Topic 3 – Bonding, Structure and the Periodic Table

Types of bond
States of matter
Structure and physical properties
Molecular shapes
Intermolecular forces
Structure and Bonding in the Periodic Table

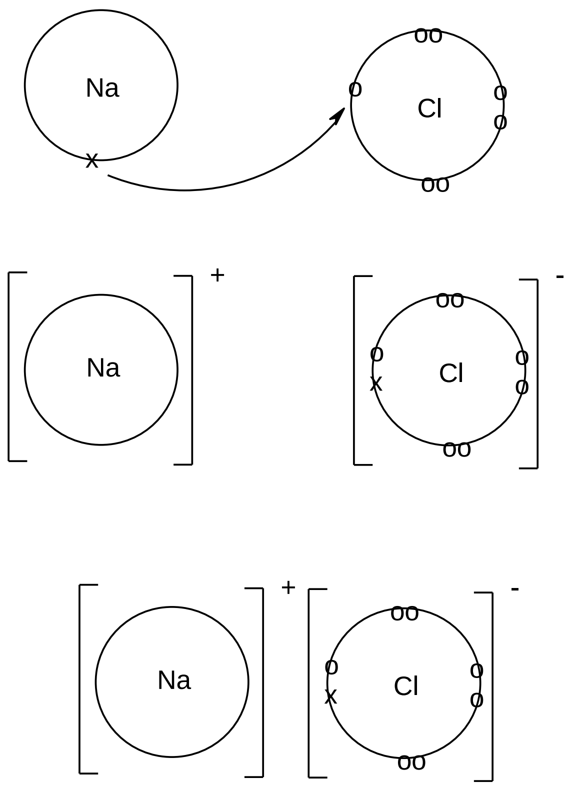
TYPES OF BOND

Atoms bond to each other in one of four ways:

i) <u>ionic bonding</u>

An ionic bond is an attraction between oppositely charged ions, which are formed by the transfer of electrons from one atom to another.

Eg In sodium chloride, each sodium atom transfers an electron to a chlorine atom. The result is a sodium ion and a chloride anion. These two ions attract each other to form a stable compound.

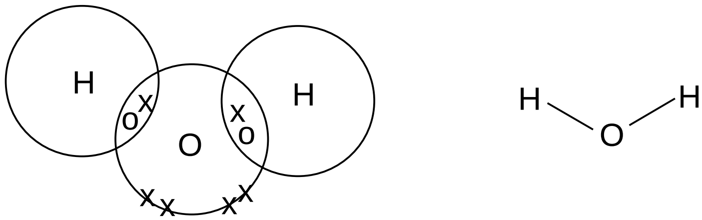


ii) <u>Covalent bonding</u>

A covalent bond is a pair of electrons shared between two atoms.

In a normal covalent bond, each atom provides one of the electrons in the bond. A covalent bond is represented by a short straight line between the two atoms.

Eg water

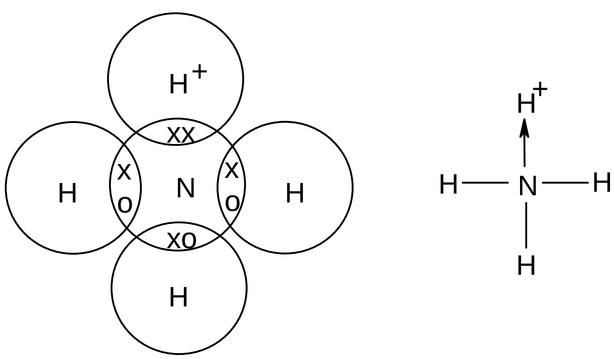


In a dative covalent bond, one atom provides both electrons to the bond.

A dative covalent bond is a pair of electrons shared between two atoms, one of which provides both electrons to the bond.

A dative covalent bond is represented by a short arrow from the electron providing both electrons to the electron providing neither.

Eg ammonium ion



Covalent bonding happens because the electrons are more stable when attracted to two nuclei than when attracted to only one.

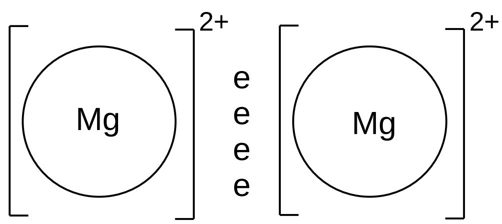
Covalent bonds should not be regarded as shared electron pairs in a fixed position; the electrons are in a state of constant motion and are best regarded more as **charge clouds**.

iii) <u>Metallic bonding</u>

A metallic bond is an attraction between cations and a sea of electrons.

Metallic bonds are formed when atoms lose electrons and the resulting electrons are attracted to all the resulting cations.

Eg Magnesium atoms lose two electrons each, and the resulting electrons are attracted to all the cations.



Metallic bonding happens because the electrons are attracted to more than one nucleus and hence more stable. The electrons are said to be delocalized – they are not attached to any particular atom but are free to move between the atoms.

IONIC OR COVALENT? - ELECTRONEGATIVITY

Electronegativity is the relative ability of an atom to attract electrons in a covalent bond.

The electronegativity of an atom depends on its ability to attract electrons and its ability to hold onto electrons. Electronegativity increases across a period as the nuclear charge on the atoms increases but the shielding stays the same, so the electrons are more strongly attracted to the atom. Electronegativity decreases down a group as the number of shells increases, so shielding increases and the electrons are less strongly attracted to the atom.

An atom which has a high electronegativity is said to be **electronegative**; an atom which does not have a high electronegativity is said to be **electropositive**.

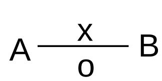
Electronegativities are relative; electronegativity has no units and is measured on a scale from 0.7 to 4.0. The electronegativities of some elements in the periodic table are shown below:

									H 2.1								He
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr

Note that the noble gases cannot be ascribed an electronegativity since they do not form bonds.

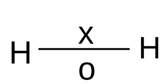
Electronegativity is a very useful concept for predicting whether the bonding between two atoms will be ionic, covalent or metallic.

Consider a covalent bond between two atoms A and B.



If both atoms have a similar electronegativity, both atoms attract the electrons with similar power and the electrons will remain midway between the two. The bond will thus be covalent - the electrons are shared between the two atoms.

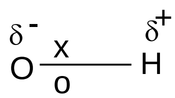
Eg H (2.1) and H (2.1)



a covalent bond

If one atom is significantly more electronegative than the other, it attracts the electrons more strongly than the other and the electrons are on average closer to one atom than the other. The electrons are still shared, but one atom has a slight deficit of electrons and thus a slight positive charge and the other a slight surplus of electrons and thus a slight negative charge. Such a bond is said to be **polar covalent**.

Eg H (2.1) and O (3.0)

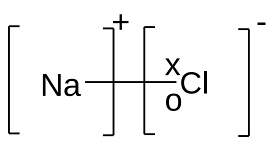


a polar covalent bond

A slight positive charge or negative charge on an atom is represented by a δ^+ or a δ^- symbol respectively.

If the difference between the two atoms is large, then the sharing of electrons is so uneven that the more electronegative atom has virtually sole possession of the electrons. The electrons are, in effect, not shared at all but an electron has essentially between transferred from one atom to the other. The more electropositive atom is positively charged and the more electronegative atom is negatively charged. The bonding is thus ionic.

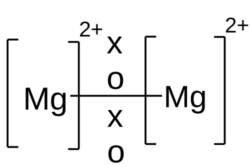
Eg Na (0.9) and Cl (3.0)



an ionic bond

If both atoms are electropositive, neither has a great ability to attract electrons and the electrons do not remain localised in the bond at all. They are free to move, both atoms gain a positive charge and the bonding is metallic.

Eg Mg (1.2) and Mg (1.2)



a metallic bond

Differences in electronegativity can be used to predict how much ionic or metallic character a covalent bond will have.

Given suitable electronegativity data, it is thus possible to predict whether a bond between two atoms will be ionic, polar covalent, covalent or metallic.

If both atoms have electronegativities less than 1.6 - 1.9 then the bond is metallic.

If either atom has an electronegativity greater than 1.9 and the difference is less than 0.5 then the bond is covalent.

If either atom has an electronegativity greater than 1.9 and the difference is more than 0.5 but less than 2.1 then the bond is polar covalent.

If the difference is greater than 2.1 then the bond is ionic.

These rules are not perfect and there are notable exceptions; for example the bond between Si (1.8) and Si (1.8) is covalent but the bond between Cu (1.9) and Cu (1.9) is metallic. The bond between Na (0.9) and H (2.1) is ionic but the bond between Si (1.8) and F (4.0) is polar covalent. However as basic giudelines they are very useful provided that their limitations are appreciated.

All bonds are assumed to be covalent in principle: differences in electronegativity can be used to predict how much ionic or metallic character a covalent bond will have.

Electronegativity differences show that bonds between non-identical atoms are all essentially intermediate in character between ionic and covalent. No bond is completely ionic, and only bonds between identical atoms are completely covalent.

Bonds between identical atoms cannot be ionic as there is no difference in electronegativity. They will therefore be either covalent or metallic.

STATES OF MATTER

Matter can exist in one of three states; solid, liquid and gas. The state in which a certain substance is most stable at a given temperature depends on the balance between the kinetic energy of the particles, which depends on temperature, and the magnitude of the force of attraction between them.

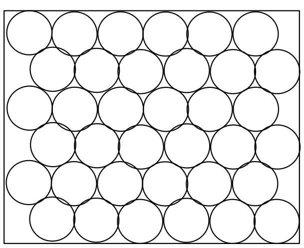
i) Solids

In a solid, the particles are tightly packed together in a lattice. A lattice is an ordered and infinitely repeating arrangement of particles. The properties of solids are dominated by the forces in between these particles which cause them to attract each other and preserve this ordered arrangement.

A solid thus has a fixed volume and a fixed shape.

At all temperatures above absolute zero, the particles have kinetic energy. In a solid, however, this kinetic energy is not enough to cause the particles to fly apart, and nor is it enough to cause significant separation of the particles. The particles are thus restricted to rotational and vibrational motion; no translational motion of the particles with respect to each other is possible.

In a solid, the kinetic energy of the particles is not nearly enough to overcome the potential energy caused by their mutual attraction.



SOLIDS

If a solid is heated, the kinetic energy of the particles increases, and they vibrate more. As they vibrate more, the bonds between the particles are weakened, some are broken and spaces appear between the particles. At this point the solid has melted.

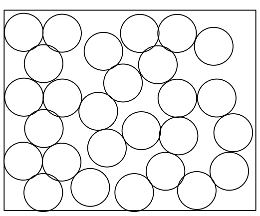
ii) Liquids

In a liquid, the particles are by and large packed together in a lattice that extends across the range of 10 - 100 particles. However over a longer range the structure breaks down, and there is enough space between the particles for them to move from one cluster to another. The properties of liquids are still dominated by the forces between the particles, but these particles have enough kinetic energy to move between each other in the spaces that exist. There is thus short-range order but no long-range order.

A liquid has a fixed volume but no fixed shape.

The kinetic energy of the particles is now significant; it forces the particles apart to the extent that the spaces between them are often wider than the particles themselves. The particles are thus permitted some translational motion with respect to each other within these spaces. All solids will melt if they are heated strongly enough.

In a liquid, the kinetic energy of the particles is still not large enough to overcome their mutual attraction, but is nevertheless significant and must be taken into account.



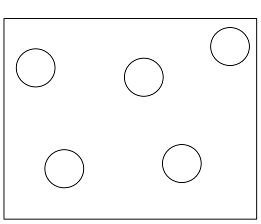
LIQUIDS

iii) gases

In a gas, all the particles are in rapid and random motion, and thus behave independently of each other. There is no ordered arrangement of any kind, and the spaces between the particles are much larger than the size of the particles themselves. The properties of a gas are dominated by the kinetic energy of the particles; the attraction between them is not significant.

A gas has neither a fixed volume nor a fixed shape.

In a gas, the kinetic energy of the particles is much greater than the forces of attraction between them. Since the kinetic energy depends only on temperature, it follows that all gases at a similar temperature behave in a similar way. All liquids can be boiled if heated strongly enough.



GASES

IONIC STRUCTURES

Bonding in ionic compounds

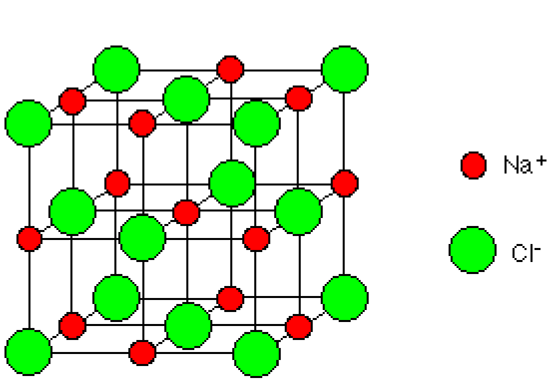
An ionic bond is an attraction between oppositely charged ions. After the ions are formed they all come together to form a **lattice**. A lattice is an infinite and repeating arrangement of particles. All the anions are surrounded by cations and all the cations are surrounded by anions.

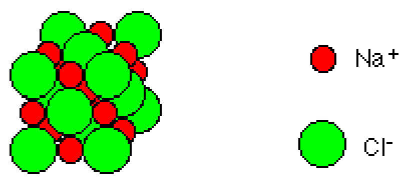
The coordination number of an ion in an ionic solid is the number of oppositely charged ions which surround it. This varies from substance to substance but is usually 4, 6 or 8.

Example – sodium chloride

In sodium chloride, NaCl, each sodium ion is surrounded by six chloride ions and vice versa.

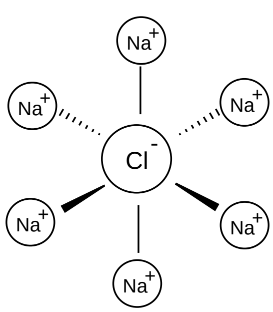
The diagram below shows the structure of sodium chloride. The pattern repeats in this way and the structure extends (repeats itself) in all directions over countless ions. You must remember that this diagram represents only a tiny part of the whole sodium chloride crystal.

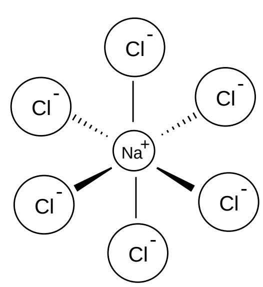




Each sodium ion attracts several chloride ions and vice versa so the ionic bonding is not just between one sodium and one chloride ion. There is a 3-D lattice.

It could also be represented as follows:





1. Melting and boiling point

The attraction between opposite ions is very strong. A lot of kinetic energy is thus required to overcome them and the melting point and boiling point of ionic compounds is very high.

In the liquid state, the ions still retain their charge and the attraction between the ions is still strong. Much more energy is required to separate the ions completely and the difference between the melting and boiling point is thus large.

Compound	NaCl	MgO
Melting point/^{o}C	801	2852
Boiling point/^{o}C	1459	3600

The higher the charge on the ions, and the smaller they are, the stronger the attraction between them will be and the higher the melting and boiling points. In MgO, the ions have a 2+ and 2- charge and thus the attraction between them is stronger than in NaCl, so the melting and boiling points are higher.

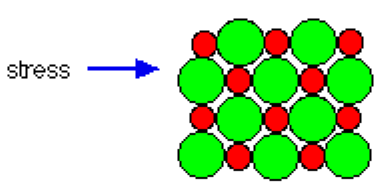
2. Electrical Conductivity

Since ionic solids contain ions, they are attracted by electric fields and will, if possible, move towards the electrodes and thus conduct electricity. In the solid state, however, the ions are not free to move since they are tightly held in place by each other. Thus ionic compounds do not conduct electricity in the solid state. Ionic solids are thus good insulators.

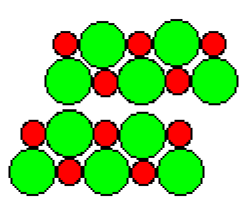
In the liquid state, the ions are free to move and so can move towards their respective electrodes. Thus ionic compounds can conduct electricity in the liquid state.

3. Mechanical properties

Since ions are held strongly in place by the other ions, they cannot move or slip over each other easily and are hence hard and brittle.



opposite ions attract


like ions repel – structure breaks

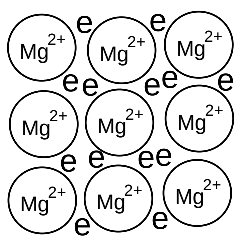
METALLIC STRUCTURES

Bonding in metals

Metallic bonding is the attraction between cations and a sea of delocalised electrons. The cations are arranged to form a lattice, with the electrons free to move between them.

The structure of the lattice varies from metal to metal, and they do not need to be known in detail. It is possible to draw a simplified form of the lattice:

Example - magnesium



This is a simplified 2D form of the metal lattice

Properties of metals

a) Electrical conductivity: since the electrons in a metal are delocalised, they are free to move throughout the crystal in a certain direction when a potential difference is applied and metals can thus conduct electricity in the solid state. The delocalised electron system is still present in the liquid state, so metals can also conduct electricity well in the liquid state.

b) Melting and boiling point: although not generally as strong as in ionic compounds, the bonding in metals is relatively strong, and as a result the melting and boiling points of metals are relatively high.

Metal	Na	K	Be	Mg
Melting point/ ^oC	98	64	1278	649
Boiling point/ ^oC	883	760	2970	1107

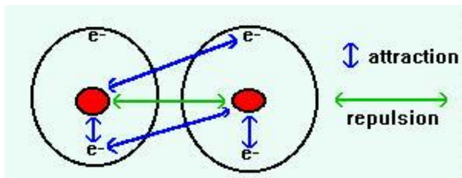
Smaller ions, and those with a high charge, attract the electrons more strongly and so have higher melting points than larger ions with a low charge. Na has smaller cations than K so has a higher melting and boiling point. Mg cations have a higher charge than Na so has a higher melting and boiling point.

c) Other physical properties: Since the bonding in metals is non-directional, it does not really matter how the cations are oriented relative to each other. The metal cations can be moved around and there will still be delocalized electrons available to hold the cations together. The metal cations can thus slip over each other fairly easily. As a result, metals tend to be soft, malleable and ductile.

COVALENT STRUCTURES

A covalent bond is a shared pair of electrons between two atoms. When a covalent bond is formed, two atomic orbitals overlap and a molecular orbital is formed. Like atomic orbitals, a molecular orbital can only contain two electrons. Overlap of atomic orbitals is thus only possible if both orbitals contain only one electron (normal covalent bond), or if one is full and the other empty (dative covalent bond).

Covalent bonding happens because the electrons are more stable when attracted to two nuclei than when attracted to only one:



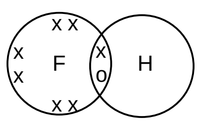
1. <u>Normal covalent bonds</u>

An overlap between two orbitals, each containing one electron, is a normal covalent bond. The number of normal covalent bonds which an atom can form depends on its number of unpaired electrons. Some atoms, like carbon, promote electrons from s to p orbitals to create unpaired electrons.

	1s	2s	2p		
F	↑↓	↑↓	↑↓	↑↓	↑

F has 1 unpaired electron in a 2p orbital – forms one covalent bond

Eg hydrogen fluoride

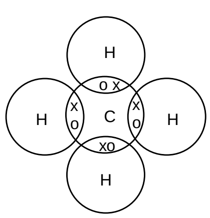


	1s	2s	2p		
C	↑↓	↑↓	↑	↑	

Carbon rearranges slightly to make more unpaired electrons –

	1s	2s	2p		
C	↑↓	↑	↑	↑	↑

C has 4 unpaired electrons – forms four covalent bonds



Eg methane

1. <u>Dative covalent bonds</u>

Any atom which has filled valence shell orbitals can provide both electrons for a dative covalent bond. This includes any element in groups V, VI, VII or 0 but is most common in N, O and Cl.

	1s	2s	2p		
N	↑↓	↑↓	↑	↑	↑

N has three unpaired electrons and one electron pair

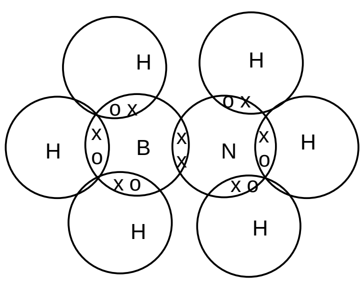
Any atom which has empty valence shell orbitals can accept a pair of electrons for a covalent bond. This includes any element in groups I, II and III but is most common in Be, B and Al.

	1s	2s	2p		
B	↑↓	↑↓	↑		

B promotes an electron from 2s to 2p to form 3 unpaired electrons:

	1s	2s	2p		
B	↑↓	↑	↑	↑	

B has 3 unpaired electrons and an empty orbital

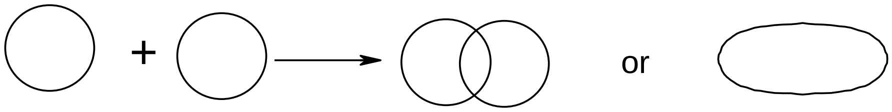


Eg BH_3NH_3

2. <u>Sigma and pi bonds</u>

Atomic orbitals can overlap in one of two ways:

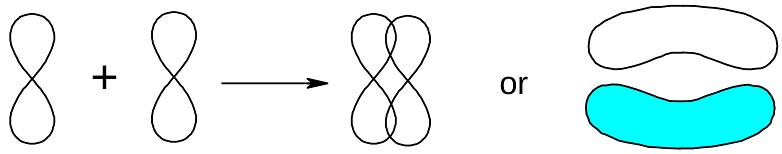
If they overlap directly along the internuclear axis, as is most common, a σ-bond is formed.



A σ-bond is a bond resulting from direct overlap of two orbitals along the internuclear axis.
All single bonds between two atoms are σ-bonds.

It is only possible to form one σ-bond between two atoms, since another would force too many electrons into a small space and generate repulsion. If double bonds are formed, therefore, the orbitals must overlap in a different way.

If two orbitals overlap above and below (or behind and in front of) the internuclear axis, then a π-bond is formed.



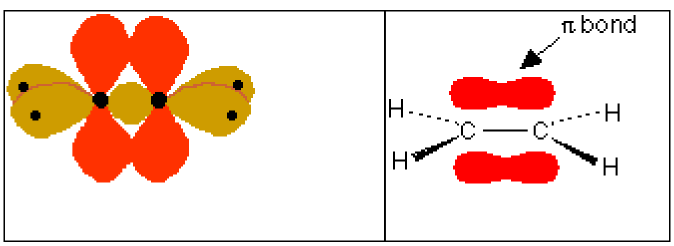
A π-bond is a bond resulting from overlap of atomic orbitals above and below the internuclear axis.
All double bonds consist of a σ-bond and a π-bond.

All triple bonds consist of a σ-bond and two π-bonds. If the first π-bond results from overlap above and below the internuclear axis, the second results from overlap behind and in front of the internuclear axis.

Note that π-bonds can only be formed by overlap of p-orbitals, since s-orbitals do not have the correct geometry.

π-bonds can also be represented by orbital diagrams.

Eg ethene:



3. Strength of covalent bonds

Covalent bonds are in general strong. The smaller the atoms, the closer the electrons are to the two nuclei and the stronger the bond.

Bond	Bond dissociation energy/ $kJmol^{-1}$
C-F	467
C-Cl	346
C-Br	290
C-I	228

4. <u>Molecular, giant covalent and layered substances</u>

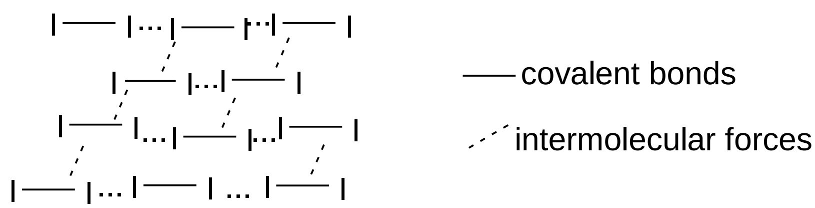
Covalent bonding can result in three very different types of substance:

a) Molecular

In many cases, the bonding capacity is reached after only a few atoms have combined with each other to form a molecule. If no more covalent bonds can be formed after this, the substance will be made up of a larger number of discreet units (molecules) with no strong bonding between them.
Such substances are called **molecular substances**, and there are many examples of them: CH_4, Cl_2, He, S_8, P_4, O_2, H_2O, NH_3 etc

The molecules are held together by **intermolecular forces**, which are much weaker than covalent bonds but are often strong enough to keep the substance in the solid or liquid state.

Example - Iodine



There are attractive forces between these molecules, known as intermolecular forces, but they are weak. In the gaseous state, the intermolecular forces are broken but the bonds within the molecule remain intact - they are not broken. The gas phase consists of molecules, not atoms.

Molecular substances have certain characteristic properties:

Melting and boiling point: these are generally low, since intermolecular forces are weak. Intermolecular forces also decrease rapidly with increasing distance, so there is often little difference in the melting and boiling points.

Substance	CH_4	H_2O	H_2	He
Melting point /^oC	-184	0	-259	-272
Boiling point /^oC	-166	100	-253	-268

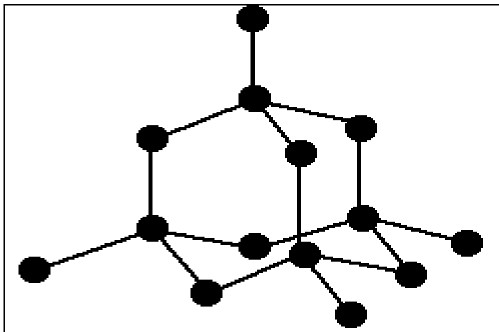
Electrical conductivity: There are no ions and no delocalised electrons, so there is little electrical conductivity in either solid or liquid state.

Other physical properties: The intermolecular forces are weak and generally non-directional, so most molecular covalent substances are soft, crumbly and not very strong.

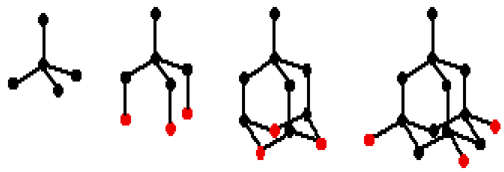
b) Giant covalent

In some cases, it is not possible to satisfy the bonding capacity of a substance in the form of a molecule; the bonds between atoms continue indefinitely, and a large lattice is formed. There are no discrete molecules and covalent bonding exists between all adjacent atoms.
Such substances are called giant covalent substances, and the most important examples are C, B, Si and SiO_2.

Example – diamond (diamond is an allotrope of carbon)



Don't forget that this is just a tiny part of a giant structure extending on all 3 dimensions.



In giant covalent compounds, covalent bonds must be broken before a substance can melt or boil.

Giant covalent compounds have certain characteristic properties:

Melting and boiling point: these are generally very high, since strong covalent bonds must be broken before any atoms can be separated. The melting and boiling points depend on the number of bonds formed by each atom and the bond strength. The difference between melting and boiling points is not usually very large, since covalent bonds are very directional and once broken, are broken completely.

Substance	C	Si	B	SiO_2
Melting point /^{o}C	3550	1410	2300	1510
Boiling point /^{o}C	4827	2355	2550	2230

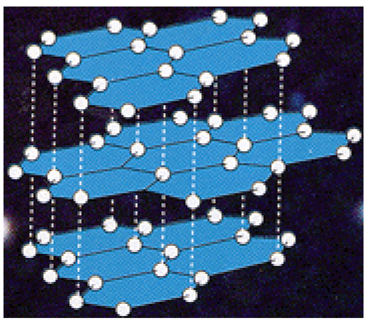
Electrical conductivity: there are no ions or delocalised electrons, so there is little electrical conductivity in either solid or liquid state.

Other physical properties: since the covalent bonds are strong and directional, giant covalent substances are hard, strong and brittle.
Diamond is in fact the hardest substance known to man. For this reason it is used in drills, glass-cutting and styluses for turntables.

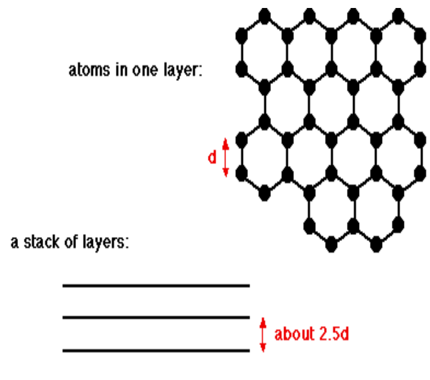
c) giant covalent layered

Some substances contain an infinite lattice of covalently bonded atoms in two dimensions only to form layers. The different layers are held together by intermolecular forces, and there are often delocalized electrons in between the layers. Examples of these structures are graphite and black phosphorus.

Example - graphite



or



In graphite, each carbon atom is bonded to three others. The spare electron is delocalized and occupies the space in between the layers. All atoms in the same layer are held together by strong covalent bonds, and the different layers are held together by intermolecular forces.

A number of characteristic properties of graphite result from this structure:

Electrical conductivity: due to the delocalised electrons in each plane, graphite is a very good conductor of electricity in the x and y directions, even in the solid state (unusually for a non-metal). However, since the delocalisation is only in two dimensions, there is little electrical conductivity in the z direction (i.e. perpendicular to the planes).

Density: graphite has a much lower density than diamond (2.25 gcm^{-3}) due to the relatively large distances in between the planes.

Hardness: graphite is much softer than diamond since the different planes can slip over each other fairly easily. This results in the widespread use of graphite in pencils and as an industrial lubricant.

SUMMARY OF DIFFERENT TYPES OF COMPOUND AND THEIR PROPERTIES

SUBSTANCE	Nature of bonding	Physical properties
IONIC **Eg NaCl**	Attraction between oppositely charged ions. Infinite lattice of oppositely charged ions in three dimensions	High mpt, bpt Good conductors in liquid state Poor conductors in solid state Hard, strong, brittle
METALLIC **Eg Mg**	Attraction between cations and delocalised electrons. Infinite lattice of cations in three dimensions, with delocalized electrons in the spaces	High mpt, bpt Good conductors in solid state Good conductors in liquid state Strong, malleable
GIANT COVALENT **Eg diamond**	Infinite lattice of atoms linked by covalent bonds in three dimensions. Covalent bonds are pairs of electrons shared between two atoms	Very high mpt, bpt Poor conductors in solid state Poor conductors in liquid state Hard, strong, brittle
MOLECULAR **Eg I_2**	Discrete molecules. Atoms in molecule linked by covalent bonds. (σ or π, normal or dative) Weak intermolecular forces between molecules.	Low mpt, bpt Poor conductors in solid state Poor conductors in liquid state Soft, weak, powdery
GIANT COVALENT LAYERED **Eg graphite**	Infinite lattice of atoms linked by covalent bonds in two dimensions to form planes. Planes held together by intermolecular forces. Delocalised electrons in between layers	High mpt, bpt Good conductors parallel to planes Poor conductors perpendicular to planes Soft

Don’t forget to learn the structures of

- Sodium chloride
- Iodine
- Diamond
- Graphite

MOLECULAR SHAPES

When an atom forms a covalent bond with another atom, the electrons in the different bonds and the non-bonding electrons in the outer shell all behave as negatively charged clouds and repel each other. In order to minimise this repulsion, all the outer shell electrons spread out as far apart in space as possible.

Molecular shapes and the angles between bonds can be predicted by the VSEPR theory
VSEPR = valence shell electron pair repulsion

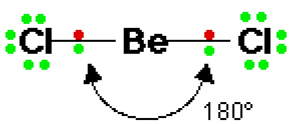
VSEPR theory consists of two basic rules:

i) All σ-bonded electron pairs and all lone pairs arrange themselves as far apart in space as is possible. π-bonded electron pairs are excluded.
ii) Lone pairs repel more strongly than bonding pairs.

These two rules can be used to predict the shape of any covalent molecule or ion, and the angles between the bonds.

a) 2 electron pairs

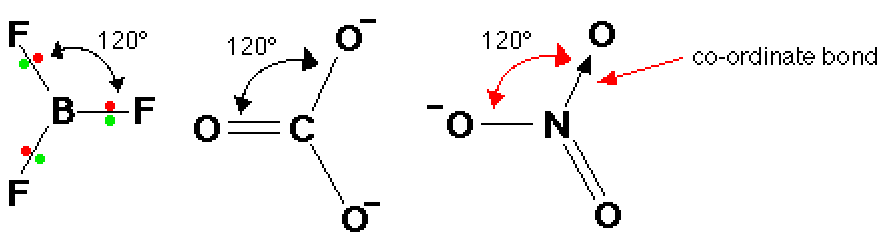
If there are two electron pairs on the central atom, the angle between the bonds is 180°.



Molecules which adopt this shape are said to be LINEAR.
E.g. $BeCl_2$, CO_2

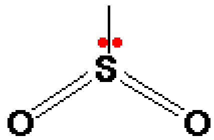
b) three electron pairs

If there are three electron pairs on the central atom, the angle between the bonds is 120°.



Molecules which adopt this shape are said to be TRIGONAL PLANAR.
E.g. BF_3, $AlCl_3$, CO_3^{2-}, NO_3^-

If one of these electron pairs is a lone pair, the bond angle is slightly less than 120° due to the stronger repulsion from lone pairs, forcing them closer together.



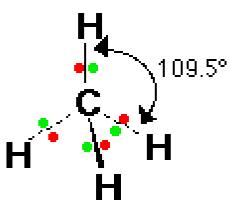
bond angle = 118°

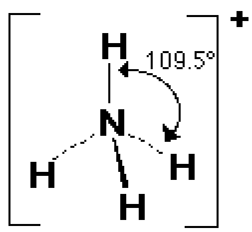
Molecules which adopt this shape are said to be BENT.

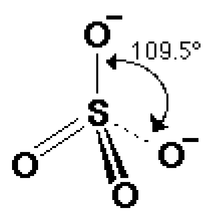
E.g. SO_2, NO_2^-

c) Four electron pairs

If there are four bonded pairs on the central atom, the angle between the bonds is approx 109°.



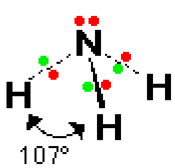




Molecules which adopt this shape are said to be TETRAHEDRAL.

E.g. CH_4, $SiCl_4$, NH_4^+, SO_4^{2-}

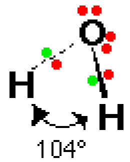
If one of the electron pairs is a lone pair, the bond angle is slightly less than 109°, due to the extra lone pair repulsion which pushes the bonds closer together (approx 107°).



Molecules which adopt this shape are said to be TRIGONAL PYRAMIDAL.

E.g. NH_3, PCl_3

If two of the electron pairs are lone pairs, the bond angle is also slightly less than 109°, due to the extra lone pair repulsion (approx 104°).

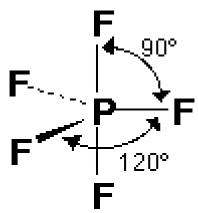


Molecules which adopt this shape are said to be BENT.

E.g. H_2O, OF_2

d) Five electron pairs

If there are five bonded pairs on the central atom, the three bonds are in a plane at 120° to each other, the other 2 are at 90° to the plane.

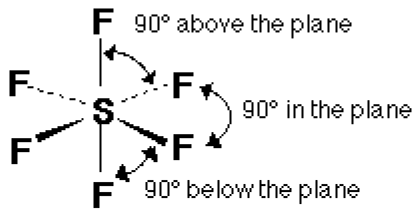


Molecules which adopt this shape are said to be TRIGONAL BYPRYMIDAL**.**

E.g. PF_5, PCl_5

d) Six electron pairs

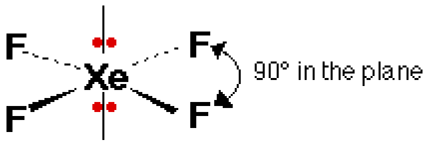
If there are six electron pairs on the central atom, the angle between the bonds is 90°.



Molecules which adopt this shape are said to be OCTAHEDRAL.

E.g. SF_6

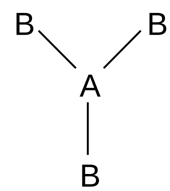
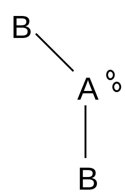
If there are 4 bonding pairs and 2 lone pairs, the bonded pairs are at 90° in the plane and the lone pairs at 180°. The angles are still exactly 90° because the lone pairs are opposite each other so their repulsion cancels out.

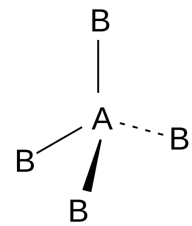
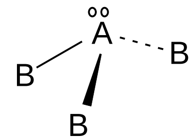
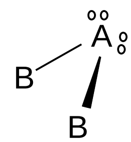
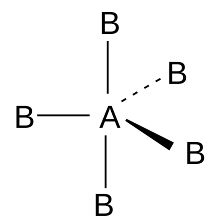
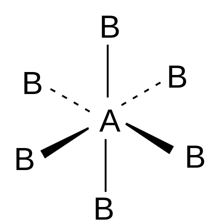
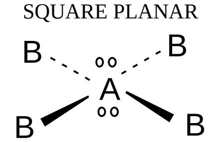


Molecules which adopt this shape are said to be SQUARE PLANAR.

E.g. XeF_4, ClF_4^-

SUMMARY OF MOLECULAR SHAPES

Valence shell electron pairs	Bonding pairs	Lone pairs	shape	Bond Angle (°)
2	2	0	LINEAR B — A — B	180
3	3	0	TRIGONAL PLANAR 	120
3	2	1	BENT 	115 - 118

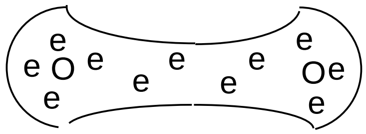
4	4	0	TETRAHEDRAL 	109.5
4	3	1	TRIGONAL PYRAMIDAL 	107
4	2	2	BENT 	104.5
5	5	0	TRIGONAL BIPYRAMIDAL 	90 and 120
6	6	0	OCTAHEDRAL 	90
6	4	2	SQUARE PLANAR 	90

INTERMOLECULAR FORCES

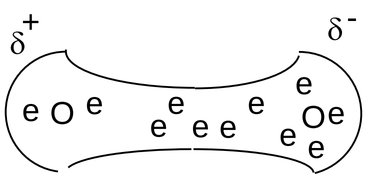
There are no covalent bonds between molecules in molecular covalent compounds. There are, however, forces of attraction between these molecules, and it is these which must be overcome when the substance is melted and boiled. These forces are known as intermolecular forces. There are three main types of intermolecular force:

1. Van der Waal's forces

Consider a molecule of oxygen, O_2.

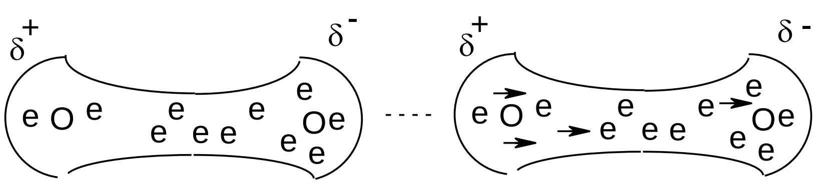


The electrons in this molecule are not static; they are in a state of constant motion. It is therefore likely that at any given time the distribution of electrons will not be exactly symmetrical - there is likely to be a slight surplus of electrons on one of the atoms.



This is known as a **temporary dipole**. It lasts for a very short time as the electrons are constantly moving. Temporary dipoles are constantly appearing and disappearing.

Consider now an adjacent molecule. The electrons on this molecule are repelled by the negative part of the dipole and attracted to the positive part, and move accordingly.



This is known as an **induced dipole**. There is a resulting attraction between the two molecules, and this known as a **Van der Waal's force**.

Van der Waal's forces are present between all molecules, although they can be very weak. They are the reason all compounds can be liquefied and solidified. Van der Waal's forces tend to have strengths between 1 $kJmol^{-1}$ and 50 $kJmol^{-1}$.

The strength of the Van der Waal's forces in between molecules depends on two factors:

a) the number of electrons in the molecule

The greater the number of electrons in a molecule, the greater the likelihood of a distortion and thus the greater the frequency and magnitude of the temporary dipoles. Thus the Van der Waal's forces between the molecules are stronger and the melting and boiling points are larger.

Eg noble gases:

Substance	He	Ne	Ar	Kr
Number of electrons	2	10	18	36
Melting point/^oC	-272	-252	-189	-157
Boiling point/^oC	-269	-250	-186	-152

Eg alkanes:

Substance	CH_4	C_2H_6	C_3H_8	C_4H_{10}
Number of electrons	10	18	26	34
Melting point/^oC	-182	-183	-190	-138
Boiling point/^oC	-164	-88	-42	0

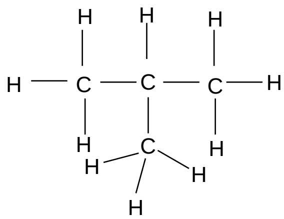
a) Surface area of the molecules

The larger the surface area of a molecule, the more contact it will have with adjacent molecules. Thus the greater its ability to induce a dipole in an adjacent molecule and the greater the Van der Waal's forces and melting and boiling points.

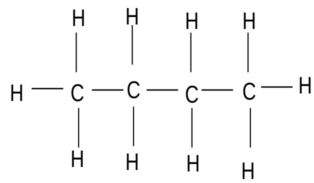
This point can be illustrated by comparing different molecules containing a similar number of electrons:

Substance	Kr	Cl_2	$CH_3CH(CH_3)CH_3$	$CH_3CH_2CH_2CH_3$
Number of electrons	36	34	34	34
Melting point/^oC	-157	-101	-159	-138
Boiling point/^oC	-152	-35	-12	0

$CH_3CH(CH_3)CH_3$ methylpropane



$CH_3CH_2CH_2CH_3$ butane

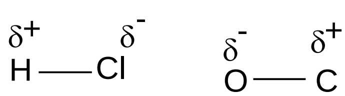


Note that butane has a larger surface area than 2-methylpropane, although they have the same molecular formula (C_4H_{10}). Straight-chain molecules always have higher boiling points than their isomers with branched chains.

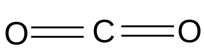
2. <u>Dipole-dipole bonding</u>

Temporary dipoles exist in all molecules, but in some molecules there is also a **permanent dipole**.

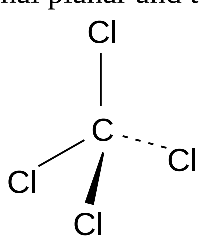
Most covalent bonds have a degree of ionic character resulting from a difference in electronegativity between the atoms. This results in a polar bond and a dipole.



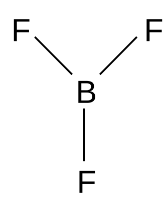
In many cases, however, the presence of polar bonds (dipoles) does not result in a permanent dipole on the molecule, as there are other polar bonds (dipoles) in the same molecule which have the effect of cancelling each other out. This effect can be seen in a number of linear, trigonal planar and tetrahedral substances:



CO_2



CCl_4

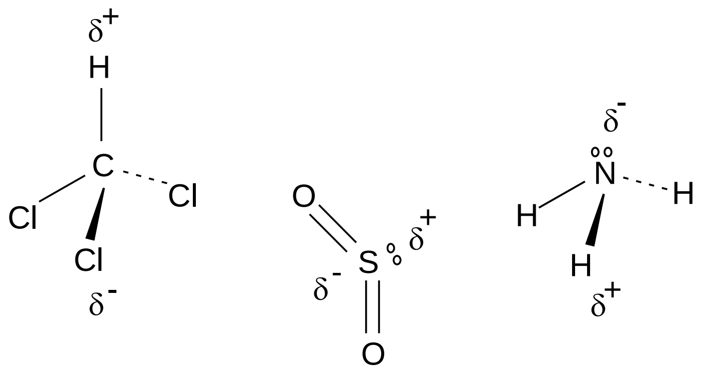


BF_3

In all the above cases, there are dipoles resulting from polar bonds but the vector sum of these dipoles is zero; i.e. the dipoles cancel each other out. The molecule thus has no overall dipole and is said to be **non-polar**.

Non-polar molecules are those in which there are no polar bonds or in which the dipoles resulting from the polar bonds all cancel each other out. The only intermolecular forces that exist between non-polar molecules are temporary-induced dipole attractions, or Van der Waal’s forces.

In other molecules, however, there are dipoles on the molecule which do not cancel each other out:

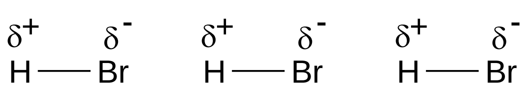


$CHCl_3$ SO_2 NH_3

In all the above cases, there are dipoles resulting from polar bonds whose vector sum is not zero; i.e. the dipoles do not cancel each other out. The molecule thus has a permanent dipole and is said to be **polar**.

Polar molecules are those in which there are polar bonds and in which the dipoles resulting from the polar bonds do not cancel out.

In addition to the Van der Waal's forces caused by temporary dipoles, molecules with permanent dipoles are also attracted to each other by **dipole-dipole bonding**. This is an attraction between a permanent dipole on one molecule and a permanent dipole on another.



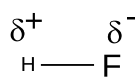
Dipole-dipole bonding usually results in the boiling points of the compounds being slightly higher than expected from temporary dipoles alone; it slightly increases the strength of the intermolecular bonding.
The effect of dipole-dipole bonding can be seen by comparing the melting and boiling points of different substances which should have Van der Waal's forces of similar strength:

Substance	Cl_2	HBr	$CH_3CH(CH_3)CH_3$	CH_3COCH_3
Number of electrons	34	36	34	32
Permanent dipole	NO	YES	NO	YES
Melting point/^oC	-101	-88	-159	-95
Boiling point/^oC	-45	-67	-73	-44

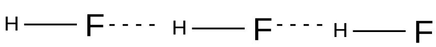
3. Hydrogen bonding

In most cases as seen above, the presence of permanent dipoles only makes a slight difference to the magnitude of the intermolecular forces. There is one exceptional case, however, where the permanent dipole makes a huge difference to the strength of the bonding between the molecules.

Consider a molecule of hydrogen fluoride, HF. This clearly has a permanent dipole as there is a large difference in electronegativity between H (2.1) and F (4.0). The electrons in this bond are on average much closer to the F than the H:



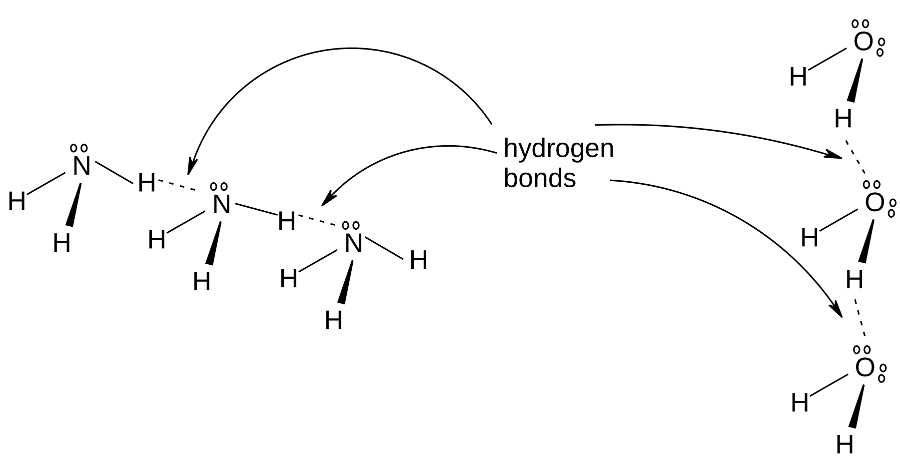
The result of this is that the H atom has on almost no electron density around its nucleus at all and is therefore very small. The H atom is therefore able to approach electronegative atoms on adjacent molecules very closely and form a very strong intermolecular dipole-dipole bond.



This is known as **hydrogen bonding**. It is only possible if the hydrogen atom is bonded to a very electronegative element; i.e. N, O or F. It is not fundamentally different from dipole-dipole bonding; it is just a stronger form of it.

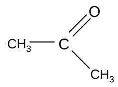
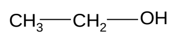
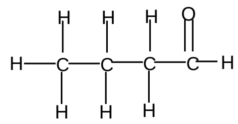
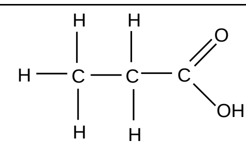
A hydrogen bond can be defined as an attraction between an electropositive hydrogen atom (ie covalently bonded to N, O or F) and an electronegative atom on an adjacent molecule.

Examples of substances containing hydrogen bonds are HF, H_2O, NH_3, alcohols, carboxylic acids, amines, acid amides and urea.



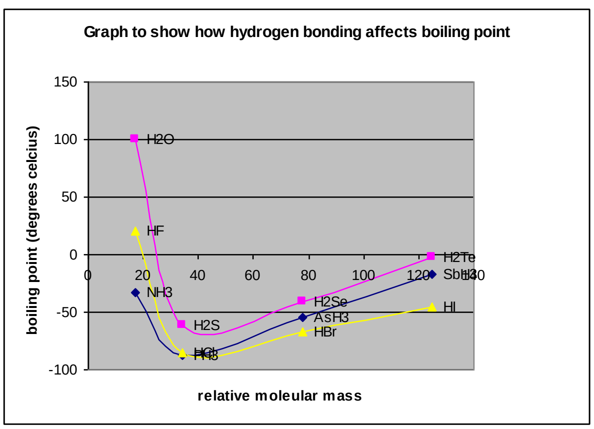
a) Effect on boiling point

The effect of hydrogen bonding on melting and boiling points of substances is huge, unlike other dipole-dipole bonds. Many substances containing hydrogen bonds have much higher boiling points than would be predicted from Van der Waal's forces alone.

Substance	CH_3OCH_3	CH_3CH_2OH	$CH_3CH_2CH_2CHO$	CH_3CH_2COOH
Structure				
Number of electrons	26	26	40	40
Hydrogen bonding	NO	YES	NO	YES
Melting point/^{o}C	-95	-117	-81	-21
Boiling point/^{o}C	-44	79	56	141

Another important series of trends are the boiling points of the hydrides of elements in groups V, VI and VII of the periodic table:
Group V: NH_3, PH_3, AsH_3, SbH_3
Group VI: H_2O, H_2S, H_2Se, H_2Te
Group VII: HF, HCl, HBr, HI

The boiling points of these graphs are shown graphically below:



In each case the hydride of period 2 shows a boiling point which is abnormally high (H_2O, NH_3 and HF).

The general increase in boiling point down the groups result from the increase in Van der Waal's forces which results from an increasing number of electrons in the molecules. There are permanent dipoles but they are not very strong.

The abnormally high boiling points of H_2O, NH_3 and HF are a result of hydrogen bonding between the molecules. Thus results in very strong intermolecular forces between the molecules despite the fact that the Van der Waal's forces are weaker than in the other hydrides.

b) other effects of hydrogen bonding

The effects of hydrogen bonding on the physical properties of a substance are not restricted to elevated melting and boiling points; it can influence the properties of substances in other ways:

The low density of ice. This is due to hydrogen bonding. In ice, the water molecules arrange themselves in such a way as to maximise the amount of hydrogen bonding between the molecules. This results in a very open hexagonal structure with large spaces within the crystal. This accounts for its low density.

When the ice melts, the structure collapses into the open spaces and the resulting liquid, despite being less ordered, occupies less space and is thus more dense.

Thus ice floats on water.

The helical nature of DNA. This is also due to hydrogen bonding. Molecules of DNA contain N-H bonds and so hydrogen bonding is possible. The long chains also contain C=O bonds and the H atoms can form a hydrogen bond with this electronegative O atom. This results in the molecule spiralling, as the C=O bonds and the N-H bonds approach each other.

This is an example of an **intramolecular** hydrogen bond, where the attraction is between a hydrogen atom and an electronegative atom on the same molecule. This must be distinguished from intermolecular hydrogen bonding, in which the attraction is between a hydrogen atom and an electronegative atom on an adjacent molecule.

STRUCTURE AND BONDING IN THE PERIODIC TABLE

The structure and bonding of the elements in period 3 of the Periodic Table varies widely. **There is a gradual decrease in metallic character in crossing a period**.

On crossing a period the ionisation energies increase so it becomes more difficult to remove electrons and form metallic structures. Thus covalent bonding becomes more common on crossing a period from left to right.

The noble gases form neither metallic nor covalent bonds with each other. The ionisation energies are very high so metallic bonding is not possible. There are no unpaired electrons so covalent bonding is not possible. Thus they form no bonds and exist as free gaseous atoms.

The trends in intramolecular bond type can be seen in the following table:

Na metallic	Mg metallic	Al metallic	Si covalent	P covalent	S covalent	Cl covalent	Ar -

The variation on bond type causes a number of differences in the structures of the Period 3 elements which in turn causes significant differences in physical properties.

a) Sodium, Magnesium and Aluminium

Sodium, Magnesium and Aluminium are metals. They consist of an infinite lattice of cations held together by a sea of delocalised electrons. There is a fairly strong attraction between the cations and the delocalised electrons and as a result metals tend to have fairly high melting points and boiling points.

The melting points increase with increasing charge and decreasing size and thus increase across a period.

Element	Sodium	Magnesium	Aluminium
Mpt/^{o}C	98	669	680
Bpt/^{o}C	883	1107	2467

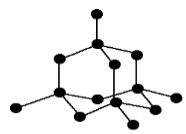
The delocalised electrons in the metal structure are free to move throughout the metal lattice and can thus behave as charge carriers. When a potential difference is applied, the electrons can move towards the positive electrode. Thus metals are good conductors of electricity.

Electrical conductivity increases from sodium to aluminium as the number of delocalized electrons per atom increases. Aluminium has three electrons per atom in the sea, magnesium two per atom and sodium only one per atom.

b) Silicon

Silicon is a giant covalent macromolecule. Silicon atoms form infinite lattices in which all the atoms are held together by strong covalent bonds. Since the structure cannot be broken up without breaking these strong covalent bonds, it follows that silicon has a very high melting and boiling point. The structure of silicon is tetrahedral, identical to diamond:

SILICON:

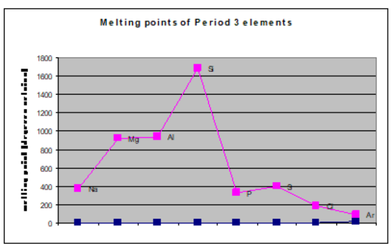
Structure	
Mpt/°C	1406
Bpt/°C	2355

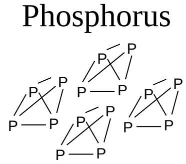
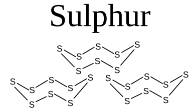
Silicon does not conduct electricity well as it has no free electrons and no free ions.

c) Phosphorus, sulphur, chlorine and argon

Phosphorus, sulphur, chlorine and argon form simple molecular structures.There are strong, covalent bonds within the molecule but the different molecules are only held together by weak Van der Waal's forces. Separating these molecules thus requires little energy and the melting and boiling points of these elements are relatively low.

The larger the molecule, the greater the magnitude of the temporary and induced dipoles and the higher the melting and boiling points.



Element	Phosphorus	Sulphur	Chlorine	Argon
Structure			Cl—Cl Cl—Cl Cl—Cl Cl—Cl Cl—Cl	Ar Ar Ar Ar Ar Ar
Mpt/°C	44	119	-101	-189
Bpt/°C	280	445	-35	-186
Formula	P_4 (or P)	S_8 (or S)	Cl_2	Ar

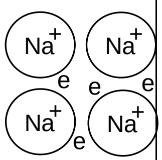
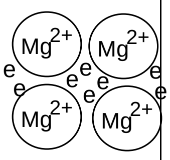
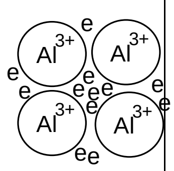
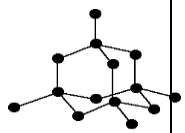
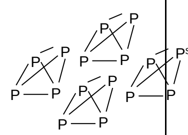
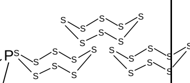
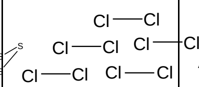
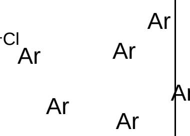
Sulphur has the highest melting point as it exists as S_8 molecules. These molecules are quite large, so the number of electrons in the molecule is high and the Van der Waal's forces are quite strong. Phosphorus exists as P_4 molecules, which have fewer electrons in them and so have weaker Van der Waal's forces. So phosphorus has a lower melting point than sulphur. Chlorine exists as molecules, which have even fewer electrons in them so the Van der Waal's forces are lower and chlorine has a lower melting point than sulphur and phosphorus. Argon has the lowest melting and boiling point of all, as it exists as single Ar atoms which have even less electrons and so only form very weak Van der Waal's forces.

These elements do not conduct electricity well as they have no free electrons and no free ions.

3. **Summary of properties of period 3 elements**

- Melting and boiling point
  – increases from Na to Al
  – increases from Al to Si
  – decreases from Si to P
  – increases from P to S
  – decreases from S to Ar

- Electrical conductivity
  – increases from Na to Al
  – is zero from Si to Ar

Element:	Sodium	Magnesium	Aluminium	Silicon	Phosphorus (white)	Sulphur	Chlorine	Argon
Bonding:	Metallic	Metallic	metallic	covalent	Covalent	covalent	covalent	-
Structure:								
Type:	Metallic	Metallic	Metallic	Giant covalent	Simple molecular	Simple molecular	Simple molecular	Simple atomic
Melting point/^oC:	98	669	680	1410	44	119	-101	-189
Boiling point/^oC:	883	1107	2467	2355	280	445	-45	-186
First IE/ $kJmol^{-1}$:	496	738	578	789	1012	1000	1251	1521
E-negativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0	-
Electrical conductivity ($x10^{-8}\Omega^{-1}m^{-1}$)	0.21	0.26	0.41	0	0	0	0	0

NB You do not need to know the exact figures, just know the trends and be able to explain them.