The shared electrons are positioned between the nuclei of each atom, and there is attraction between the positive nucleus of each atom and the shared electrons which holds the atoms together.

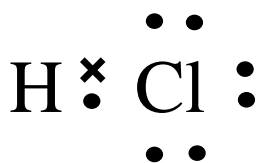


This is called covalent bonding. The two electrons which are shared are called the bonding pair.

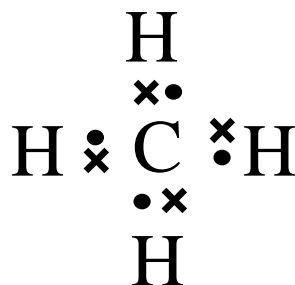
Key Points on Covalent Bonding

- Electron deficient atoms share a pair of electrons to form stable electronic structures.
- The shared electron pair is attracted to the nuclei of each atom holding the atoms together strongly.
- Atoms joined in this way form molecules.
- Covalent materials may consist of simple molecules, polymers or giant molecules

Further examples

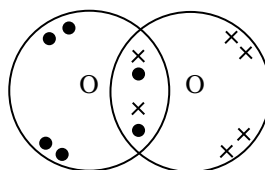
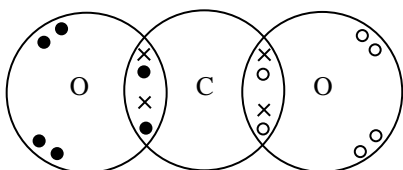


Hydrogen chloride



Methane

If two electron pairs are shared between the same atoms, they form a double bond, as in CO_2 , O_2 :



If three electron pairs are shared between the same atoms, they form a triple bond, as in N_2 :



Note that non-bonding electrons are paired up as “lone pairs”.

Physical Properties of covalently bonded compounds

Covalent compounds composed of simple molecules have weak intermolecular forces between the molecules. Little energy is needed to overcome these forces, so the melting and boiling points of these substances are low.

Giant molecular substances have strong covalent bonds throughout the structure and so require a large amount of energy to overcome them and these substances have high melting and boiling point.

In general covalent substances do not have free electrons, so they are non-conductors of electricity.

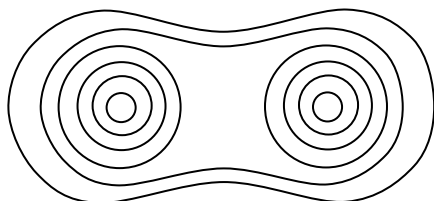
Graphite is exceptional as a covalent material in that it does have free electrons and so is a conductor.

(Details of diamond and graphite are covered in the “Shapes of Molecules and Ions” section).

Electron density maps

Electron density maps for covalent molecules can be plotted.

The electron density map for a molecule such as iodine is shown below.



The even distribution of electron density between the two atoms can be seen in this diagram.

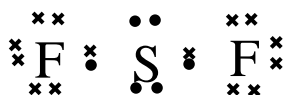
Expansion of the octet

Although the octet is a particularly stable structure, it is possible for other stable structures to form. An atom can increase the number of single electrons it has, and so the number of bonds it can form by "splitting" an electron pair.

Sulphur is an example.

What would you expect the formula of sulphur fluoride to be? SF_2

Draw a dot and cross diagram of sulphur fluoride.

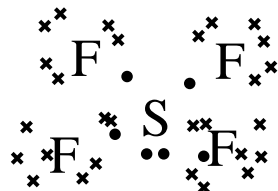


It is possible for an electron pair in sulphur to split. Splitting an electron pair takes in energy, but the extra energy produced by forming extra bonds makes it possible.



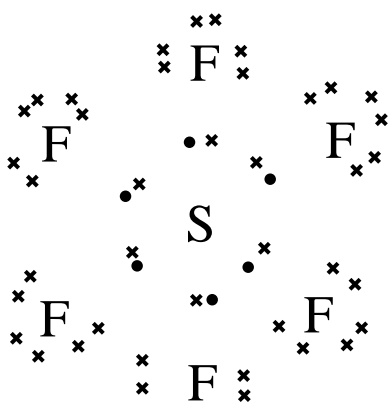
If an electron pair in sulphur is split, the sulphur can then form four bonds.

Example, SF_4

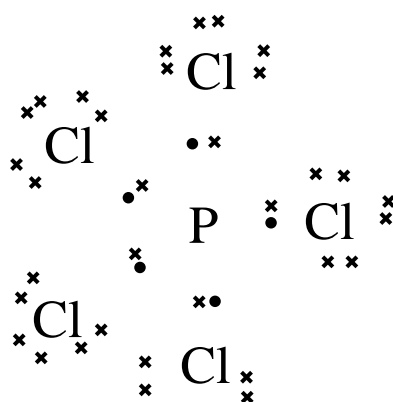


This process splitting electron pairs means that an atom in a compound can have more than 8 electrons, and it is referred to as expanding the octet.

Other examples are SF_6 and PCl_5 .



Sulphur hexafluoride, SF_6



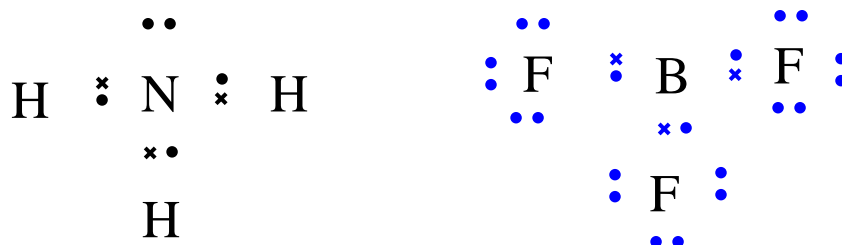
Phosphorus pentachloride, PCl_5

The elements in the second period do not do this because the energy to split the electron pair is too great to be compensated for by the formation of extra bonds, but elements below Period 2 form a number of compounds of this type.

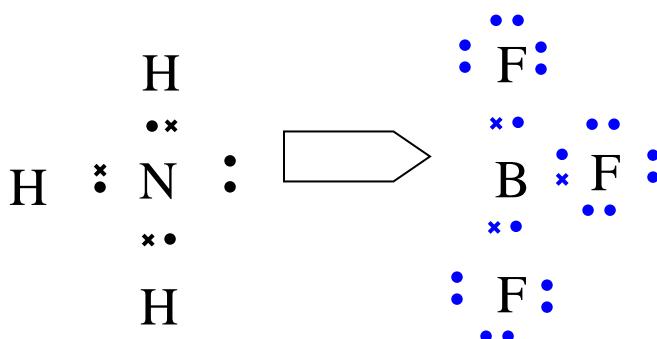
Dative covalent bonding

Coordinate bonding or **dative covalent bonding** is similar to normal covalent bonding in that the bond consists of an electron pair. It is different in that instead of one electron coming from each atom, both the electrons come from a single atom.

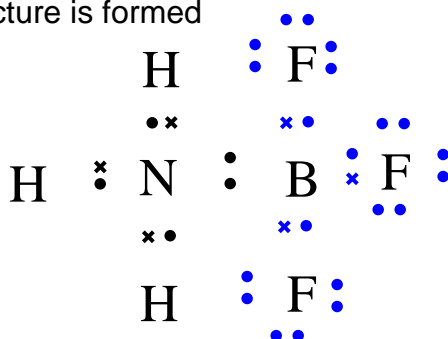
Consider the structure of boron trifluoride and ammonia;



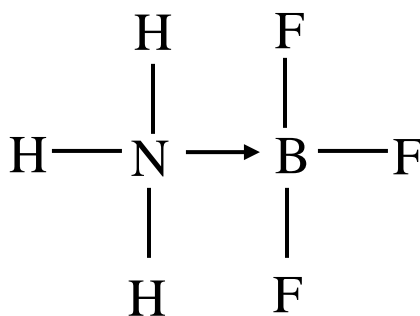
The boron only has three electron pairs in the outer shell. The nitrogen has a lone pair of electrons. These two molecules form a dative bond by the nitrogen using the lone pair to donate to the vacant site on the boron.



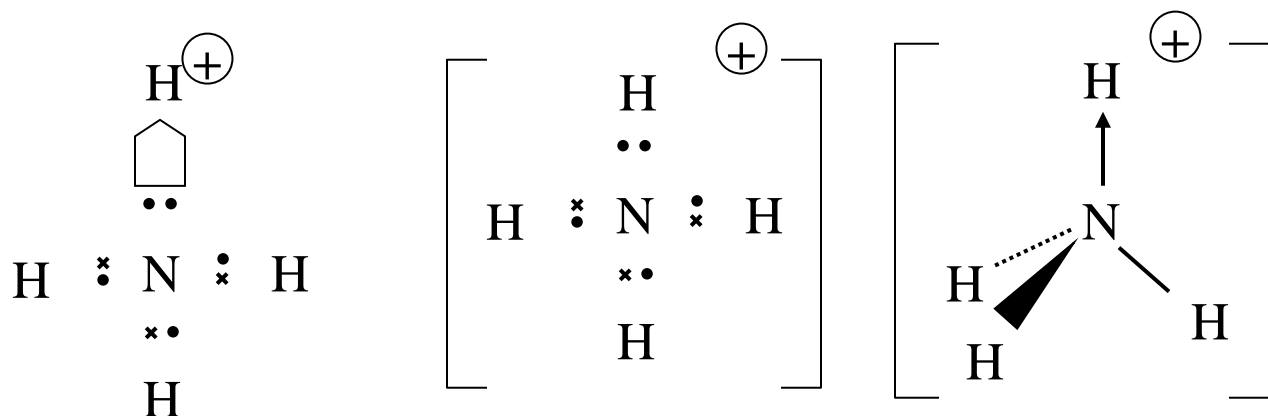
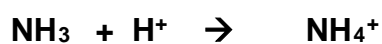
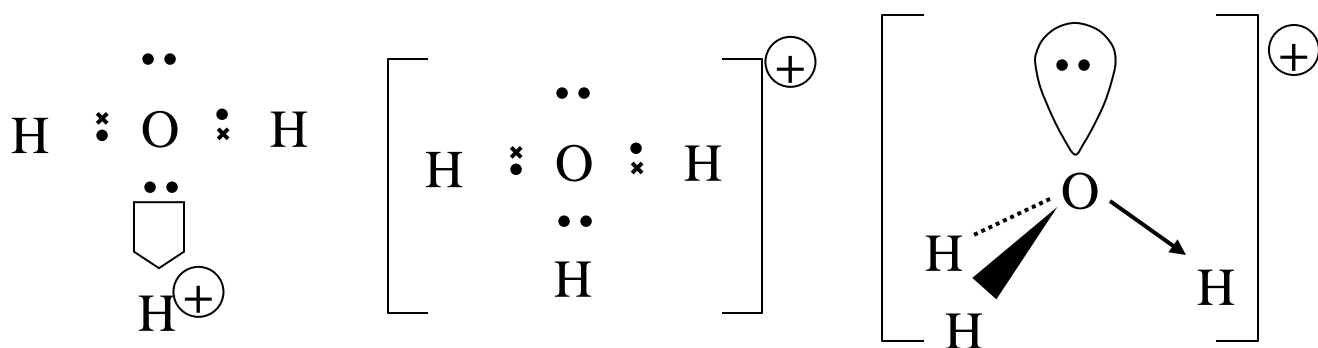
The following structure is formed



This can be represented as follows, with the dative bond represented by an arrow;



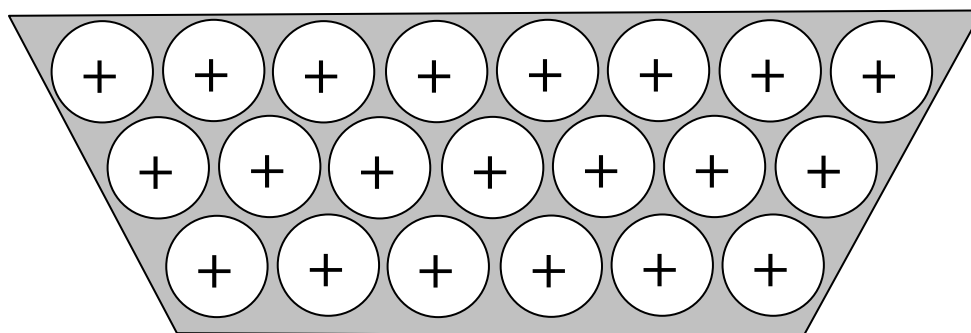
Other examples of the dative bond occur in the formation of the hydroxonium and ammonium ions;



Metallic bonding

Metals can be visualised as being made up of positive ions surrounded by a cloud of electrons. Metals are electropositive; that is they tend to release their valence electrons and form positive ions. It is these electrons which make up the electron cloud.

The structure is held together by the attraction between these positive ions and the electron cloud or delocalised electrons.



This structure gives metals their properties. Since the bonding electrons are not fixed they are said to be **delocalised**, it means that a small potential difference will cause the electrons to move - making metals good electrical conductors.

Electron movement also assists in the conduction of heat energy- making metals good conductors of heat. The absence of fixed bonds allows the ions to move giving the characteristics of malleability and ductility.

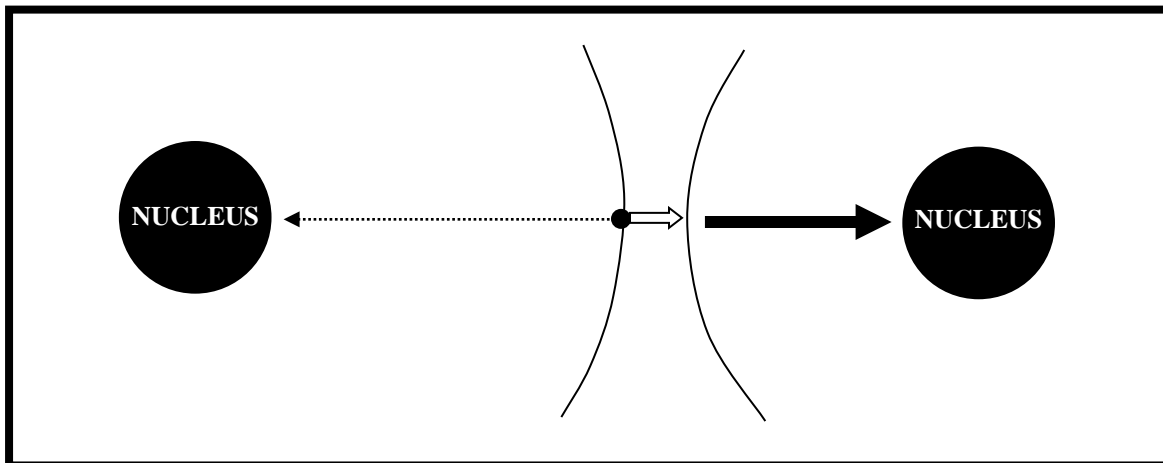
Factors effecting the strength of metallic bonding:

1. The more valence electrons the stronger the bonding; as there is a higher charge on the cations and there is a higher charge in the electron fields.
2. The smaller the metal ion the stronger the bonding; as the electrons become closer to the centre of the positive charge.

The metallic bonding determines physical properties of metals. The more valence electrons there are, the better the conductivity. The stronger the metallic bonding the higher the melting and boiling points.

Ionic bonding

Metal atoms hold their outer (valence) electrons weakly. Non-metals have a strong pull for the outer electrons. There is a tendency for metal atoms to transfer electrons to non-metal atoms.



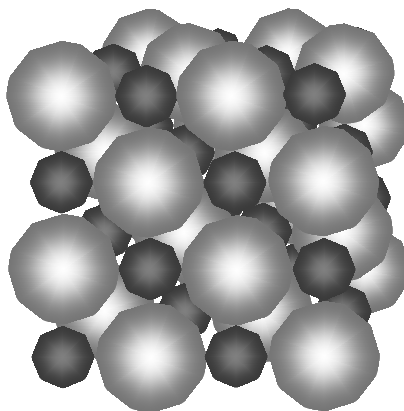
When this happens the metal atom forms a positive ion (so metals are termed electropositive) and the non-metal atom forms a negative ion (non-metals are said to be electronegative). The ions formed have a stable "octet structure"

The strong electrostatic attraction between the cation and the anion lead to a strong ionic bond. This forms a giant structure built up of these oppositely charged ions.

The strong electrostatic forces within the giant structure mean that it requires a large amount of energy to break them down. As a result of this, ionic compounds have high melting and boiling points.

The ionic compounds are unable to conduct electricity in solid form, but when dissolved in water or in molten form the ions are free to move and so they conduct.

Sodium chloride is an ionic compound. The structure of this compound is shown here.



Key Points on Ionic Bonding

- An electron (or electrons) is transferred from one atom to another to form stable electronic structures.
- In this process positive and negative ions are formed
- The oppositely charged ions attract and have very strong electrostatic forces
- A giant structure of ions is formed
- The compounds have high melting and boiling points
- The compounds do not conduct as solids, but do when molten or in solution.

Representing ionic compounds

Ionic substances are giant structures, but the essential electronic structure of an ionic compound can be represented by showing one set of ions.

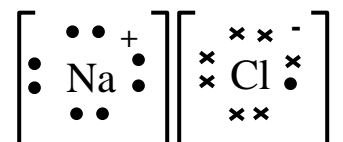
Example - Sodium chloride

Simple electronic configuration Sodium: 2, 8, 1 Chlorine: 2, 8, 7

To form stable structures an electron is transferred from sodium to chlorine.

Sodium ion: 2, 8 Chloride ion: 2, 8, 8

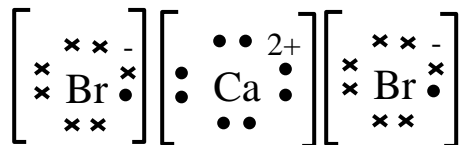
A diagram to the ionic compound shows just the outer shell.



Example 2 - Calcium bromide Calcium: 2, 8, 8, 2 Bromine: 2, 8, 18, 7

To form stable structures two electrons are transferred from calcium one each to two bromine atoms.

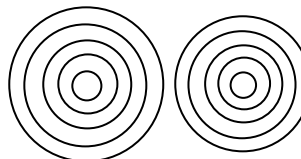
Calcium ion: 2, 8, 8 Bromide ion: 2, 8, 18, 8



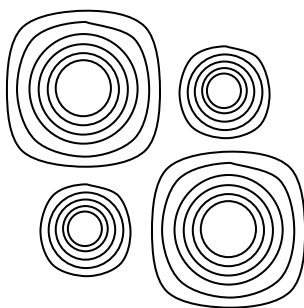
Electron density maps

X rays can be deflected off solids to give us information about their structure. X ray diffraction of ionic solids can be presented as an electron density map. An electron density map shows lines which represent areas of equal electron density.

An idealised electron map for an ion pair in an ionic compound is shown to the right. It is important to remember that the lines do not represent shells.



In practice the situation is more complex as the cation can distort the electron field of the anion.



The electron density map for sodium chloride is shown to the left. The distortion of the ions, particularly the chloride can be seen.

Sizes of ions in a Group

Going down a group of the Periodic Table, the ions formed have the same charge. As the atoms from which they were formed become larger so do the ions.

Sizes of isoelectronic ions

Isoelectronic ions are ions that have the same number of electrons.

Atom	N	O	F	Na	Mg	Al
Number of electrons	7	8	9	11	12	13
Forms ions by	Gaining 3 electrons	Gaining 2 electrons	Gaining 1 electron	Losing 1 electron	Losing 2 electrons	Losing 3 electrons
Formula of ion	N^{3-}	O^{2-}	F^{-}	Na^{+}	Mg^{2+}	Al^{3+}
Number of electrons	10	10	10	10	10	10
Size of ion /nm	0.171	0.140	0.136	0.095	0.065	0.050

As the ions all have the same number of electrons, the size of the ion is determined by the charge on the nucleus. As the nuclear charge increases from N to Al so does the attraction of the electrons to the nucleus and so the ionic size decreases.

Ionic compounds and Energy

Energy changes take place when ionic compounds are formed.

The process of bond breaking is endothermic and the process of bond breaking is exothermic. The energy changes that take place when an ionic compound forms are shown below.

Bond breaking

- Energy taking in - to convert the metal lattice into individual metal atoms.
- Energy taking in - to convert the non-metal molecules to individual non-metal atoms.

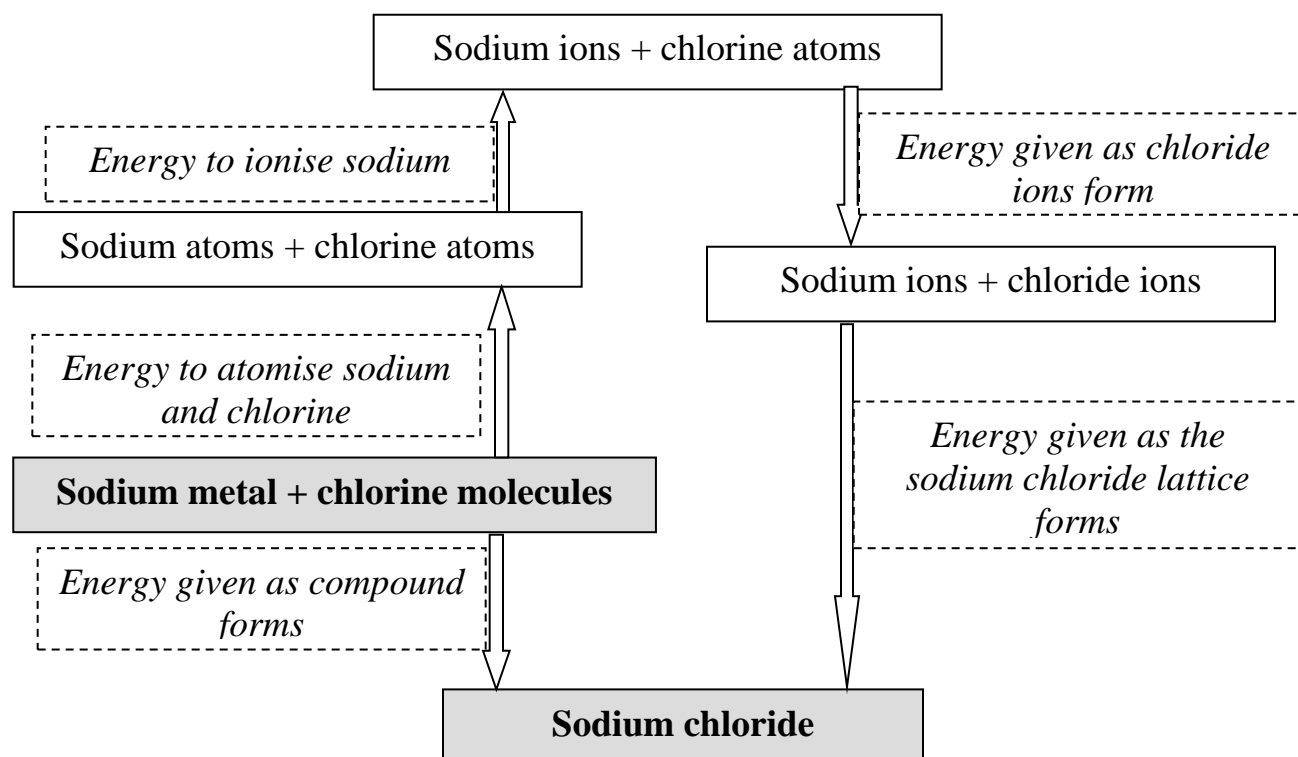
Ion formation

- Energy taking in - to convert the individual metal atoms into individual metal ions.
- Energy given out - when the individual non-metal atoms gain an electron to form an anion.

Bond forming

- Energy given out – as the cations and anions come together to form an ionic lattice - the **Lattice Enthalpy**.

This process is shown below for sodium chloride.



Such an energy diagram is called a **Born-Haber cycle**.

(It is not necessary to construct a Born-Haber cycle for Unit 1).

The Lattice Enthalpy can be calculated from this.

$$\Delta H_{\text{Lat}} = \Delta H_f - (\Delta H_{\text{at}}\{\text{Na}\} + \Delta H_{\text{at}}\{\text{Cl}\} + \text{IE}\{\text{Na}\}) - \text{EA}(\text{Cl})$$

For sodium chloride

$$\Delta H_{\text{Lat}} = -411 - (109 + 121 + 494) - -364 = -771 \text{ kJmol}^{-1}$$

The values obtained from these Born-Haber cycles have to be found by experimental measurement of the various energy values and so are often referred to as **experimentally determined lattice enthalpies**.

They represent the actual lattice enthalpy, as opposed to a theoretical lattice enthalpy, which is based on a theoretical model for ionic compounds.

Considering Born-Haber cycles allows us to see why compounds have the formulae they do.

Take calcium chloride as an example.

Relevant values

1 st ionization energy of calcium	590 kJmol ⁻¹
2 nd ionization energy of calcium	1150 kJmol ⁻¹
3 rd ionization energy of calcium	4940 kJmol ⁻¹
Electron affinity of chlorine	-364 kJmol ⁻¹
Lattice enthalpy of CaCl	-720 kJmol ⁻¹
Lattice enthalpy of CaCl ₂	-2237 kJmol ⁻¹
Atomization enthalpy of Ca	193 kJmol ⁻¹
Atomization enthalpy of Cl	121 kJmol ⁻¹

The enthalpy of formation can be found by rearranging the equation used above.

$$\Delta H_{\text{Lat}} = \Delta H_f - (\Delta H_{\text{at}}\{\text{Ca}\} + \Delta H_{\text{at}}\{\text{Cl}\} + \text{IE}\{\text{Ca}\}) - \text{EA}(\text{Cl})$$

$$\Delta H_f = \Delta H_{\text{Lat}} + (\Delta H_{\text{at}}\{\text{Ca}\} + \Delta H_{\text{at}}\{\text{Cl}\} + \text{IE}\{\text{Ca}\}) + \text{EA}(\text{Cl})$$

$$\text{For CaCl} \quad \Delta H_f = -720 + 193 + 121 + 590 - 364 = -180 \text{ kJmol}^{-1}$$

$$\text{For CaCl}_2 \quad \Delta H_f = -2237 + 193 + 121 + 590 + 1150 + 2 \times -364 = -790 \text{ kJmol}^{-1}$$

More energy is needed to form Ca²⁺ but this is outweighed by the much larger lattice enthalpy, so the formation CaCl₂ is energetically more favourable than for CaCl.

The lattice enthalpy of CaCl₃ is greater than for CaCl₂, but the extremely large amount of energy needed to form the Ca³⁺ makes the process energetically unfavourable.

Factors influencing lattice enthalpy.

The lattice enthalpy of an ionic compound is affected by the size and charge on the ions which make it up.

A decrease in the size of any ion increases the lattice enthalpy. This is because small ions can be close together and the smaller distance of separation the larger the attractive force between the ions.

An increase in charge also increases lattice enthalpy. This is because the force of attraction between ions increases as the charge on the ion increases.

Theoretical determination of lattice enthalpy

It is possible to calculate the lattice enthalpy by visualizing the ionic lattice as made up of perfectly spherical ions in a lattice. The lattice enthalpy is determined theoretically by calculating all the forces of attraction and repulsion in the lattice.

A simplified version of this is given below:

$$\Delta H_{LE}^{\ominus} = -\text{constant} \times \frac{z_+ \times z_-}{r_+ + r_-} \quad \text{i.e.} \propto [\text{product of charges}] \div [\text{sum of radii}]$$

Here, the constant depends on the type of structure (the way in which the ions pack together). z_+ and z_- are the charge on the cation and anion respectively, and r_+ and r_- are the radii of cation and anion.

A comparison of the lattice energies of NaCl (-770 kJ mol^{-1}) and MgCl_2 ($-2500 \text{ kJ mol}^{-1}$) shows a much more negative value for the magnesium compound: not only is z_+ double for Mg^{2+} , but also its ion has a smaller radius (r_+), and this too leads to a larger lattice energy.

Comparing experimental and theoretical values for lattice enthalpy

The lattice energy is the energy change which occurs when well separated gaseous ions are brought together to form a crystal. As stated above, it is possible to obtain a theoretical value of the lattice energy by considering all the attractions and repulsions between the ions in the lattice.

The values obtained by using Born-Haber cycles are determined by experiment and reflect the actual value.

The table below compares theoretical lattice energies with experimental lattice energies.

Compound	Experimental value / kJ mol^{-1}	Theoretical value / kJ mol^{-1}	Difference in values / kJ mol^{-1}
MgF_2	-2957	-2913	44
MgI_2	-2327	-1944	383

The compound magnesium fluoride has theoretical values which agree quite well with the experimental value, but the magnesium iodide values agree less well. In general the iodides tend to show a greater difference between these values than fluorides.

The experimental values show that lithium halides are actually more stable than would be expected by regarding them as purely ionic compounds. In the same way, iodides are in reality more stable than would be expected by treating them theoretically as purely ionic compounds. This discrepancy is caused by a covalent character which exists in the ionic lattice.

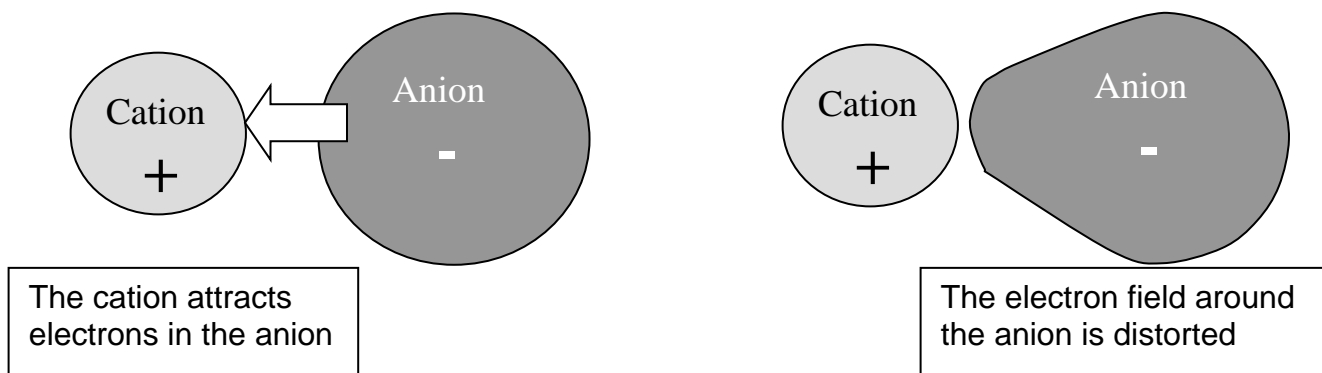
The greater the difference between the experimental value and the theoretical value, the greater the degree of covalency in the lattice.

This covalency is caused by **polarisation**.

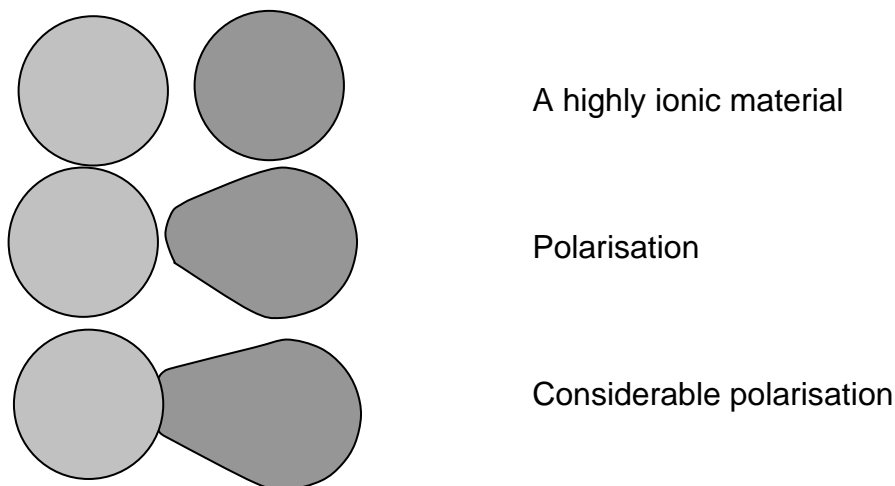
Polarisation in Ionic Bonding

When an ionic bond is formed, the metal atom transfers one or more electrons to the non-metal and a cation (+) and an anion (-) are formed.

In perfect ionic bonding there is complete separation of charge. In polarised ionic bonding some of the electron charge on the anion is pulled back towards the cation.



Polarisation occurs to different extents according to the ions involved



The extent of the polarisation depends on how much the cation pulls on the electrons; the **polarising power**, and on how much the anion allows the electrons to be pulled away: the **polarisability**.

Polarising power is increased by higher positive charge and smaller cation.

Polarisability is increased by higher negative charge and larger anion.

Factors which increase polarisation in ionic compounds

1. increased charge on anion or cation,
2. increased size of anion,
3. decreased size of cation.

Low polarisation

low charge (+1,-1)
small anion
large cation

e.g. K^+F^-

High polarisation

high charge (+3,-3)
large anion
small cation

e.g. $Al^{3+} (I^-)_3$

It is of course incorrect to regard ion pairs in isolation, because they actually exist in a lattice.

Polarisation of ionic compounds gives the compounds a covalent character.

The greater the polarisation, the greater the covalent character.

The extent of this polarisation can be found by comparing theoretical and experimental lattice enthalpies.

When such a comparison was carried out with selected compounds in the previous section, it was seen that lithium and iodide compounds demonstrate significant covalent character.

Lithium has a high polarising power and iodides have a high polarisability.

The more polarised the compound, the greater the difference between the theoretical values and the experimental values.

Further example

compound	Lattice enthalpy value based on theoretical ionic model	Lattice enthalpy value based on experiment
sodium chloride	-766.1 kJmol ⁻¹	-776.4 kJmol ⁻¹
silver chloride	-768.6 kJmol ⁻¹	-916.3 kJmol ⁻¹

Sodium chloride is almost 100% ionic, hence the good agreement.

Silver chloride has a poor agreement and so has some covalent nature in its bonding.