Higher

Chemistry

HSN11300
Unit 1 Topic 3

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Topic 3 – Patterns in the Periodic Table

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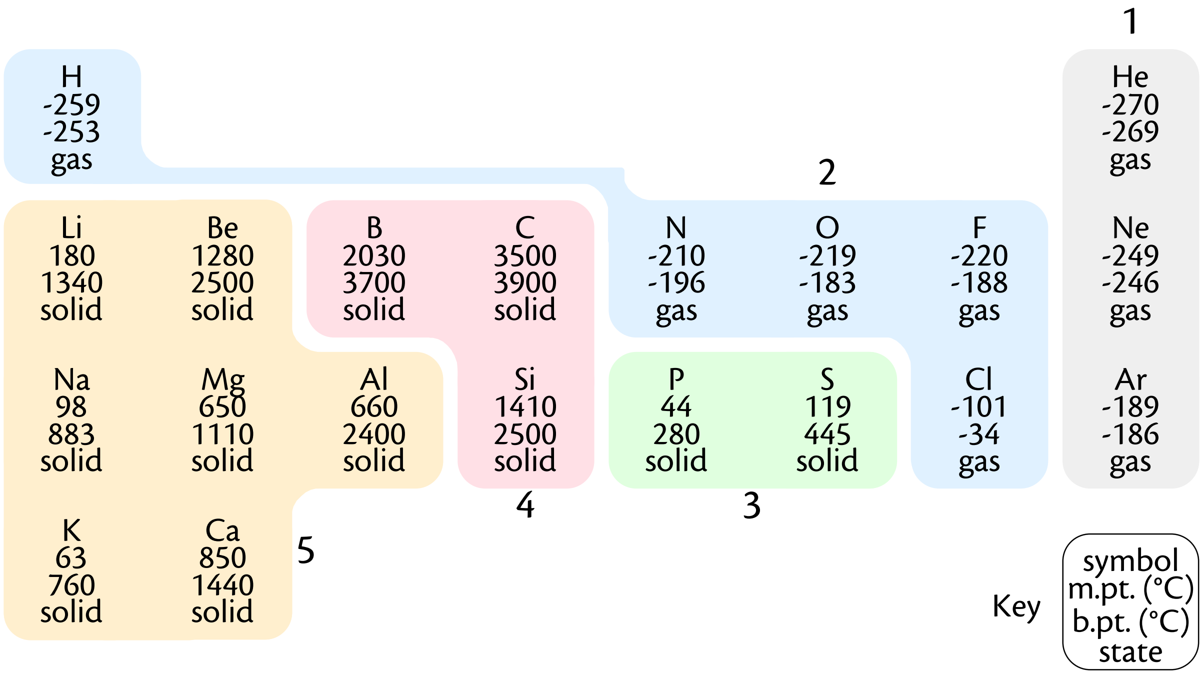
The Periodic Table

The modern periodic table is based on that first drawn up by the Russian chemist, Mendeleev, in about 1870. He listed the known elements in order of increasing atomic mass and then arranged them so that those with similar chemical properties fell into the same vertical column. He left gaps for elements not yet discovered, like germanium, and predicted their properties with accuracy. The periodic table that we use is very similar to Mendeleev's but has all the elements arranged in order of their Atomic Number. The vertical columns are called groups and the horizontal rows are called periods. Make sure you know the work on the periodic table covered at Standard Grade.

We are now going to see how the structures of the elements affect physical properties.

Melting Points and Boiling Points of the Elements

Look at the melting and boiling points (in °C) of the elements in the table below. There is a very large range of values but they can quite easily be put into 5 groups. The state in which the element exists at room temperature is also given.

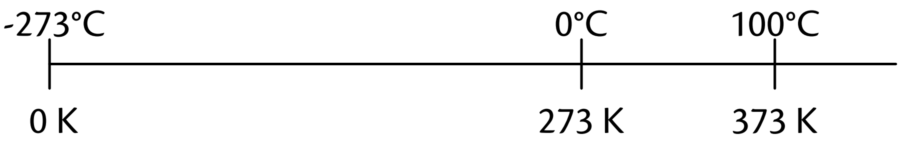


H -259 -253 gas							He -270 -269 gas
Li 180 1340 solid	Be 1280 2500 solid	B 2030 3700 solid	C 3500 3900 solid	N -210 -196 gas	O -219 -183 gas	F -220 -188 gas	Ne -249 -246 gas
Na 98 883 solid	Mg 650 1110 solid	Al 660 2400 solid	Si 1410 2500 solid	P 44 280 solid	S 119 445 solid	Cl -101 -34 gas	Ar -189 -186 gas
K 63 760 solid	Ca 850 1440 solid						

Key

symbol
m.pt. (°C)
b.pt. (°C)
state

A very similar table is on page 4 of your Data Book but note that the temperatures are given on the Kelvin scale. The relationship between degrees Celsius and Kelvin is shown below.



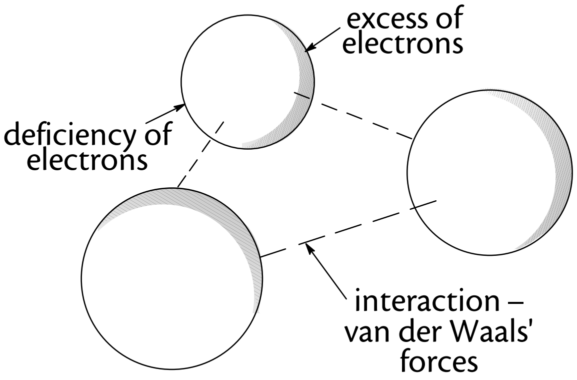
By studying the bonding in each group of elements we can explain the range of melting points. The melting point temperature of a solid is a measure of the amount of energy needed to break the bonds which hold the basic particles (atoms or molecules) together. So high melting points indicate strong bonds are being broken.

1. Noble Gases

Helium atoms have only 2 electrons. They fill the 1st shell and this is a stable arrangement. All the other noble gases have 8 electrons in their outer shells. We know that this is a stable arrangement. Because the atoms are already stable, they don't join with each other. They exist as separate single discrete atoms – they are monatomic.

Although they have very low melting points, the Noble gases can be obtained in the solid state. This means that there must be some force holding the atoms together. The force is called van der Waals force and it arises as follows:

The electrons in an atom are constantly in motion resulting in uneven distribution of the electrons round the atom. This causes temporary dipoles in which one side of the atom is slightly negative and so the other side becomes slightly positive. These temporary dipoles attract each other (see diagram).

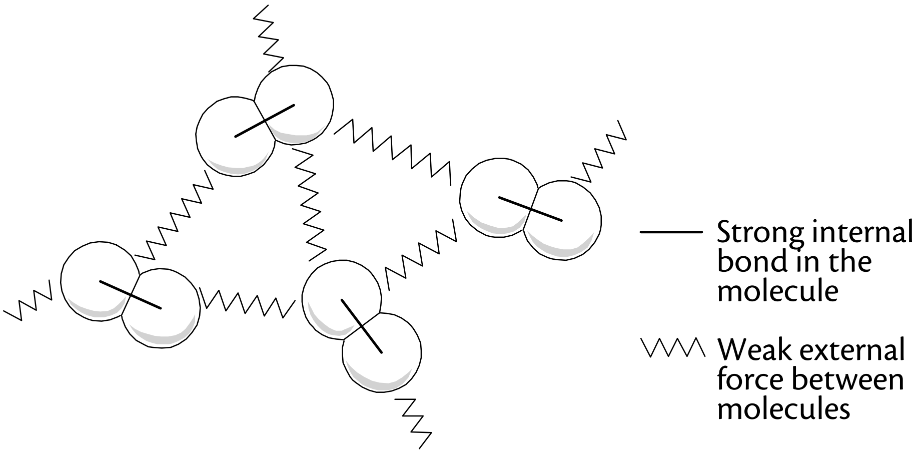


This attraction is called van der Waals force. The electrons are always in motion so the dipoles are constantly changing but they are always present. The more electrons in an atom, the larger the resulting dipole, so the larger the van der Waals force. This means more energy will be needed to overcome the force so the higher the melting point. We can see this effect if we look down the noble gas group – the increasing number of electrons in the atoms causes melting points to increase.

Note: Van der Waals forces are weaker than all other forms of bonding.

2. The Diatomic Gases (2 atoms to a molecule)

They exist as discrete diatomic molecules. Each molecule contains two atoms held together by a covalent bond, hence N_2, O_2 etc. In the solid state the molecules are held together by van der Waals forces.



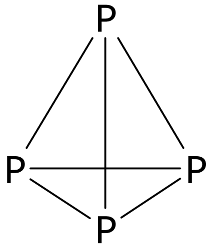
The size of the van der Waals force and hence the melting point depends on the number of electrons in the molecule, so the bigger the molecule, the bigger the Van der Waals force. Check this trend in the diatomic gases.

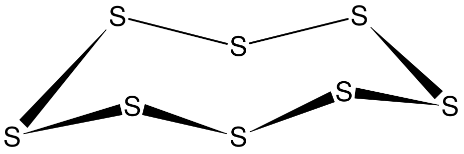
Note: Van der Waals forces are important only in the solid and liquid states. In the gas state the molecules are too far apart to experience any attraction.

3. Phosphorus and Sulphur

Nitrogen and phosphorus are in the same group, but they have very different melting points. This would suggest different structures. Similarly we would expect oxygen and sulphur to have differences in their bonding because they have very different melting points.

Both phosphorus and sulphur do exist as discrete (separate) molecules but they are not diatomic like N_2 and 0_2. Phosphorus has P_4 molecules and Sulphur S_8 molecules as shown.



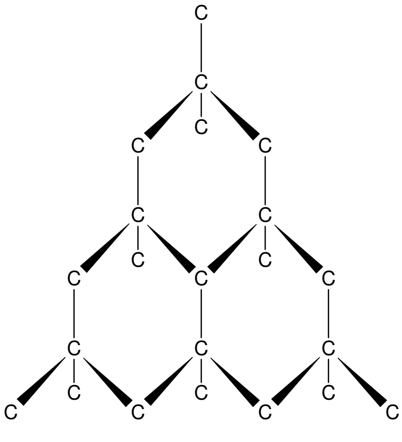


In the solid these molecules pack in layers held together by van der Waals forces. Because the molecules are bigger, with more electrons, the van der Waals forces are strong enough to hold the molecules together as a solid at room temperature.

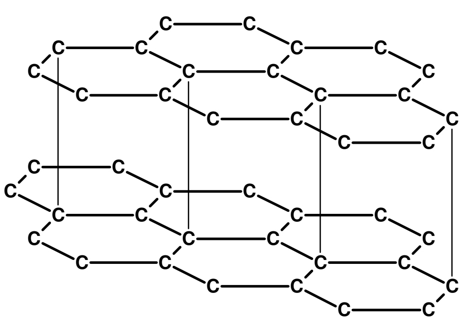
4. Carbon, Silicon and Boron

The element carbon exists in three forms – diamond, graphite and the recently discovered fullerenes. When an element can exist in more than one form it is called polymorphism.

The forms, diamond, graphite and fullerenes are called polymorphs.

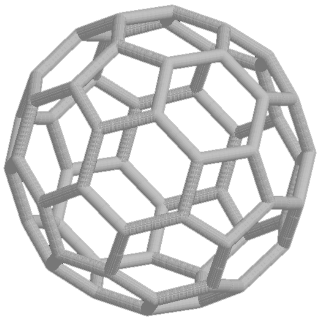


Diamond is a 3-dimensional network of carbon atoms. Each carbon atom is covalently bonded to 4 other carbon atoms that are arranged tetrahedrally round it. This gives a very rigid structure making diamond one of the hardest substances known. There are no discrete molecules in diamond so there are no weak forces. The structure is a covalent network lattice held together by strong covalent bonds. To melt diamond involves breaking these covalent bonds. This requires a lot of energy so the melting point is very high. Note also that all 4 outer shell electrons on each carbon are used in bonding so none is available to let diamond conduct electricity – diamond is a non-conductor.



Graphite is a layered structure. Each carbon is covalently bonded to only 3 other carbon atoms. The result is a hexagonal flat layer held together by strong covalent bonds. As you can see the layers are relatively far apart – too far to be covalently bonded to each other. The layers are held together by relatively weak van der Waals forces. These weak forces allow the layers to slide over each other fairly easily giving graphite a greasy feel. For this reason graphite is used as a lubricant between moving metal parts. More commonly, writing with a pencil involves sliding the graphite layers onto the paper.

As we saw above in graphite, only 3 of carbon's 4 outer shell electrons are used in bonding. These spare electrons are free to move so graphite, unlike diamond, is a conductor of electricity. It finds use as electrodes in dry cells and in industrial electrolyses.



a C_{60} molecule

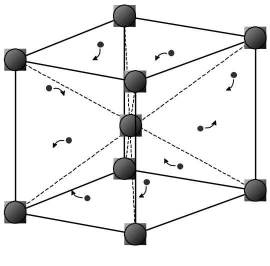
Fullerenes were discovered in the late 1980s. They are a form of carbon in which the atoms join to form large discrete molecules, eg C_{60} and C_{70}. These molecules are spherical in shape and are named after the American, Richard Buckminster Fuller, who developed the geodesic dome. They are at present the subject of a lot of research.

Silicon has a 3-dimensional covalent network lattice similar to diamond so it too has a very high melting point.

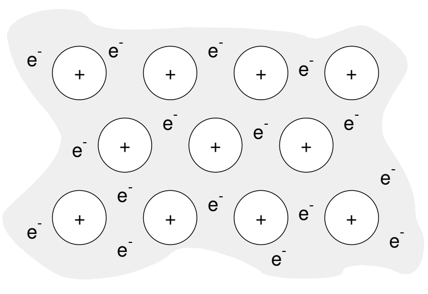
Boron The bonding in boron is complicated but it has a covalent network structure so again a high melting point.

5. The Metals

Metal elements have 1, 2 or 3 electrons in their outer shell and they all have the same basic structure. The outer shell electrons do not remain with the atom but are free to move throughout the whole structure – they are said to be delocalised. The atoms which have lost their electrons effectively become positive ions.



We can think of the metallic structure are being positive ions fixed in place in a lattice with a 'sea' of electrons moving through them. Metallic bonding is the attraction between the positive ions and the sea of electrons.



This attraction is not destroyed by altering the metal structure, so metals are malleable (can be hammered into shape) and are ductile (can be drawn out to form wires).

When a metal is molten these attractions between electrons and positive ions are still present so the process of melting does not break these attractions, so melting points are relatively low. Boiling a metal would separate the ions from the electrons so the attraction would need to be overcome, so boiling points are very high. As we go down a Group the melting points of the metals decrease. This is because the attraction between the sea of electrons and the positive ions decreases as the size of the ion increases. This decrease in attraction means that the strength of metallic bonding decreases down a group.

In general melting points for Group 2 metals are higher than those of group 1 because group 2 atoms have 2 electrons to contribute to the 'sea' and the positive ions have a 2+ charge. The result is a greater attraction and so stronger metallic bonding in Group 2 than in Group 1.

As we have seen, the 'sea' of electrons is free to move so metals conduct electricity.

Metallic Character of the Elements

By metallic character we mean being shiny, conductors of heat and electricity, malleable and ductile. The free moving 'sea' of electrons is responsible for these metallic properties.

Trends in metallic character

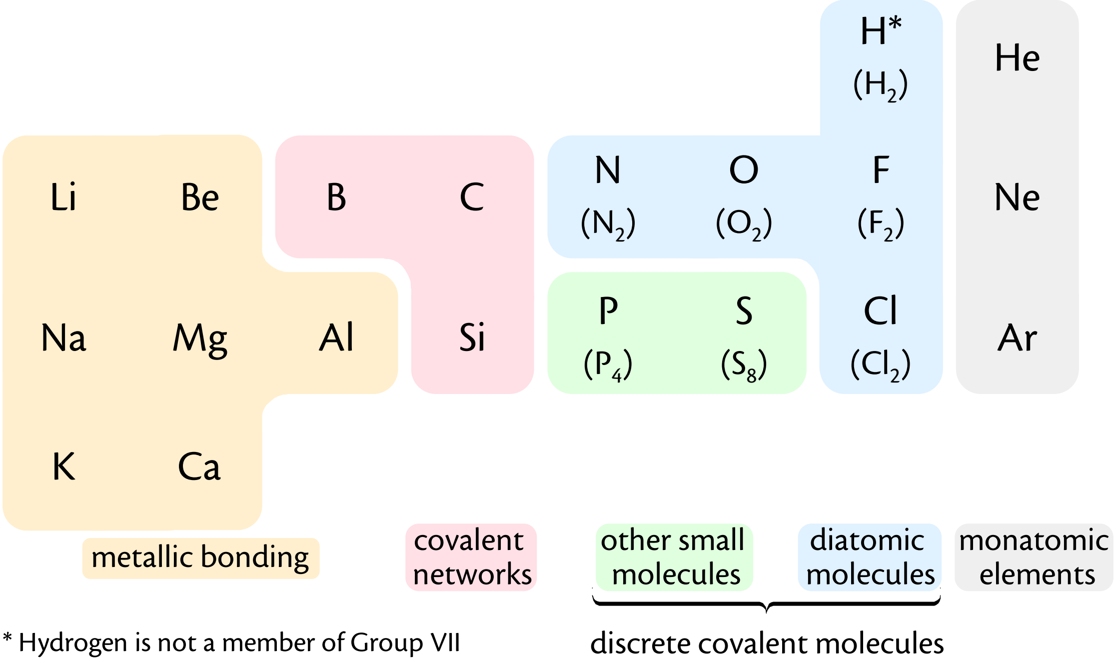
(a) across a period – metallic character decreases.
This is because ionisation enthalpies (see page 10) increase across a period and it therefore becomes more difficult for atoms to release the electrons needed to give the delocalised 'sea'.

(b) down a group – metallic character increases.
Ionisation enthalpy decreases down a group so increasing the delocalisation of electrons giving increased metallic character.

Note: the stronger the metallic bond the less the metallic character and vice versa.

Taking the two trends together the most metallic elements are found in the bottom left of the periodic table and the least metallic elements at the top right.

Here is a summary of the bonding in the elements:

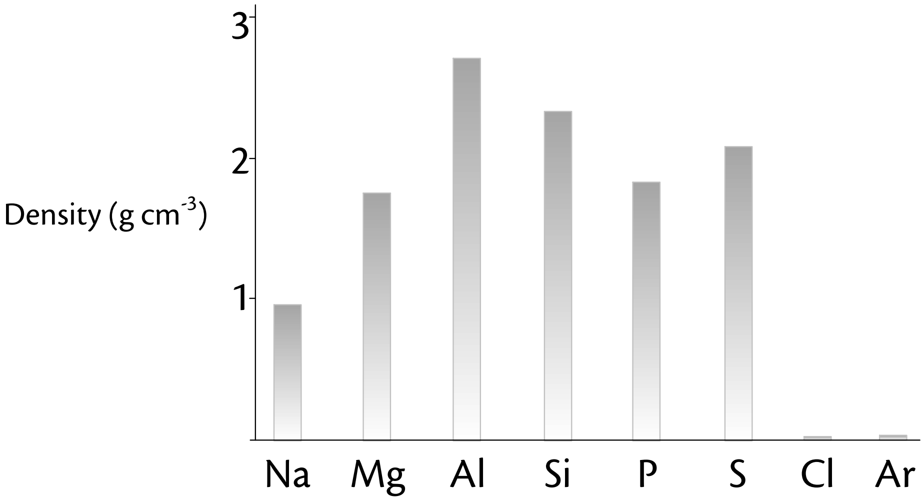


* Hydrogen is not a member of Group VII

We will now try to explain other physical properties of the elements in terms of bonding.

Density

The density of a substance is its mass per unit volume, usually measured in g cm^{-3}. The graph shows the variation in density across a period.



Na, Mg and Al have metallic bonding which is the attraction between the delocalised outer shell electrons and the fixed positive ions. The greater the number of outer shell electrons the greater the charge on the positive ion and so the greater the attraction. This means as we go from Na to Mg to Al the metallic bonding becomes stronger and the ions are pulled more closely together, leading to an increase in density.

Phosphorus and sulphur atoms are heavier than silicon atoms so we might expect their densities to be higher. However silicon is a covalent network of tightly packed atoms whereas the P_4 and S_8 molecules are only loosely held by van der Waals forces. Chlorine and argon are gases at room temperature. The chlorine molecules and argon atoms are well spread out so their densities are very low.

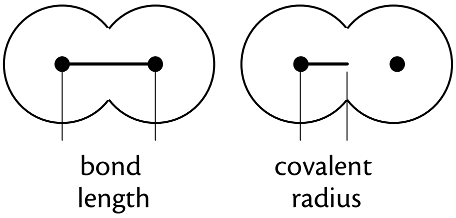
Covalent Radius

The size of an atom is very difficult to measure because atoms do not have a sharp boundary. However an X-ray technique can measure the distance between the nuclei of covalently bonded atoms – this distance is called the bond length.

The covalent radius of an element is half the distance between the nuclei of two of its covalently bonded atoms.

eg the covalent bond length in a chlorine molecule is 198 pm.

(pm = picometre; 10^{-12} metre)



So the covalent radius of a chlorine atom = $\frac{198}{2}$ = 99 pm

Trends in covalent radii

(a) down a group – covalent radii increase

	Electron arrangement	Covalent radius (pm)
Li	2, 1	123
Na	2, 8, 1	157
K	2, 8, 8, 1	203
Rb	2, 8, 18, 8, 1	216
Ca	2, 8, 18, 18, 8, 1	235

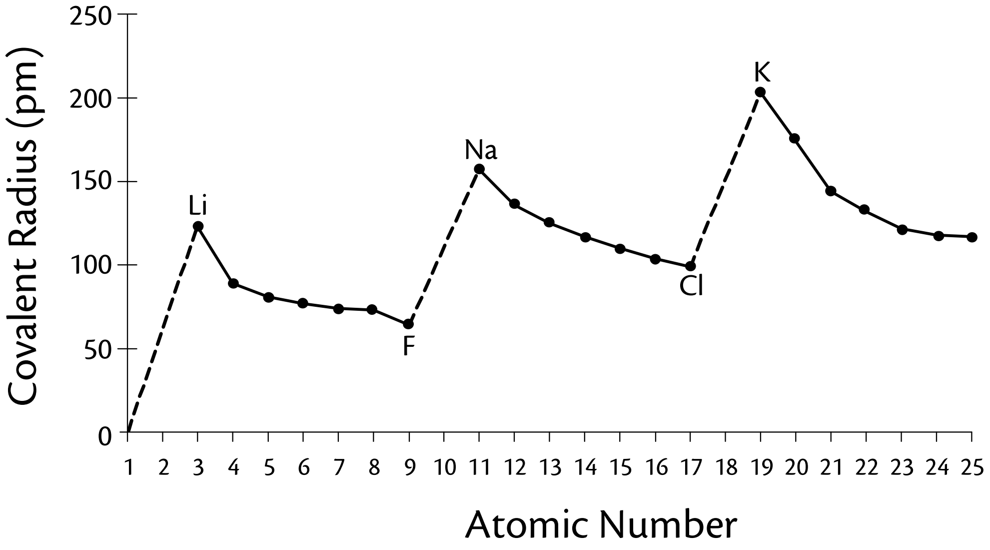
As we go down a group each member has an extra shell of electrons so the covalent radius increases. The positive charge on the nucleus increases down a group which tends to pull the electrons closer but the effect of adding an extra shell outweighs this.

(b) across a period – covalent radii decrease

	Na	Mg	Al	Si	P	S	Cl
covalent radius (pm)	136	136	125	117	110	104	99

As we go across a period electrons are being added to the same shell and protons are being added to the nucleus. This increasing positive charge pulls in the outer shell of electrons more closely so the radius decreases.

The graph shows how Covalent Radius varies with Atomic Number:



Bond Lengths from Covalent Radii

Single bond lengths between atoms of different elements can be found by adding their individual covalent radii.

e.g. the covalent radii of hydrogen and chlorine are respectively 37 and 99 pm.

so the bond length in HCl = 37 + 99 pm = 136 pm

Ionisation Enthalpy

The 1st ionisation enthalpy is the energy required to remove 1 mole of electrons from 1 mole of atoms in the gas state to form 1 mole of ions in the gas state. This is always an endothermic process.

eg $$Mg_{(g)} \longrightarrow Mg^{+}_{(g)} + e^{-} \qquad \Delta H = +744\ \text{kJmol}^{-1}$$

The above equation represents the 1st Ionisation Enthalpy of magnesium. The table below gives values for 1st Ionisation Enthalpies. The values are in kJ mol^{-1}.

Li 526	Be 905	B 807	C 1090	N 1410	O 1320	F 1690	Ne 2090
Na 502	Mg 744	Al 584	Si 792	P 1020	S 1010	Cl 1260	Ar 1530
K 425	Ca 596	Ga 577	Ge 762	As 953	Se 941	Br 1150	Kr 1350
Rb 409	Sr 556	In 556	Sn 715	Sb 816	Te 870	I 1020	Xe 1170

decrease down group ↓

overall increase along period →

Trends in Ionisation Enthalpies

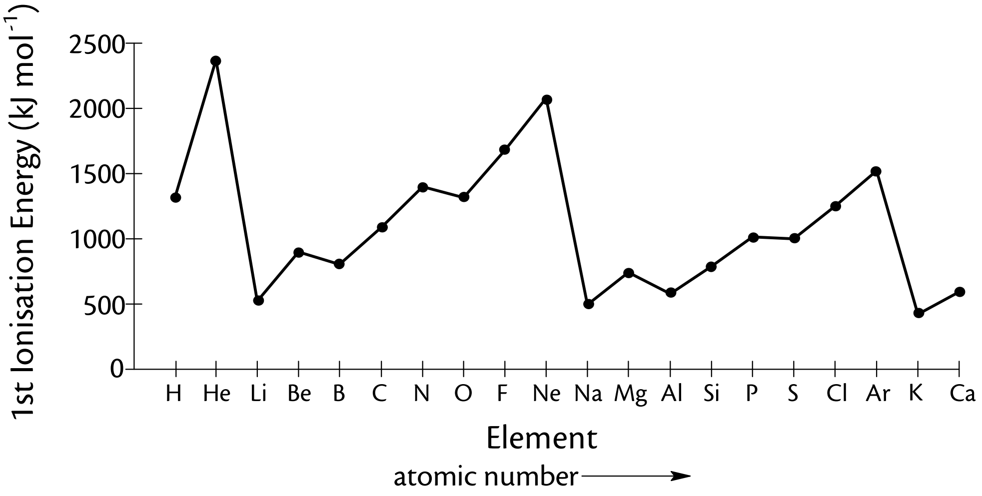
(a) down a group – ionisation enthalpies decrease

As we go down a group the outer shell electron we are removing is progressively further away from the nucleus and so is less tightly held and so easier to remove. However as we go down a group the nucleus is becoming more positive and should hold the outer electron more tightly, making ionisation enthalpies increase. This effect is diminished by the screening effect of the intervening electron shells. The outer shell electron does not feel the full attraction of the positive nucleus – so the increasing size argument wins.

(b) across a period – ionisation enthalpies increase

Across a period the nucleus becomes more positive. This makes the outer shell electron more difficult to remove. Also, across a period the atoms become smaller so the outer electron is closer to the nucleus and so is held more tightly. The result of this trend is that metals have relatively low ionisation enthalpies and can form positive ions but for non metal atoms forming positive ions is energetically impossible.

The graph shows the variation of 1st Ionisation Energies with Atomic Number.



The 2nd Ionisation Enthalpy of an element is the energy required to remove the 2nd mole of electrons.

eg $$Mg^{+}_{(g)} \longrightarrow Mg^{2+}_{(g)} + e^{-} \qquad \Delta H = +1460\ kJmol^{-1}$$

So the total energy to remove 2 moles of electrons from an atom is the sum of the 1st and 2nd Ionisation Enthalpies.

eg $$Mg_{(g)} \longrightarrow Mg^{2+}_{(g)} + 2e^{-} \qquad \Delta H = +2204\ kJmol^{-1}$$

The 2nd Ionisation energy of an atom is always larger than the first because it involves removing an electron from a species that is already positively charged. This table contains data from page 10 of the SQA Chemistry data book.

		Ionisation Energies (kJ mol^{-1})			
Element	Symbol	First	Second	Third	Fourth
lithium	Li	526	7310	11800	—
beryllium	Be	905	1770	14800	—
boron	B	807	2440	3660	25000
carbon	C	1090	2360	4640	6220
nitrogen	N	1410	2860	4580	7470
oxygen	O	1320	3400	5320	7470
fluorine	F	1690	3380	6060	8410
neon	Ne	2090	3960	6140	9360

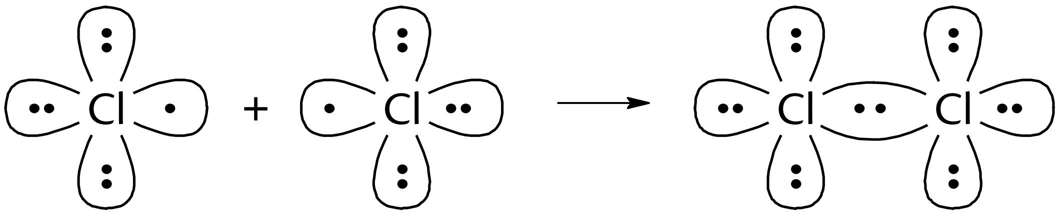
Note

1. The large increase from the 1st to 2nd Ionisation energy of sodium. The 1st ionisation energy removes the single outer shell electron from the sodium atom so the 2nd ionisation energy involves breaking into a stable octet of electrons – this requires a lot of energy.

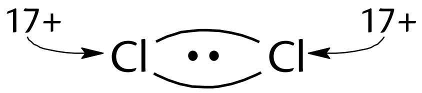
2. With magnesium the large increase in ionisation energy comes once the 2 outer shell electrons of the magnesium atom have been removed. The 3rd ionisation energy breaks into a stable octet.

Bonding in Compounds

Let's start by looking at the covalent bond in the element chlorine



A covalent bond is a pair of electrons shared by 2 atoms. Atoms in a covalent bond are held together by the electrostatic attraction between the negatively charged shared electrons and the 2 positively charged nuclei.



If the two bonded atoms are the same as in a chlorine molecule, then the pair of electrons is shared equally by the two atoms. We call this a non-polar covalent bond.

If the two bonded atoms are different, one nucleus will have a stronger attraction for the shared electrons than the other so the electrons will not be shared equally.

Electronegativity values are useful in predicting how electrons will be shared. Electronegativity is a measure of the attraction an atom involved in a covalent bond has for the electrons of the bond. In hydrogen iodide, H–I, the iodine atom is more electronegative than the hydrogen so the iodine has the greater attraction for the shared electrons. This means the shared pair are attracted nearer to iodine, which as a result becomes slightly negatively charged, δ–. The hydrogen becomes slightly positive, δ+, because the shared electrons have moved nearer the iodine. When the sharing of the bonding electrons is unequal we call it a polar covalent bond.

$$^{\delta+}\mathrm{H}\text{——}\mathrm{I}^{\delta-}$$

In hydrogen fluoride, H–F, the difference in electronegativities is greater so this covalent bond is more polar.

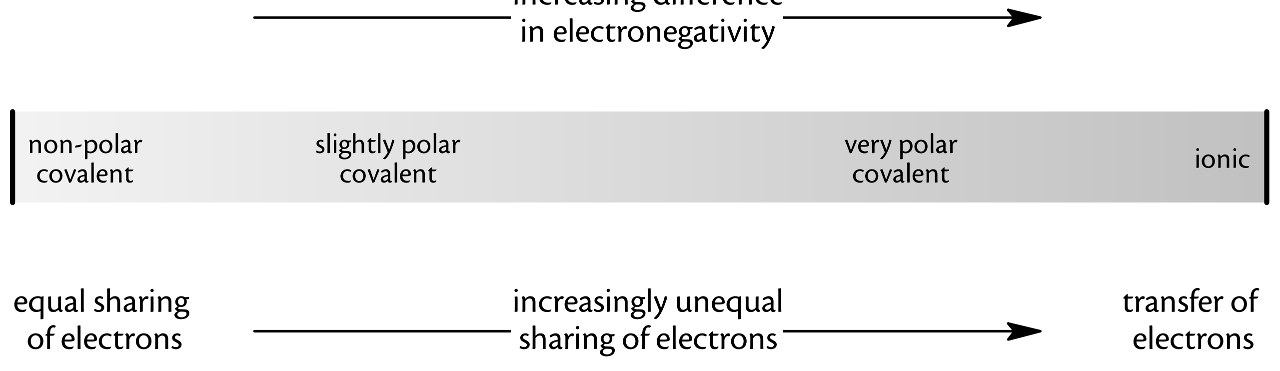
In some compounds one atom is so much more electronegative than the other that there is no sharing of electrons at all.

eg in lithium fluoride the electronegativities are:

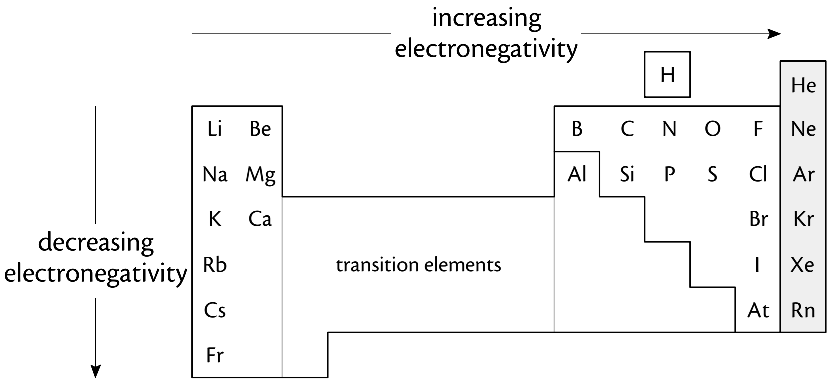
$$^{0.9}\mathrm{Li}\text{——}\mathrm{F}^{3.5}$$

This difference is so great that the bonding electron originally belonging to lithium is transferred to the fluorine. This forms two ions of opposite charge, Li^+ and F^-. These are attracted to each other – this electrostatic attraction is called the ionic bond.

Don't think of non-polar covalent, polar covalent and ionic as 3 completely separate types of bonding. Rather think of them as being on a continuous scale. At one end is non-polar covalent with its equal sharing of electrons, moving on to progressively more and more polar covalent. Eventually the sharing is so unequal that an electron is effectively transferred from one atom to the other forming ions, and therefore ionic bonding.



The diagram below indicates the variation in electronegativity of the atoms.



The main trends are

(a) increasing electronegativity across a period.

(b) decreasing electronegativity down a group.

The greater the difference in electronegativity between atoms, the less likely they are to share electrons and form covalent bonds and the more likely they are to form ionic bonds. So the more widely separated atoms are in the Periodic table the more likely they will bond ionically.

e.g. sodium chloride and magnesium oxide are ionic and caesium fluoride is the compound with the greatest ionic character.

Structure and Properties of Compounds

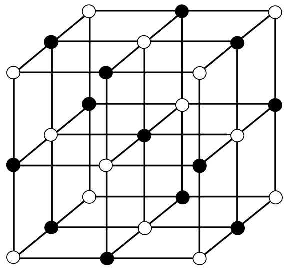
In the previous section we saw that compounds have ionic bonding or covalent bonding. We now must see, just as we did with elements, how the bonding affects the properties.

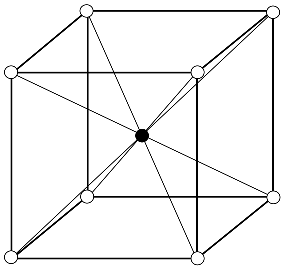
Ionic Compounds

Ionic compounds do not form molecules. The electrostatic attraction between positive and negative ions forms giant 3 dimensional lattice structures. The relative numbers of positive and negative ions is such that the overall charge is neutral.

eg $Ca^{2+}(Cl^{-})_2$

The energy given out when the lattice is formed is called the lattice energy. This is therefore the energy that must be supplied to separate the ions and break down the lattice it is therefore a measure of the strength of the electrostatic attraction. All ionic compounds are solids at room temperature and generally they have very high melting points. This shows that the electrostatic attraction – the ionic bond – between the ions is very strong. The diagrams below show the structures of NaCl and CsCl. Although they both have similar formulae the structures are different because of the different relative sizes of Na^+ and Cl^-; and of Cs^+ and Cl^-.


sodium chloride lattice


caesium chloride lattice

Note: in an ionic compound (e.g. $MgCl_2$) the formula does not suggest the presence of molecules. It is showing that in the giant crystal lattice there is 1 Mg^{2+} ion for every 2 Cl^- ions.

Covalent Compounds

Covalent bonding in compounds can result in either discrete molecules or covalent network structures.

Discrete Molecules

Covalent compounds made of discrete molecules have strong covalent bonds within the molecules but relatively weak forces between the molecules. (The weak forces between the molecules are called intermolecular forces and we will look at them in more detail later). When a covalent molecular compound is melted or boiled it is the weak intermolecular forces that are overcome and not the covalent bonds in the molecule. This means melting points and boiling points are relatively low. Covalent molecular compounds can be solid, liquid or gaseous at room temperature;

eg carbon dioxide (g), water (l) and candle wax (s) are all covalent molecular.

Covalent Network

Both carbon and silicon are in Group 4 and their oxides have formulae CO_2 and SiO_2. However, as we have seen, CO_2 is a gas at room temperature but SiO_2 is a solid that only melts at 17000°C. This suggests very different bonding in the two compounds. CO_2 consists of discrete molecules so has weak forces between its molecules, so CO_2 exists as a gas above –78°C. Silicon oxide, commonly known as silica, is the main chemical in sand. Its structure is a 3 dimensional covalent network. There are no discrete molecules so melting involves breaking strong covalent bonds. A lot of energy is required so the melting point is very high.

Abrasives

The very strong covalent network structure of silica, SiO_2 makes it very hard. Other substances with strong covalent networks are also very hard.

Diamond, a polymorph of carbon
Silicon carbide, SiC, commonly called carborundum
Boron nitride, BN
Fused alumina, Al_2O_3

These all have covalent network structures. Because they are very hard they all find use as abrasives, cutting tools or in polishing.

Compounds and Conduction of Electricity

Ionic compounds do not conduct when solid. They do conduct when melted or dissolved in water. This sets the ions free so they can be attracted to the electrode of opposite charge.

Covalent compounds do not conduct when solid or when melted or in solution because they contain no ions.

However there are a few covalent compounds that ionise when dissolved in water. Obviously their solutions will conduct electricity.

eg $HCl_{(g)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$

Polar Bonds and Polar Molecules

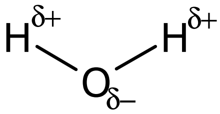
We saw earlier that covalent bonds between different atoms are polar because of the differing electron attracting powers of the atoms, for example:

$$^{\delta+}H\text{—}Cl^{\delta-}$$

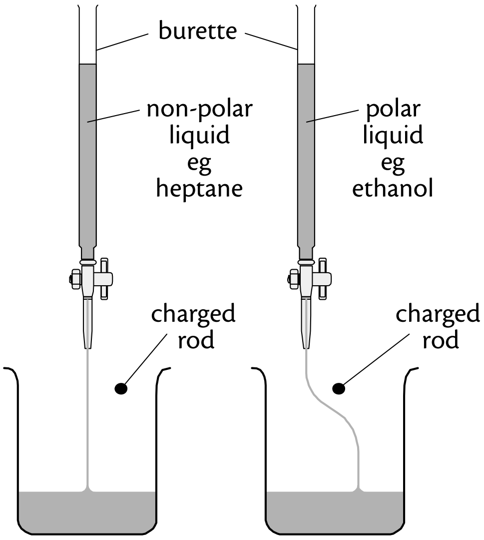
The presence of polar bonds in a molecule does not necessarily mean that the molecule as a whole will be polar. Carbon dioxide has two polar bonds,

$$\overset{\delta-}{O}=\overset{\delta+}{C}=\overset{\delta-}{O}$$

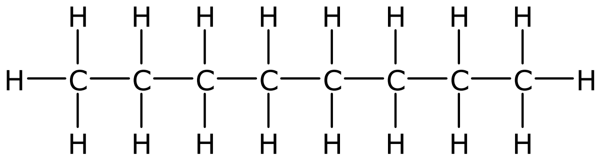
but because they are symmetrically arranged the polarity cancels out and as a whole the molecule is non-polar. Water has two polar bonds,



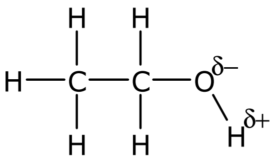
but they are not symmetrically arranged and don't cancel out, so water molecules are polar. The water molecule is said to be a permanent dipole.

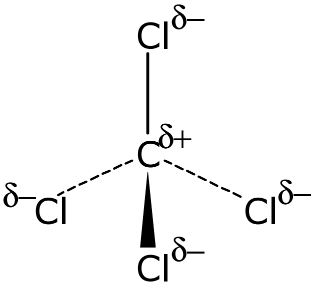


Liquids with polar molecules are easily distinguished from those with non-polar molecules. Polar molecules are attracted to a charged rod but non-polar molecules are not attracted.
Heptane has almost non-polar bonds so the molecules are non-polar.



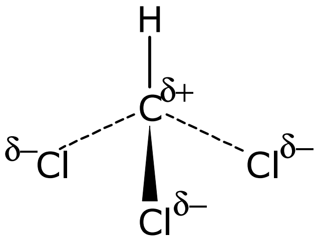
Ethanol has one polar O–H bond so the molecule is polar.





Two molecules worth noting are CCl_4 and $CHCl_3$. Molecules of CCl_4 have 4 polar C–Cl bonds but being symmetrically arranged (tetrahedrally) the polarities cancel and the molecule is non-polar because it has no permanent dipole.

$CHCl_3$ has 3 polar C–Cl bonds and one C–H bond which is almost non-polar. In this case the polarities don't cancel; we have a permanent diplole, so $CHCl_3$ has polar molecules.



Intermolecular Forces

We now look in more detail at the relatively weak intermolecular forces that exist in covalent molecular compounds.

Van der Waals Forces

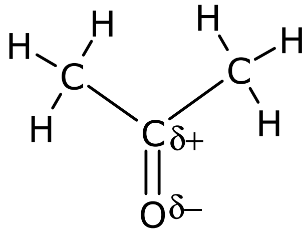
We met them already when we discussed bonding in the elements but they also occur between molecules. They are the weakest of the intermolecular forces but in the absence of any others they are important. The bigger the molecule the bigger the Van der Waals force.

We know that as we go up the alkane series the molecules get bigger so the Van der Waals force between the molecules increases. The result is that more energy has to be put in to overcome this force when melting or boiling the alkanes. This explains why melting and boiling points increase up the alkane series and indeed up every homologous series.

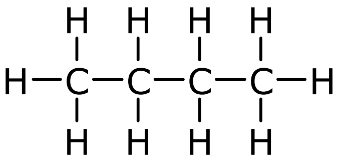
Permanent dipole–permanent dipole attractions

Propanone molecules have a permanent dipole so the molecules are polar. As well as Van der Waals force, the permanent dipole interactions between propanone molecules are an additional electrostatic attraction holding the molecules together.

The example below shows the effect. Both compounds have the same formula mass but the one with polar molecules has the higher boiling point.



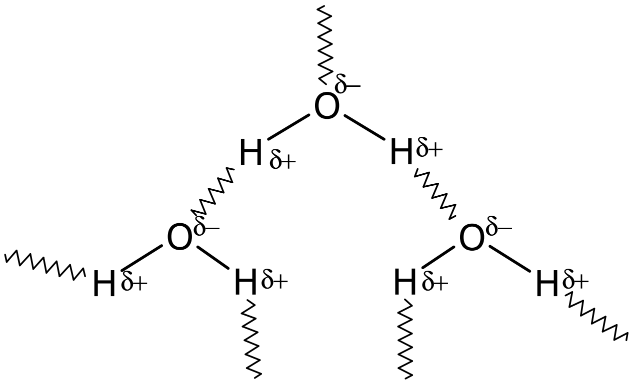
Propanone
formula mass 58
boiling point 56°C



Butane
formula mass 58
boiling point 0°C

Hydrogen Bonds

Hydrogen atoms have a very low electronegativity. If hydrogen is bonded to a very electronegative atom (N, O and F) then the covalent bond will be very polar. Consider water molecules:

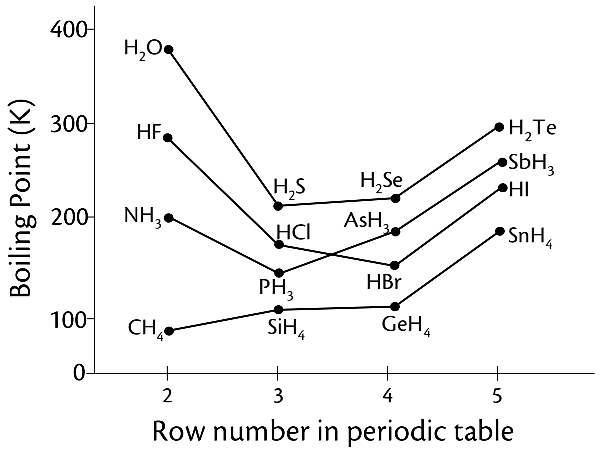


There are relatively strong forces of attraction between the δ+ hydrogen in one molecule and the δ– oxygen in a neighbouring molecule. These forces are called hydrogen bonds and are additional to Van der Waals forces. Hydrogen bonds are the strongest of the intermolecular forces but they are much weaker than covalent bonds.

Effects of Hydrogen Bonding

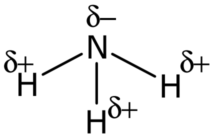
Physical Properties of Hydrides

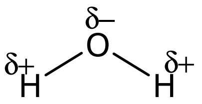
Look at the graph of the boiling points of the Group 4, 5, 6 and 7 hydrides.

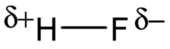


Only the boiling points in Group 4 follow the expected trend; as we go down group 4 the hydride molecules become bigger so increasing van der Waals forces resulting in gradually increasing boiling points. In groups 5, 6 and 7 the boiling points of the first members are much higher than expected. This means more energy than expected has to be supplied to separate the molecules, indicating that they are held together by more than just van der Waals forces. The extra force is called hydrogen bonds which, remember, is present only in molecules in which hydrogen is bonded to a small electron attracting atom like N, O or F.

The covalent bonds within the molecules are very polar with the result that $H^{\delta+}$ on one molecule attracts δ– on another molecule. It is this additional bond that gives NH_3, H_2O and HF higher than expected boiling points.

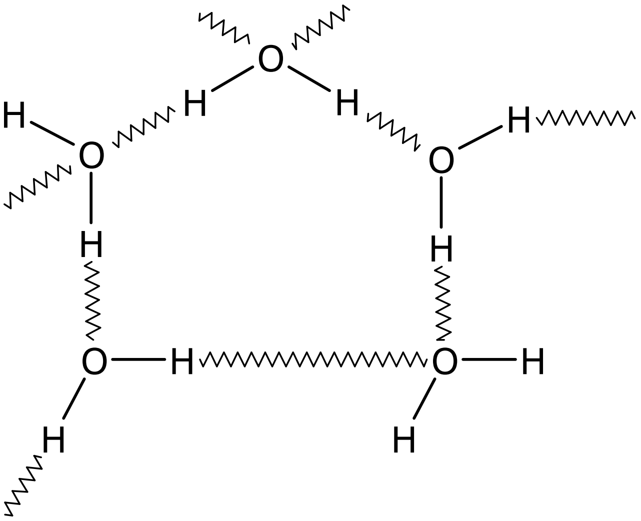






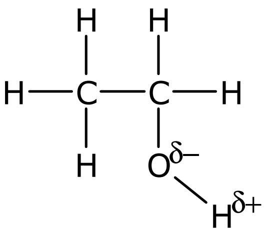
Hydrogen bonding in Ice

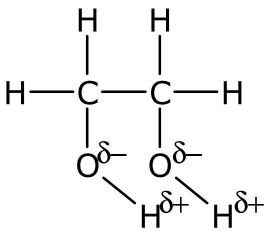
Usually when a substance is cooled its molecules/atoms lose kinetic energy and move closer and closer together increasing the density until the substance solidifies. So normally a substance has a greater density in the solid state than in the liquid state. As water is cooled, its density increases as the temperature falls, until 40°C is reached where water has its maximum density. Further cooling causes the molecules to start to move apart, forming hydrogen bonds until it freezes in an open cage like structure. The result is that ice is less dense than water. This is the reason that ice floats on water.

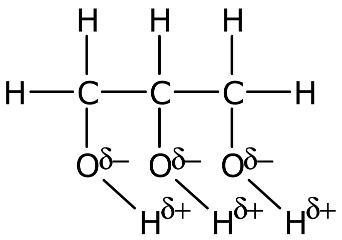


Viscosity

Viscosity is the thickness of a liquid and can be measured by timing how long it takes a ball bearing to fall through the liquid – the more viscous, the longer it takes. The more hydrogen bonds in a molecule the more the molecules will hold together and the more viscous the liquid will be. Hexane, C_6H_{14}, has no hydrogen bonds between its molecules (only Van der Waals forces) so is not very viscous. However, consider the following 3 molecules which have respectively 1, 2, and 3 polar O–H bonds. The more O–H bonds per molecule, the more hydrogen bonds the molecule can make and, therefore, the more viscous the molecule is.


ethanol

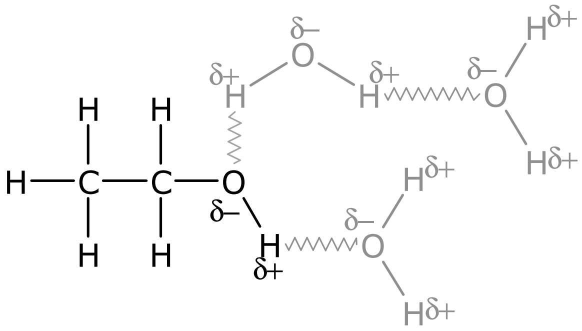

ethane-1,2-diol

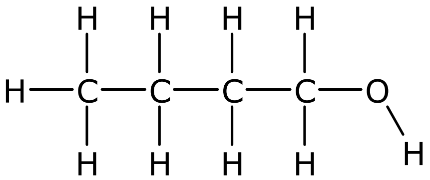

propane-1,2,3-triol

increasing viscosity →

Miscibility with water

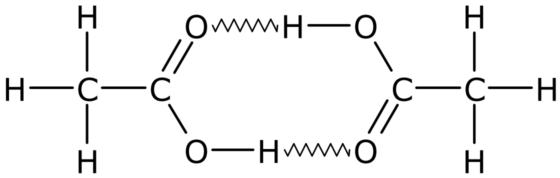
In general, organic molecules are insoluble in water. However, small molecules like ethanol, with a polar O–H functional group, are soluble in water because the ethanol molecules can form hydrogen bonds with the water molecules. Larger molecules, like butanol, are insoluble even though they have the same polar group, because the larger non-polar hydrocarbon chain is the dominant influence.


ethanol is soluble


butanol is insoluble

Formula mass

Ethanoic acid has a formula mass of 60. Some methods of determining formula mass give the value as 120 because in solution hydrogen bonds hold the molecules together in pairs.

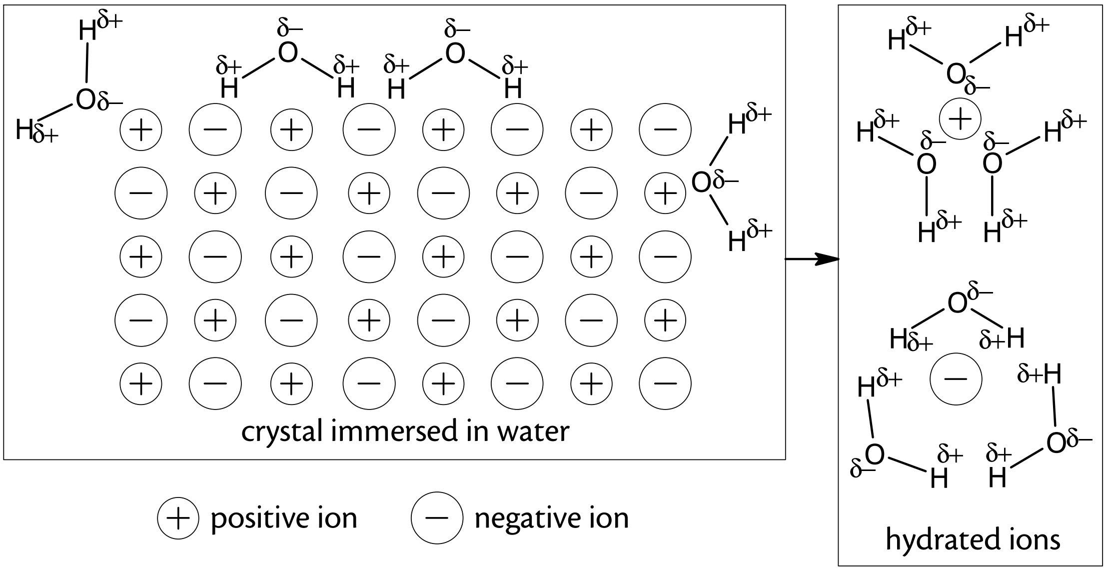


Dissolving

As a general rule, water will be the best solvent for ionic solids and substances with polar molecules. Non-polar solutes are likely to dissolve in non-polar solvents like heptane or tetrachloromethane. It is sometimes stated as ‘like dissolves like’.

Water as a Solvent

The diagram shows what happens when an ionic crystal dissolves in water.



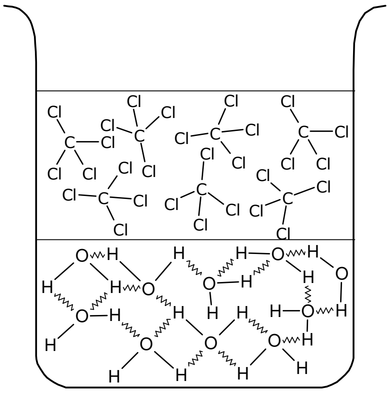
The polar water molecules are attracted to the ions in the crystal lattice. The attraction drags the ions out of the crystal ‘into solution’, where the ions are surrounded by water molecules.

Using sodium chloride dissolving in water as an example, the equation for the above process is:

$$NaCl_{(s)} \longrightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

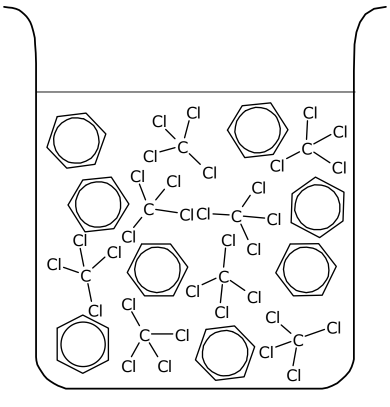
The (aq) in the equation indicates that the ions are hydrated, ie they are surrounded by polar water molecules, held by the electrostatic attraction of opposite charges.

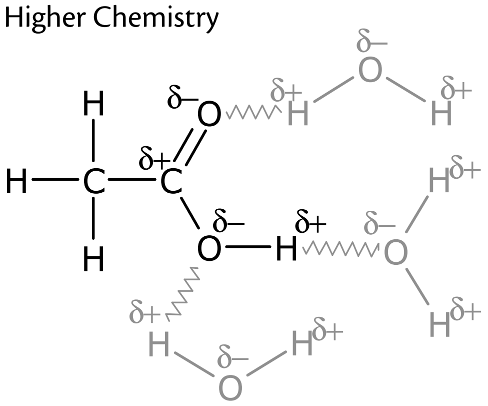
Non-polar compounds, like tetrachloromethane do not dissolve in water.



Non-polar molecules cannot hydrogen bond with water molecules and if they were to go into water, they would separate the water molecules and reduce the number of hydrogen bonds. This is energetically unfavourable so they don’t dissolve.

Non-polar compounds are miscible with each other because the only attractions present are van der Waals forces and they can exist between different non polar molecules.
eg tetrachloromethane and benzene (2 non-polar molecules) are miscible.





Small polar molecules, like ethanol or ethanoic acid, dissolve in water because the polar functional groups are able to hydrogen bond with water molecules.

However, as we go up their homologous series, the increasing length of the non-polar hydrocarbon chain means that higher members are insoluble in water.

Some polar covalent molecules ionise when they dissolve in water:

$$^{\delta+}H{-}Cl^{\delta-}{}_{(g)} \longrightarrow H^+{}_{(aq)} + Cl^-{}_{(aq)}$$

Let's now see how our ideas on bonding affect the properties of some compounds of the first 20 elements.

Hydrides

Compounds of the elements with hydrogen are called hydrides. The hydrides of the period 2 elements along with the trend in polarity are shown below.

LiH	BeH_2	B_2H_6	CH_4	NH_3	H_2O	HF
H^-	$H^{\delta-}$	H	H	$H^{\delta+}$	$H^{\delta+}$	$H^{\delta+}$

Note the trend from ionic to covalent across the period. This follows from a decreasing difference in electronegativity between hydrogen and the other element as we go from left to right. Most of these compounds are already familiar to you but Li^+H^- containing the hydride ion is probably new. The H^- ion is found only in hydrides of elements that have a very low electronegativity.

eg Li^+H^-, Na^+H^-, K^+H^- etc.

All the ionic hydrides are white solids. When they are melted and electrolysed, hydrogen gas is evolved at the positive electrode confirming the presence of H^- ions. As we move right, we pass the non-polar hydrides, CH_4 and SiH_4.

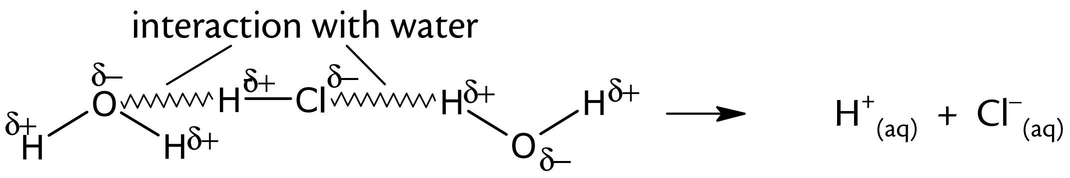
At the right of Periodic Table are the hydrides of the halogens. These are all gases with polar covalent bonding.

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

In aqueous solution these molecules ionise completely to give acidic solutions.

$$HCl_{(g)} \longrightarrow H^+{}_{(aq)} + Cl^-{}_{(aq)}$$

This happens as follows:

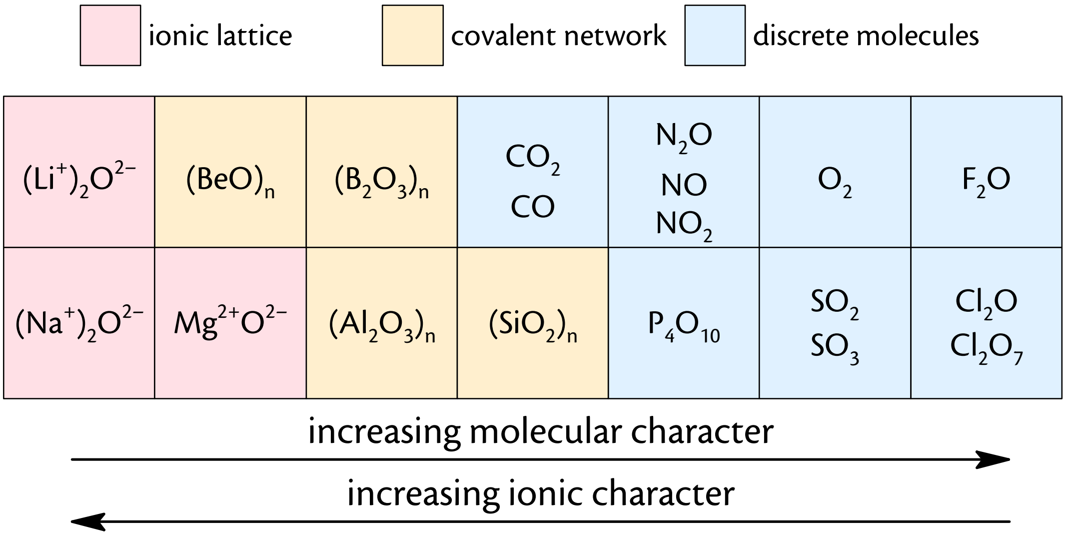


The attraction between the slightly negative oxygen in water and the slightly positive hydrogen in HCl helps break the H–Cl bond.

Oxides

Structure of Oxides

The trend from ionic to covalent bonding is as expected from electronegativities.



🟥 ionic lattice 🟨 covalent network 🟦 discrete molecules

🟥 $(Li^+)_2O^{2-}$	🟨 $(BeO)_n$	🟨 $(B_2O_3)_n$	🟦 CO_2 CO	🟦 N_2O NO NO_2	🟦 O_2	🟦 F_2O
🟥 $(Na^+)_2O^{2-}$	🟥 $Mg^{2+}O^{2-}$	🟨 $(Al_2O_3)_n$	🟨 $(SiO_2)_n$	🟦 P_4O_{10}	🟦 SO_2 SO_3	🟦 Cl_2O Cl_2O_7

Group 1 & 2 Metal oxides (except BeO) form **ionic lattices**. They are solids at room temperature and have high melting points and boiling points. When melted, these ionic oxides conduct electricity.

Oxides of Be, B, Al, Si exist as **covalent networks**. They have very high melting points and boiling points but unlike the ionic oxides, covalent network oxides do not conduct electricity when molten. SiO_2 as we have already seen is a very hard substance because the 3-dimensional arrangement of strong covalent bonds in the covalent network is very rigid.

Oxides of C, N, P, S, F, Cl consist of **discrete small molecules**. They have low melting points and boiling points because there are only weak van der Waals forces to be overcome. They do not conduct in the molten state because they are molecular.

Acid/Base Character of Oxides

This is Standard Grade work but repeating it will do no harm.

Basic oxides are the oxides of metals and, if they are soluble in water, they give alkaline solutions. Basic oxides react with acids. The ionic oxides, Li_2O, Na_2O, MgO are basic oxides. They are soluble in water so they form alkaline solutions.

eg $$(Na^+)_2O^{2-}{}_{(s)} + H_2O_{(l)} \longrightarrow 2Na^+{}_{(aq)} + 2OH^-{}_{(aq)}$$

sodium hydroxide solution (an alkali)

They react with acids to form a salt and water.

eg $$MgO_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_2O_{(l)}$$

Note: many metal oxides (e.g. CuO) are insoluble in water so do not give alkaline solutions. However they are basic oxides because they react with acid.

Acidic Oxides are the oxides of non-metals and if they are soluble in water they form acidic solutions. Acidic oxides react with alkalis to form salts and water.

The equations below show the acids formed when some acidic oxides dissolve in water.

$$\begin{array}{rcll} CO_2 + H_2O & \longrightarrow & H_2CO_3 & \text{carbonic acid} \\ SO_2 + H_2O & \longrightarrow & H_2SO_3 & \text{sulphurous acid} \\ SO_3 + H_2O & \longrightarrow & H_2SO_4 & \text{sulphuric acid} \\ P_4O_{10} + 6H_2O & \longrightarrow & 4H_3PO_4 & \text{phosphoric acid} \\ 2NO_2 + H_2O & \longrightarrow & HNO_3 + HNO_2 & \text{niric/nitrous acid} \end{array}$$

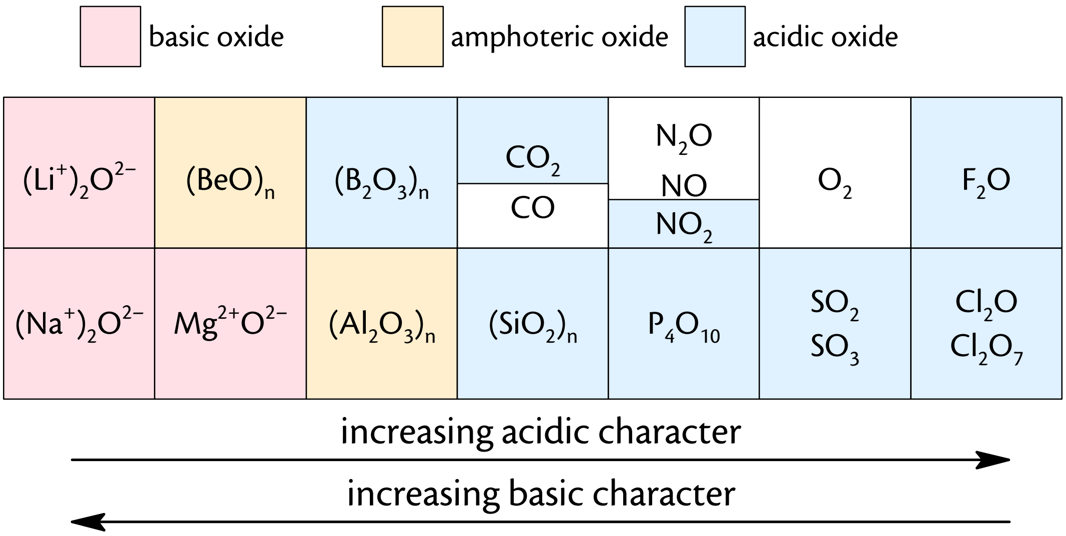
SiO_2 is insoluble in water so does not give an acid solution but, being an acidic oxide, it reacts with alkalis.

$$2NaOH + SiO_2 \longrightarrow \underbrace{(Na^+)_2SiO_3^{2-}}_{\text{sodium silicate}} + H_2O$$

Amphoteric Oxides behave as both an acidic oxide and a basic oxide.

Neutral oxides are oxides which react with neither acid nor alkali. CO, NO and N_2O are neutral oxides.

The properties of these oxides are now summarised:



🟥 basic oxide 🟨 amphoteric oxide 🟦 acidic oxide

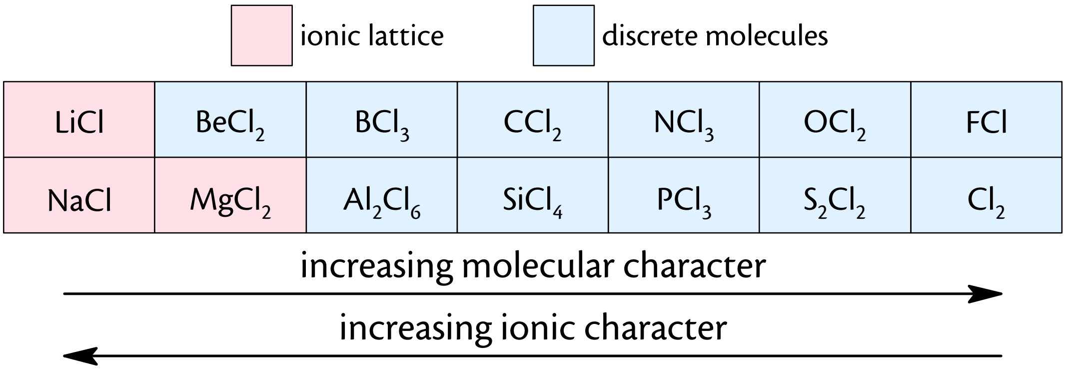
$(Li^+)_2O^{2-}$	$(BeO)_n$	$(B_2O_3)_n$	CO_2 CO	N_2O NO NO_2	O_2	F_2O
$(Na^+)_2O^{2-}$	$Mg^{2+}O^{2-}$	$(Al_2O_3)_n$	$(SiO_2)_n$	P_4O_{10}	SO_2 SO_3	Cl_2O Cl_2O_7

increasing acidic character →

← increasing basic character

Chlorides

Chlorine is very reactive and combines directly with most elements. The bonding (as in the oxides) varies from ionic to covalent across the periodic table. As expected, the metals form ionic lattices and the non-metals form discrete molecules. This again is in line with electronegativities.



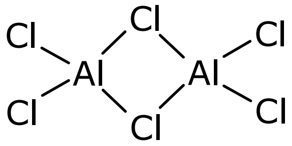
🟥 ionic lattice 🟦 discrete molecules

LiCl	$BeCl_2$	BCl_3	CCl_2	NCl_3	OCl_2	FCl
NaCl	$MgCl_2$	Al_2Cl_6	$SiCl_4$	PCl_3	S_2Cl_2	Cl_2

increasing molecular character →

← increasing ionic character

The formula of aluminium chloride is surprising, and the fact that it is molecular is surprising. The melting point is only 1900°C and it is a poor conductor when molten which indicates that the bonding in aluminium chloride is likely to be covalent rather than ionic. It appears to exist as Al_2Cl_6 molecules as shown:



Summary of Bond Types and Strengths

This is a very rough guide to the strengths of bonds we have met in this topic.

Bond Type	Strength (kJ mol^{-1})
Metallic bond	80 to 600
Ionic bond	100 to 500
Covalent bond	100 to 500
Hydrogen bond	40
Permanent dipole-permanent dipole	30
Van der Waals force	1 to 20