Edexcel

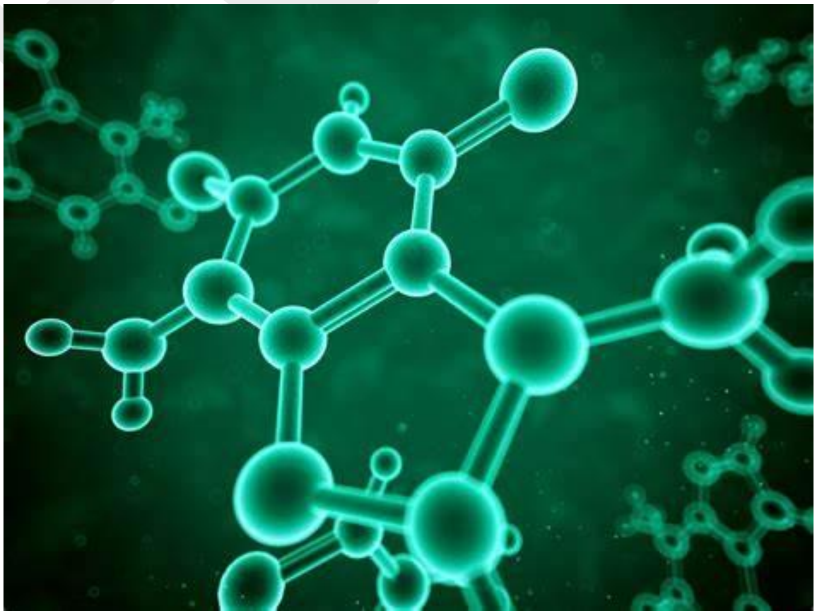
AS - Level

Chemistry

CODE: (WCH11)

Topic 3

Bonding and structure



FOCUS

3A – 1 The nature of ionic bonding

THE FORMATION OF CATIONS AND ANIONS

Some ionic compounds can be formed by the direct combination of two elements.

FORMATION OF SODIUM AND CHLORIDE IONS

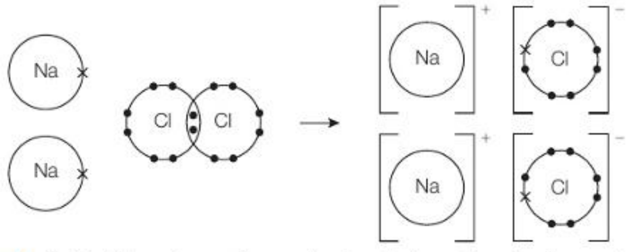
For example, sodium chloride can be formed by burning sodium in chlorine:

2Na(s) + Cl2(g) → 2NaCl(s)

We can represent the reaction that occurs by two ionic half-equations:
2Na→ 2Na+ + 2e and Cl_2+ 2e→ $2C1^-$

Each sodium atom has lost one electron to become a positive sodium ion. The chlorine molecule has gained two electrons to become two chloride ions.

We can represent the electronic changes involved by dot-and- cross diagrams.



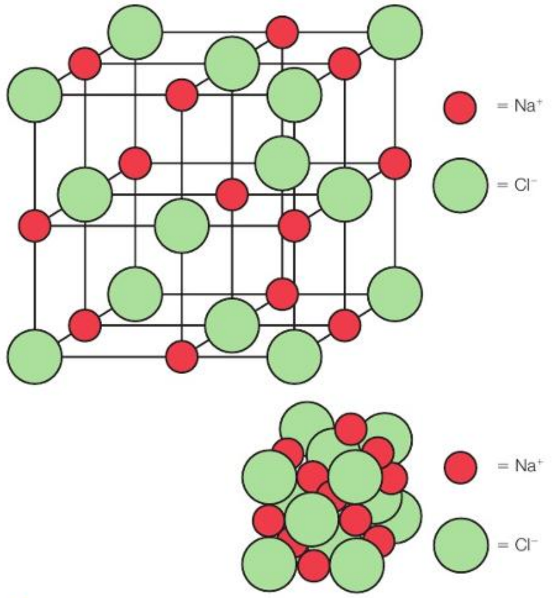
▲ **fig A** Dot-and-cross diagram showing the formation of sodium and chloride ions.

FORMATION OF MAGNESIUM AND OXIDE IONS

Here is the equation for the formation of magnesium oxide:
2Mg(s) + O_2(g) → 2MgO(s)

THE NATURE OF IONIC BONDING

Ionic bonding occurs in solid materials consisting of a regular array of oppositely charged ions extending throughout a giant lattice network.



▲ **fig C** Structure of sodium chloride.

The most familiar ionic compound is sodium chloride, NaCl. It consists of a regular array of sodium ions, Na+, and chloride ions, Cl, as shown in fig C.

The electrostatic interaction between ions is not directional: all that matters is the distance between two ions, not their orientation with respect to one another. (Compare this with covalent bonding in Topic 3B.)
When ions are present, the electrostatic interaction between them tends to be dominant.

THE STRENGTH OF IONIC BONDING

You can determine the strength of ionic bonding by calculating the amount of energy required in one mole of solid to separate the ions to infinity (i.e. in the gas phase). When they are at an infinite distance from one another, the ions can no longer interact.

FOCUS

Table A below shows the energy required to separate to infinity the ions in one mole of various alkali metal halides.

	AMOUNT OF ENERGY REQUIRED TO SEPARATE THE IONS TO INFINITY / kJ mol^{-1}			
	F^-	Cl^-	Br^-	I^-
Li^+	1031	848	803	759
Na^+	918	780	742	705
K^+	817	711	679	651
Rb^+	783	685	656	628

table A Energy required to break up a lattice of an ionic compound.

For ions of the same charge, the smaller the ions the more energy is required to overcome the electrostatic interactions between the ions and to separate them.

The size of the ions is one factor that affects the strength of ionic bonding, which in turn determines how closely packed the ions are in the lattice.

There is no simple mathematical relationship to describe the effects that ionic radius and ionic charge have on the strength of ionic bonding. The situation is complicated by the way in which the ions pack together to form the lattice, and by the extent to which there are covalent interactions between the ions. In general, however, the smaller the ions and the larger the charge on the ions, the stronger the ionic bonding.

EVIDENCE FOR THE EXISTENCE OF IONS

Ionic compounds can conduct electricity and undergo electrolysis when either molten or in aqueous solution. This is the most convincing evidence for the existence of ions.

For example, when you pass a direct electric current through molten sodium chloride (fig D), sodium is formed at the negative electrode and chlorine is formed at the positive electrode.

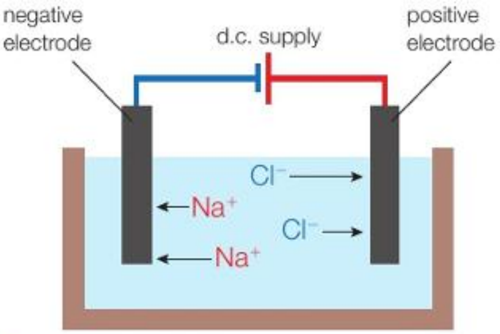


fig D Electrolysis of molten sodium chloride.

The explanation for this phenomenon is that:

- the positive sodium ions migrate towards the negative electrode where they gain electrons and become sodium atoms
- the negative chloride ions migrate towards the positive electrode where they lose electrons and become chlorine molecules.

At the negative electrode: $2Na^+ + 2e^- \rightarrow 2Na$

At the positive electrode: $2Cl^- \rightarrow Cl_2 + 2e^-$

Overall equation: $2NaCl \rightarrow 2Na + Cl_2$

We can demonstrate the movement of ions by passing a direct current through copper(II) chromate (VI) solution (fig E). Aqueous copper(II) ions, Cu^{2+} (aq), are blue and aqueous chromate(VI) ions, CrO_4^{2-} (aq), are yellow.

The Cu^{2+}(aq) ions migrate towards the negative electrode and the solution around this electrode turns blue. The CrO_4^{2-} (aq) ions migrate towards the positive terminal and the solution around this electrode turns yellow.

Further evidence for the existence of ions is supplied by electron density maps.
Fig F is an electron density map for sodium chloride.

Fig F is an electron density map for sodium chloride.

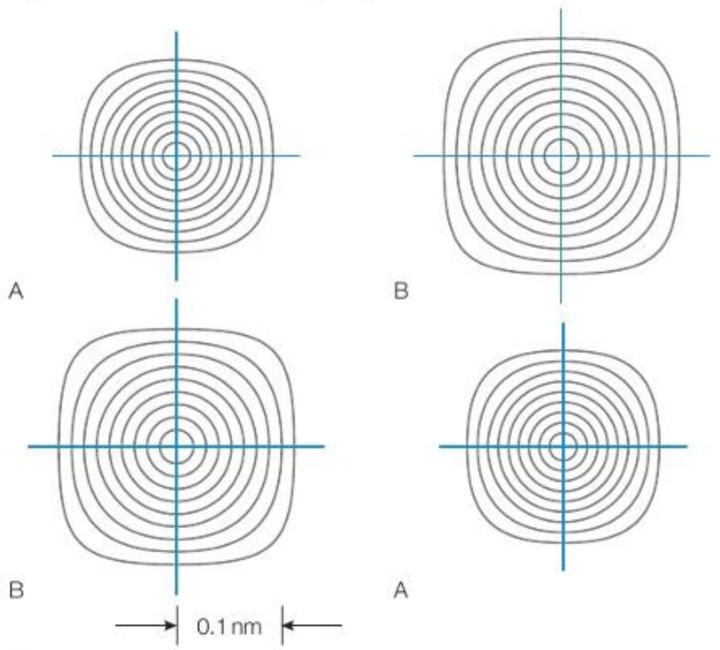


fig F Electron density map of sodium chloride produced from X-ray diffraction patterns.

3A – 2 Ionic radii and polarization of ions

TRENDS IN IONIC RADII

Ionic radii are difficult to measure accurately and vary according to the environment of the ion. For example, it is important how many oppositely charged ions are touching it (i.e. the co-ordination number). The nature of the ions is also important.

There are several different ways of measuring ionic radii and they all produce slightly different values. If you are going to make reliable comparisons using ionic radii, all the values must come from the same source.

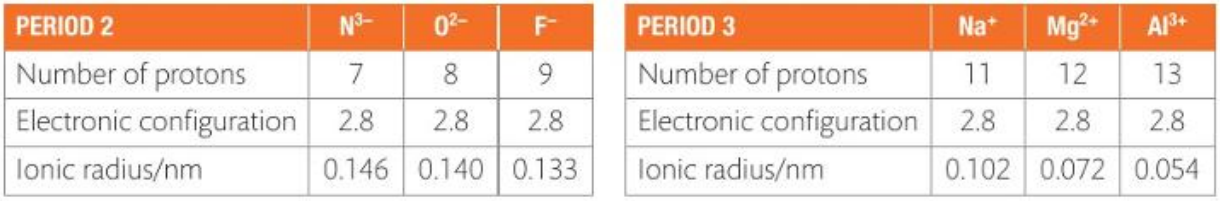
Remember that there are quite large uncertainties when using ionic radii. Trying to explain things in detail is made difficult because of those uncertainties.

GROUP 1		
ION	ELECTRONIC CONFIGURATION	IONIC RADIUS / nm
Li^+	2	0.076
Na^+	2.8	0.102
K^+	2.8.8	0.138
Rb^+	2.8.18.8	0.152

GROUP 7		
ION	ELECTRONIC CONFIGURATION	IONIC RADIUS / nm
F^-	2.8	0.133
Cl^-	2.8.8	0.181
Br^-	2.8.18.8	0.196
I^-	2.8.18.18.8	0.220

table A Trends in ionic radii in Groups 1 and 7.

As you go down each group, the ions have more electron shells; therefore, the ions get larger.



PERIOD 2	N^{3-}	O^{2-}	F^-
Number of protons	7	8	9
Electronic configuration	2.8	2.8	2.8
Ionic radius/nm	0.146	0.140	0.133

PERIOD 3	Na^+	Mg^{2+}	Al^{3+}
Number of protons	11	12	13
Electronic configuration	2.8	2.8	2.8
Ionic radius/nm	0.102	0.072	0.054

table B Trends in ionic radii across a period.

POLARISATION AND POLARISING POWER OF IONS

In an ionic lattice, the positive ion will attract the electrons of the anion. If the electrons are pulled towards the cation, the anion is polarised since the even distribution of its electron density has been distorted.

The extent to which an anion is polarised by a cation depends on several factors. The two main factors are known as Fajan's rules and are summarised here.

Polarisation will be increased by:

- high charge and small size of the cation (i.e. high charge density of the cation)
- high charge and large size of the anion.

HIGH CHARGE AND SMALL SIZE OF CATIONS

The ability of a cation to attract electrons from the anion towards itself is called its polarising power. A cation with a high charge and a small radius has a large polarising power.

An approximate value for the polarising power of a cation can be obtained by calculating its charge density. The charge density of a cation is the charge divided by the surface area of the ion. If the ion is assumed to be a sphere, its surface area is equal to $4\pi r^2$, where r is the ionic radius.

An approximation to the charge density can be determined by dividing the charge by the square of its ionic radius.

$$\text{charge density} \sim \frac{\text{charge}}{r^2}$$

HIGH CHARGE AND SMALL SIZE OF ANIONS

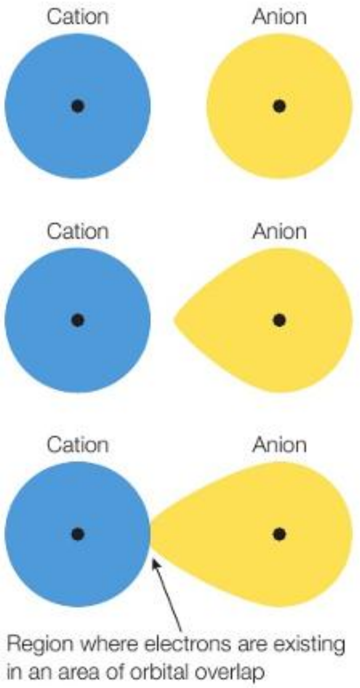
The ease with which an anion is polarised depends on its charge and its size. Anions with a large charge and a small size are polarised the most easily.

In an ionic lattice, the polarisation of the anions creates some degree of sharing of electrons between the two nuclei. That is, some degree of covalent bonding exists. You will learn more about this concept in Topic 12B (Book 2: IAL).

SUBJECT VOCABULARY

polarising power the ability of a positive ion (cation) to distort the electron density of a neighbouring negative ion (anion)

polarisation the distortion of the electron density of a negative ion (anion)



Region where electrons are existing in an area of orbital overlap

fig A A representation of a cation attracting the electrons of an anion in an ionic lattice.

3A – 3 Physical properties of ionic compounds

Ionic compounds typically have the following physical properties:

- high melting temperatures
- brittleness
- poor electrical conductivity when solid but good when molten often soluble in water.

HIGH MELTING TEMPERATURES

Ionic solids consist of a giant lattice network of oppositely charged ions (see Topic 2B.2). There are many ions in the lattice and the combined electrostatic forces of attraction among all of the ions is large.

A large amount of energy is required to overcome the forces of attraction sufficiently for the ions to break free from the lattice and slide past one another.

BRITTLENESS

If a stress is applied to a crystal of an ionic solid, then the layers of ions may slide over one another.

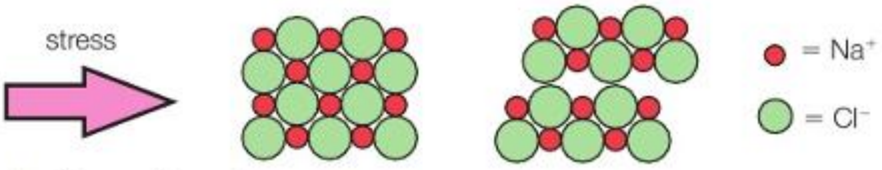


fig A Effect of stress on an ionic crystal.

ELECTRICAL CONDUCTIVITY

Solid ionic compounds do not, in general, conduct electricity. This is because there are no delocalised electrons and the ions are also not free to move under the influence of an applied potential difference.

However, molten ionic compounds will conduct since the ions are now mobile and will migrate to the electrodes of opposite sign when a potential difference is applied. If direct current is used, the compound will undergo electrolysis as the ions are discharged at the electrodes.

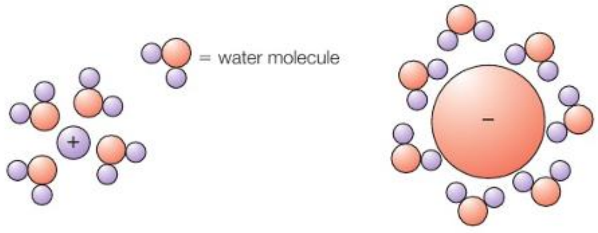
SOLUBILITY

Many ionic compounds are soluble in water. We will explain this solubility more fully in Topic 12A including the part played by entropy changes.

At the moment, you just need to understand that the energy required to break apart the lattice structure and separate the ions can, in some instances, be supplied by the **hydration** of the separated ions produced. Both positive and negative ions are attracted to water molecules because of the polarity that water molecules possess (see Topic 3B for an explanation of polarity).

SUBJECT VOCABULARY

hydration the process of water molecules being attracted to ions in solution and surrounding the ions; the oxygen ends of the water molecules are attracted to the positive ions (cations); the hydrogen ends of the water molecules are attracted to the negative ions (anions); hydration of ions is an exothermic process (i.e. heat energy is released)



The oxygen ends of the water molecules are attracted to positive ions.

The hydrogen ends of the water molecules are attracted to negative ions.

fig B Hydration of ions.

3B – 1 Covalent bonding

FORMATION OF COVALENT BONDS

A covalent bond forms between two atoms when an atomic orbital containing a single electron from one atom overlaps with an atomic orbital, which also contains a single electron, of another atom. The two electrons in the area of overlap are the bonding electrons.

They are sometimes referred to as a 'shared pair of electrons'. The covalent bond is the electrostatic attraction between the two nuclei of the bonded atoms and the pair of electrons shared between them.

The atomic orbitals involved can be any of those found in the atoms, but we shall limit our discussion to those involving only s- and p-orbitals.

Fig A shows three ways in which these orbitals may overlap.

Fig A shows three ways in which these orbitals may overlap.

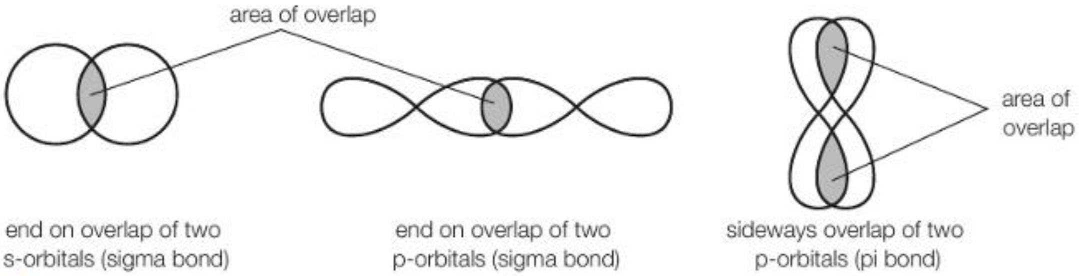


fig A Formation of sigma bonds by end-on overlap of atomic orbitals and a pi bond by sideways overlap of p-orbitals.

EXAMPLE 1. HYDROGEN

A hydrogen atom has an electronic configuration of $1s^1$. When two hydrogen atoms bond together to form a hydrogen molecule, the two s-orbitals overlap to form a new molecular orbital. The two electrons then exist in this new orbital. The highest electron density is between the two nuclei.

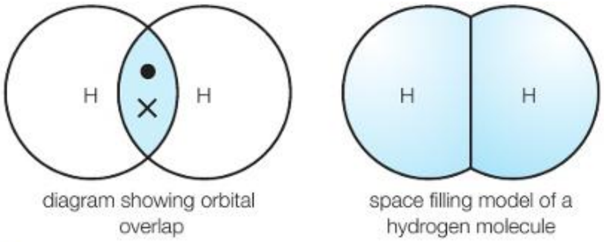


diagram showing orbital overlap

space filling model of a hydrogen molecule

▲ **fig C** Formation of the σ bond in hydrogen.

EXAMPLE 2. CHLORINE

A chlorine atom has an electronic configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$.

When two chlorine atoms bond together, the two p orbitals (each containing a single electron) overlap.

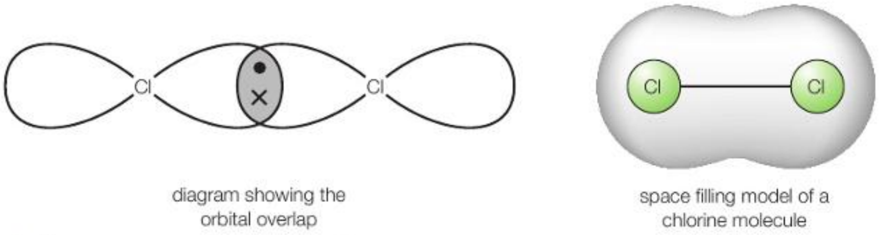


diagram showing the orbital overlap

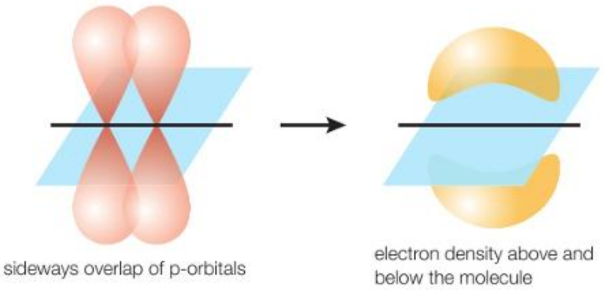
space filling model of a chlorine molecule

▲ **fig D** Formation of the σ bond in chlorine

EXAMPLE 3. π BOND FORMATION

Once a σ bond has been formed, it is possible, in certain circumstances, for a π bond to form.

The π bond results in a high electron density both above and below the molecule, as shown in **fig E**.



sideways overlap of p-orbitals

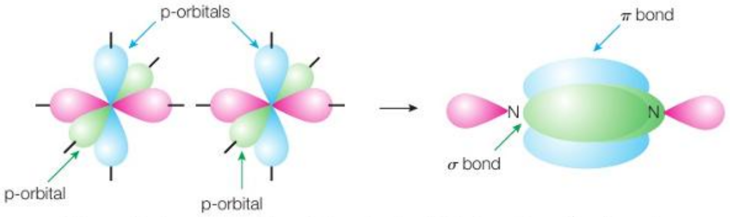
electron density above and below the molecule

▲ **fig E** Formation of a π bond.

This is what happens in the ethene molecule. One of the bonds between the carbon atoms is a σ bond; the other is a π bond.

The π bond in ethene is weaker than the σ bond. This is the reason for the increased reactivity of alkenes compared with alkanes, and why alkenes can easily undergo addition reactions. (See **Topic 5** for more information.)

The triple bond in the nitrogen molecule (N≡N) is made up of one σ bond and two π bonds.



The p-orbitals marked are those that are involved in the formation of the pi bonds.

▲ **fig F** Formation of the two π bonds in nitrogen.

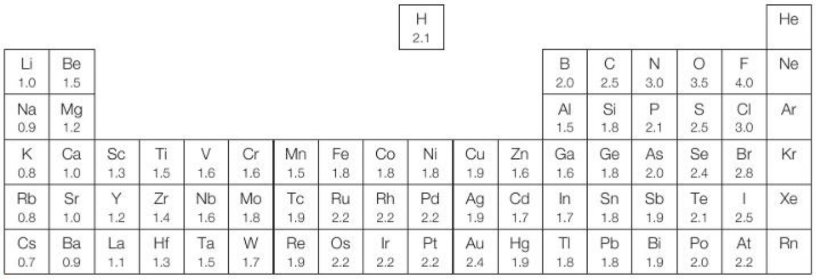
3B – 2 Electronegativity and bond polarity

WHAT IS ELECTRONEGATIVITY?

Electronegativity is the ability of an atom to attract a bonding pair of electrons.
The electronegativity of elements, in general:

- decreases down a group of the Periodic Table, that is, from top to bottom
- increases from left to right across a period.

This is demonstrated in the following section of the Periodic Table (fig A).



									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
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn

fig A able of electronegativities.

DISTRIBUTION OF ELECTRON DENSITY

If two atoms of the same element are bonded together by the overlap of atomic orbitals, the distribution of electron density between the two nuclei will be symmetrical. This is because the ability of each atom to attract the bonding pair of electrons is identical.

The diagram in fig B is an electron density map for chlorine (Cl_2):

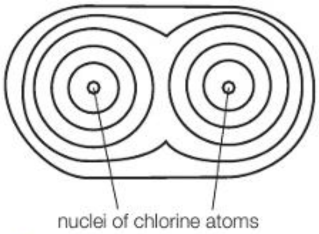


fig B Electron density map of a chlorine molecule.

POLAR COVALENT BONDS

However, if the two atoms bonded together are from elements that have different electronegativities, then the distribution of electron density will not be symmetrical about the two nuclei. This is shown in fig C by the electron density map for the hydrogen chloride (HCl) molecule.

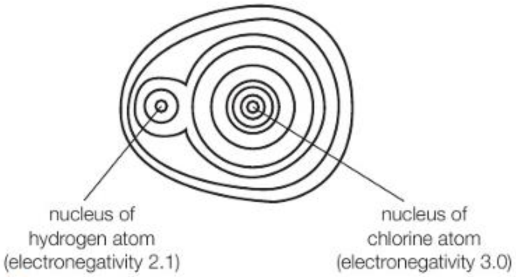


fig C Electron density map of a hydrogen chloride molecule.

Since the electron density is higher around the chlorine atom, that end of the molecule has acquired a slightly negative charge. This is represented by the symbol δ–. The other end of the molecule carries a slightly positive charge, represented by the symbol δ+.

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

A bond like this is called a **polar covalent bond** or sometimes just a 'polar bond'.

Another way of representing a polar covalent bond is to use an arrow to show the direction of electron drift.

$$\mathrm{H} \rightarrow \mathrm{Cl}$$

Other examples of polar covalent bonds are:

$$\mathrm{C}^{\delta+} \rightarrow \mathrm{Cl}^{\delta-} \qquad \mathrm{H}^{\delta+} \rightarrow \mathrm{O}^{\delta-} \qquad \mathrm{H}^{\delta+} \rightarrow \mathrm{N}^{\delta-} \qquad \mathrm{H}^{\delta+} \rightarrow \mathrm{C}^{\delta-}$$

CONTINUUM OF BONDING TYPE

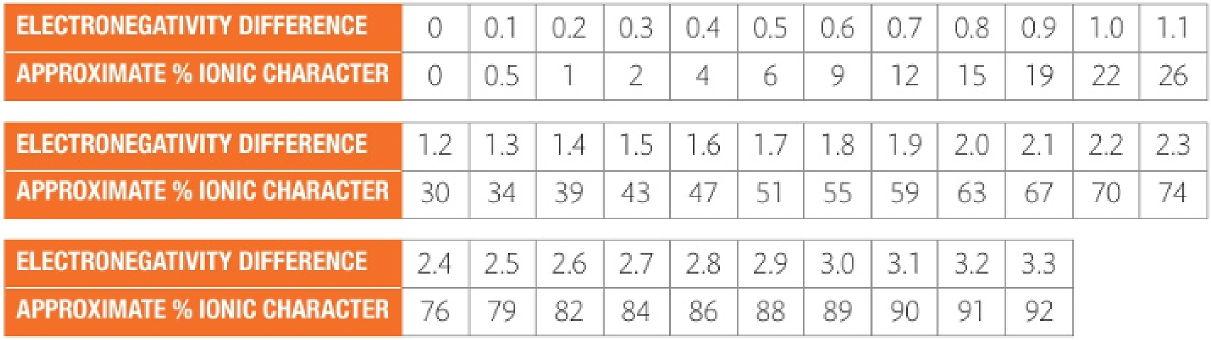
Polar covalent bonds can be thought of as being between two ideals of bonding types. These ideals are:

- pure (100%) covalent
- pure (100%) ionic.

Consider a polar covalent bond as a covalent bond that has some degree of ionic character.

If the electronegativity difference is large enough, then the main type of bonding is ionic.

A very approximate measure of the degree of ionic bonding in a compound is given in table A.

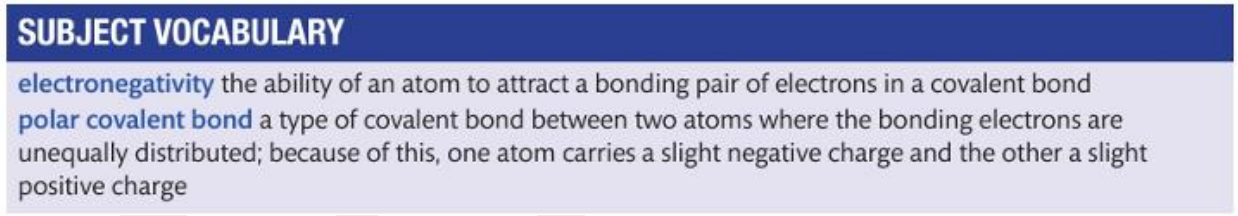


ELECTRONEGATIVITY DIFFERENCE	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1
APPROXIMATE % IONIC CHARACTER	0	0.5	1	2	4	6	9	12	15	19	22	26

ELECTRONEGATIVITY DIFFERENCE	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3
APPROXIMATE % IONIC CHARACTER	30	34	39	43	47	51	55	59	63	67	70	74

ELECTRONEGATIVITY DIFFERENCE	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2	3.3
APPROXIMATE % IONIC CHARACTER	76	79	82	84	86	88	89	90	91	92

table A Relationship between percentage ionic character and difference in electronegativity.



SUBJECT VOCABULARY

electronegativity the ability of an atom to attract a bonding pair of electrons in a covalent bond

polar covalent bond a type of covalent bond between two atoms where the bonding electrons are unequally distributed; because of this, one atom carries a slight negative charge and the other a slight positive charge

3B – 3 Bonding in discrete (simple) molecules

DISCRETE MOLECULES

A discrete (simple) molecule is an electrically neutral group of two or more atoms held together by covalent bonds.

DOT-AND-CROSS DIAGRAMS

Covalent and polar covalent bonding in discrete molecules can be shown by dot-and-cross diagrams.

Fig A shows the example of hydrogen, H_2.

Further examples of dot-and-cross diagrams are shown in table A.

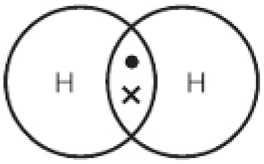


fig A Dot-and-cross diagram for hydrogen with overlapping circles.

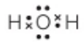
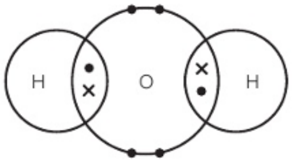
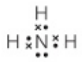
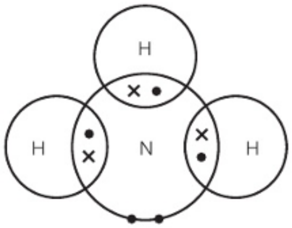
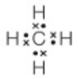
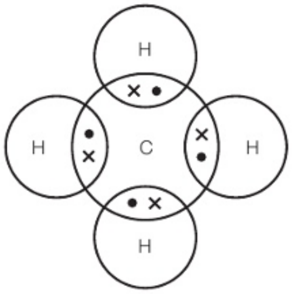
SUBSTANCE	DOT-AND-CROSS DIAGRAM	
Water, H_2O		
Ammonia, NH_3	 nucleus of hydrogen atom (electronegativity 2.1)	
Methane, CH_4		

table A Dot-and-cross diagrams for water, ammonia and methane.

THE OCTET RULE

You might read that in order to form a stable compound, the outer shell of each atom must have the same number of electrons as the outer shell of a noble gas. In most cases this will be eight electrons. This has led to a rule that is often referred to as the 'octet rule'.

This is not always true, as you can see from the examples in table B. In each case, the outer shell of the central atom of the molecule does not contain eight electrons.

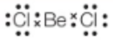
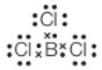
SUBSTANCE	DOT-AND-CROSS DIAGRAM	NUMBER OF ELECTRONS AROUND CENTRAL ATOM
Beryllium chloride, $BeCl_2$		4
Boron trichloride, BCl_3		6
Phosphorus(V) chloride, PCl_5		10
Sulfur hexafluoride, SF_6		12

table B Examples breaking the octet rule.

DOT-AND-CROSS DIAGRAMS OF MOLECULES CONTAINING MULTIPLE BONDS

Table C shows the dot-and-cross diagrams for three molecules (O_2, N_2, CO_2) that contain a double or triple bond.

DISPLAYED FORMULAE (FULL STRUCTURAL FORMULAE)

A **displayed (full structural) formula** shows each bonding pair as a line drawn between the two atoms involved.

Table C gives some examples of dot-and-cross diagrams together with the displayed formulae.

Table C gives some examples of dot-and-cross diagrams together with the displayed formulae.

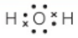
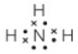
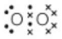
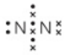
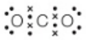
SUBSTANCE	DOT-AND-CROSS DIAGRAM	DISPLAYED FORMULA
Water, H_2O		H–O–H
Ammonia, NH_3		H | H–N–H
Oxygen, O_2		O=O
Nitrogen, N_2		N≡N
Carbon dioxide, CO_2		O=C=O

table C Examples of displayed formulae with the corresponding dot-and-cross diagram.

SUBJECT VOCABULARY

discrete (simple) molecule an electrically neutral group of two or more atoms held together by covalent bonds

displayed (full structural) formula a formula that shows each bonding pair as a line drawn between the two atoms involved

3B – 4 Dative covalent bonds

DATIVE COVALENT BOND FORMATION

A dative covalent bond is formed when an empty orbital of one atom overlaps with an orbital containing a non-bonding pair (lone pair) of electrons of another atom.

The bond is often represented by an arrow from the atom providing the pair of electrons, to the atom with the empty orbital. Below are three examples of dative covalent bonds.

THE HYDROXONIUM ION, H_3O^+

The dot-and-cross diagram and the displayed formula of a hydroxonium ion are shown in **fig A**.

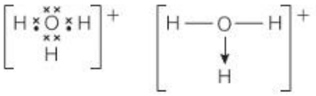


fig A Dot-and-cross diagram and displayed formula for the hydroxonium ion.

The empty 1s orbital of the H^+ ion overlaps with the orbital of the oxygen atom that contains the lone pair of electrons.

THE AMMONIUM ION, NH_4^+

The dot-and-cross diagram and the displayed formula of an ammonium ion are shown in **fig B**.

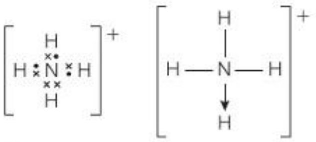
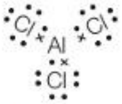


fig B Dot-and-cross diagram and displayed formula for the ammonium ion.

The empty 1s orbital of the H^+ ion overlaps with the orbital of the nitrogen atom that contains the lone pair of electrons.

ALUMINIUM CHLORIDE, Al_2Cl_6

The aluminium atom in the $AlCl_3$ molecule has only six electrons in its outer shell and so has an empty orbital (**fig C**).

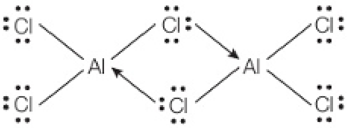


▲ **fig C** Dot-and-cross diagram for aluminium chloride.

In the gas phase, just above its sublimation temperature, aluminium chloride exists as Al_2Cl_6 molecules (**fig D**).

Two $AlCl_3$, molecules bond together. One of the atomic orbitals of a chlorine atom of one $AlCl_3$, molecule that contains a lone pair overlaps with the empty orbital of the aluminium atom of a second $AlCl_3$, molecule. The same happens between the chlorine atom of the second molecule and the aluminium atom of the first molecule.
One chlorine atom from each molecule acts as a bridge connecting the two molecules with dative covalent bonds.

One chlorine atom from each molecule acts as a bridge connecting the two molecules with dative covalent bonds.



▲ **fig D** Displayed formula for the aluminium dimer.

SUBJECT VOCABULARY

dative covalent bond the bond formed when an empty orbital of one atom overlaps with an orbital containing a lone pair of electrons of another atom

3C – 1 Shapes of molecules and ions

ELECTRON PAIR REPULSION THEORY

The electron pair repulsion (EPR) theory states that:

- the shape of a molecule or ion is caused by repulsion between the pairs of electrons, both bond pairs and lone (non-bonding) pairs, that surround the central atom
- the electron pairs arrange themselves around the central atom so that the repulsion between them is at a minimum
- lone pair-lone pair repulsion > lone pair-bond pair repulsion > bond pair-bond pair repulsion.

THE SHAPES OF MOLECULES AND IONS

To obtain the shape of a molecule or ion it is first necessary to obtain the number of bond pairs and lone pairs of electrons around the central atom.

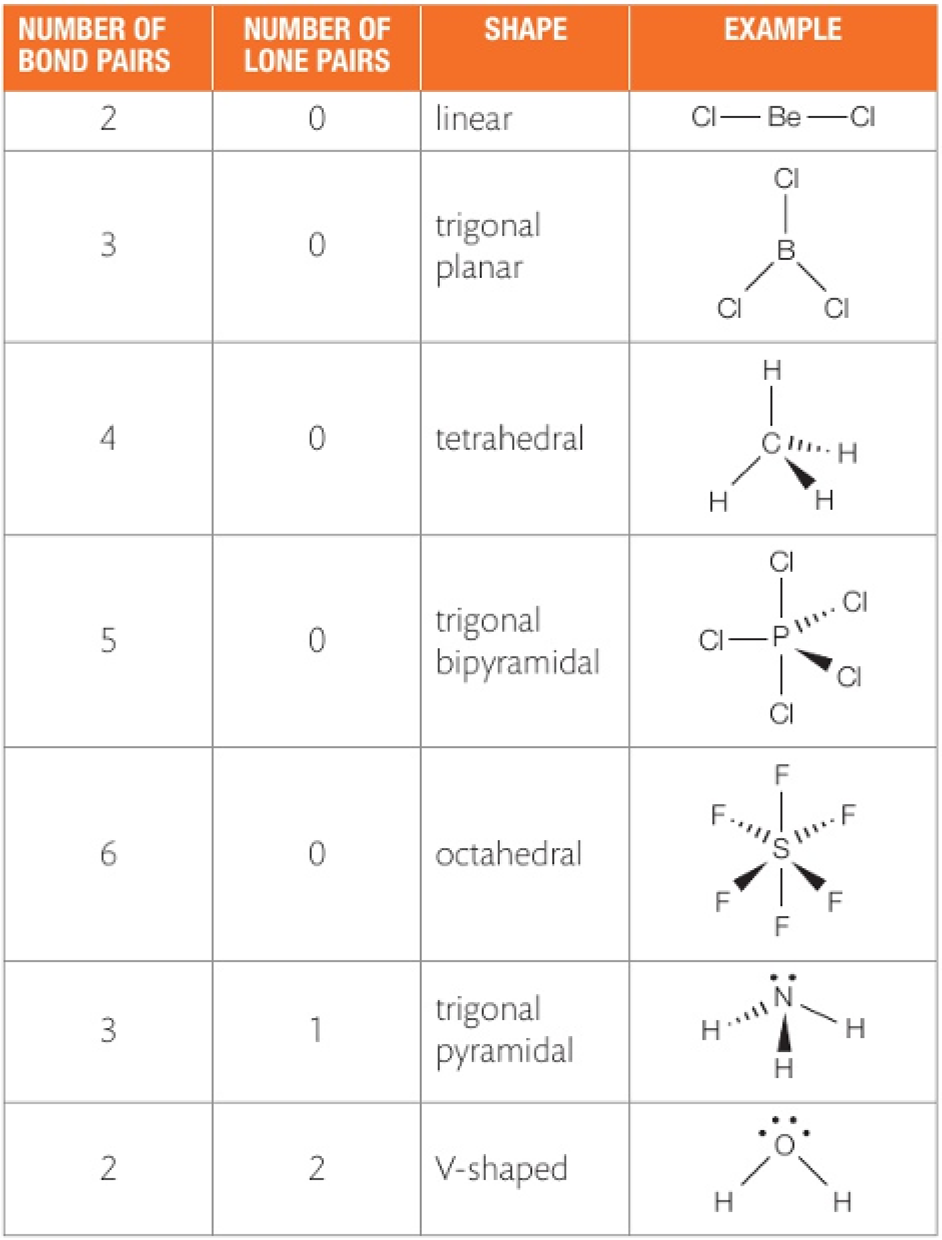
The easiest way to do this is by drawing a dot-and-cross diagram. You can then apply the guidelines listed in table A.

MOLECULES WITH MULTIPLE BONDS

To determine the shape of a molecule containing one or more multiple bonds, treat each multiple bond as if it contained only one pair of electrons.

EXAMPLE 1. CARBON DIOXIDE, CO_2

The displayed formula for carbon dioxide is O=C=O. There are no lone pairs on the carbon atom.

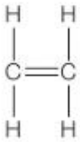


NUMBER OF BOND PAIRS	NUMBER OF LONE PAIRS	SHAPE	EXAMPLE
2	0	linear	Cl—Be—Cl
3	0	trigonal planar	
4	0	tetrahedral	
5	0	trigonal bipyramidal	
6	0	octahedral	
3	1	trigonal pyramidal	
2	2	V-shaped	

table A Shapes of molecules.

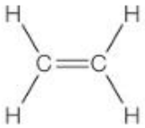
EXAMPLE 2. ETHENE, C_2H_4

The displayed formula of ethene is:



There are no lone pairs on either carbon atom.

Treating each double bond as an electron pair produces a planar molecule with 120° bond angles.



THE BOND ANGLES IN MOLECULES AND IONS

Table B shows the bond angles of a range of molecules and ions.

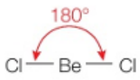
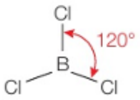
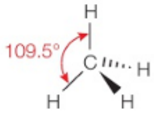
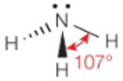
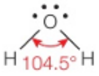
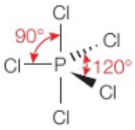
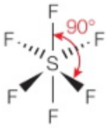
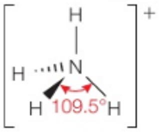
Linear, e.g. $BeCl_2$ The bond angle is 180°. 	Trigonal planar, e.g. BCl_3 The bond angle is 120°. 
Tetrahedral, e.g. CH_4 The bond angle is 109.5°. 	Trigonal pyramidal, e.g. NH_3 The bond angle is 107°.  Lone pair–bond pair repulsion is greater than bond pair–bond pair repulsion, so the angle is slightly less than 109.5°.
V-shaped, e.g. H_2O The bond angle is 104.5°.  Lone pair–lone pair repulsion is greater than lone pair–bond pair repulsion, so the bond angle is even further depressed from 109.5°, and is slightly less than the 107° in NH_3.	Trigonal bipyramidal, e.g. PCl_5 There are two bond angles: 90° and 120°. 
Octahedral, e.g. SF_6 There are two bond angles: 90° and 180°.  The angle between the bonds of two fluorine atoms opposite one another is 180°.	Tetrahedral, e.g. NH_4^+ As with CH_4, the bond angles are 109.5°.  Note the change from 107° in ammonia to 109.5° in the ammonium ion.

table B The bond angles of a range of molecules and ions.

SUBJECT VOCABULARY

electron pair repulsion (EPR) theory the electron pairs on the central atom of a molecule or ion arrange themselves in order to create the minimum repulsion between them; lone pair-lone pair repulsion is greater than lone pair-bond repulsion, which in turn is greater than bond pair-bond pair repulsion

3C – 2 Non – polar and polar molecules

SHAPE AND POLARITY

The drift of bonded electrons towards the more electronegative element (see Topic 3B.2) results in a separation of charge. This separation of charge is called a dipole.

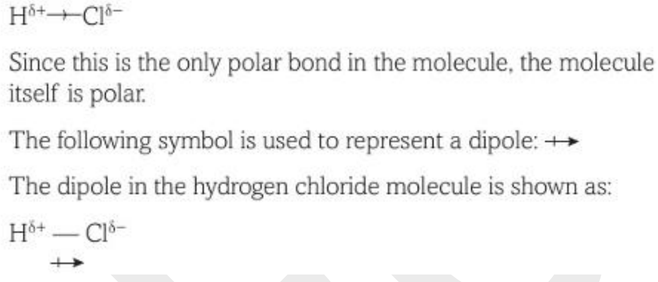
Each of the bonds in a molecule has its own dipole associated with it. The overall dipole of a molecule depends on its shape. Depending on the relative angles between the bonds, the individual dipoles can either reinforce one another or cancel out each other.

- If the cancellation is complete, the resulting molecule will have no overall dipole and is said to be 'non-polar'.
- If the dipoles reinforce one another, the molecule will possess an overall dipole and is said to be 'polar'.

DIATOMIC MOLECULES

Hydrogen and chlorine are examples of diatomic molecules that are non-polar. The two atoms in each molecule are the same and so have the same electronegativity. The distribution of electron density of the bonding electrons in either molecule is totally symmetrical (see Topic 3B.2). The bond in each is therefore non- polar, making the molecules non-polar.

However, the bond in the hydrogen chloride molecule is polar because the electronegativity of chlorine (3.0) is greater than that of hydrogen (2.1).



$\mathrm{H}^{\delta+}{+\!\!\!\rightarrow}\mathrm{Cl}^{\delta-}$

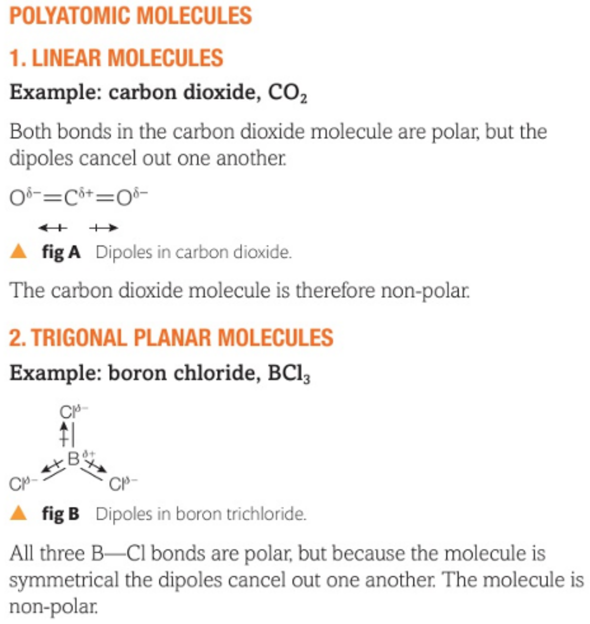
Since this is the only polar bond in the molecule, the molecule itself is polar.

The following symbol is used to represent a dipole: ${+\!\!\!\rightarrow}$

The dipole in the hydrogen chloride molecule is shown as:

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

${+\!\!\!\rightarrow}$



POLYATOMIC MOLECULES

1. LINEAR MOLECULES

Example: carbon dioxide, CO_2

Both bonds in the carbon dioxide molecule are polar, but the dipoles cancel out one another.

$\mathrm{O}^{\delta-}{=}\mathrm{C}^{\delta+}{=}\mathrm{O}^{\delta-}$

${\leftarrow\!\!\!+}\quad{+\!\!\!\rightarrow}$

▲ **fig A** Dipoles in carbon dioxide.

The carbon dioxide molecule is therefore non-polar.

2. TRIGONAL PLANAR MOLECULES

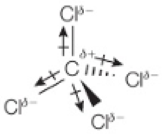
Example: boron chloride, BCl_3

▲ **fig B** Dipoles in boron trichloride.

All three B—Cl bonds are polar, but because the molecule is symmetrical the dipoles cancel out one another. The molecule is non-polar.

3. TETRAHEDRAL MOLECULES

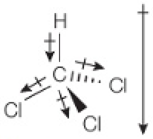
Example 1: tetrachloromethane, CCl_4



▲ **fig C** Dipoles in tetrachloromethane.

All four C—Cl bonds are polar, but because the molecule is symmetrical the dipoles cancel out one another. The molecule is non-polar.

Example 2: trichloromethane, $CHCl_3$



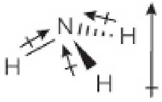
▲ **fig D** Dipoles in trichloromethane.

All four bonds are polar but, although the molecule is symmetrical, the dipoles reinforce one another and so the molecule is polar.

4. TRIGONAL PYRAMIDAL MOLECULES

Example: ammonia, NH_3

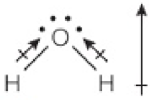
All three N—H bonds are polar and the dipoles reinforce one another. The molecule is polar.



▲ **fig E** Dipoles in ammonia.

5. V-SHAPED MOLECULES

Example: water, H_2O



▲ **fig F** Dipoles in water.

Both O—H bonds are polar and the dipoles reinforce one another. The molecule is polar.

SUBJECT VOCABULARY

dipole exists when two charges of equal magnitude but opposite signs are separated by a small distance

dipole moment the difference in magnitude between δ+ and δ− multiplied by the distance of separation between the charges

3D – Metallic bonding

THE NATURE OF METALLIC BONDING

Metals typically have the following physical properties:

- high melting temperatures
- good electrical conductivity
- good thermal conductivity
- malleability
- ductility.

Any theory of the way that the atoms in a metal are bonded together must explain the above properties.
Metals typically have one, two or three electrons in the outer shell of their atoms and have low ionisation energies.

The electrical conductivity of a metal generally increases as the number of outer-shell electrons increases.

Since electrical conductivity depends on the presence of mobile carriers of electric charge, we can build a picture of a metal as consisting of an array of atoms with at least some of their outer-shell electrons removed and free to move throughout the structure.

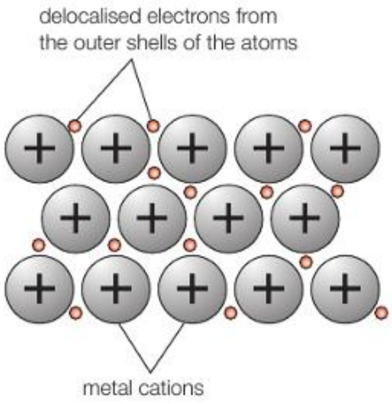


fig A Diagram showing the particles present in a metal.

The electrons are said to be delocalised since they are free to move throughout the structure and are not confined, i.e. localised, between any pair of cations.
There are electrostatic forces of attraction between the cations and the delocalised electrons. This is known as **metallic bonding.**

EXPLAINING THE PHYSICAL PROPERTIES OF METALS

MELTING TEMPERATURE

In order to melt a metal, it is necessary to partially overcome the forces of attraction between the cations and the delocalised electrons to such an extent that the cations are free to move around the structure. Metals have a giant lattice structure where many of these forces must be overcome. The energy required to do this is usually very large, so the melting temperatures are typically high.

The number of delocalised electrons per cation plays a part in determining the melting temperature of a metal.
- Group 1 metals have low melting temperatures.
- Group 2 metals have higher melting temperatures.
- Metals in the d-block typically have high melting temperatures because they have more delocalised electrons per cation.

Another factor that affects the melting temperature is the charge-to-radius ratio of the cation. The greater the charge-to-radius ratio, the stronger the attraction for the delocalised electrons. Therefore, for two cations of the same charge, the smaller cation will attract the delocalised electrons more strongly. This is why, for example, the melting temperature of lithium is greater than that of sodium.

ELECTRICAL CONDUCTIVITY

When a potential difference is applied across the ends of a metal, the delocalised electrons will be attracted to, and move towards, the positive terminal of the cell. This flow of electrons constitutes an electric current.

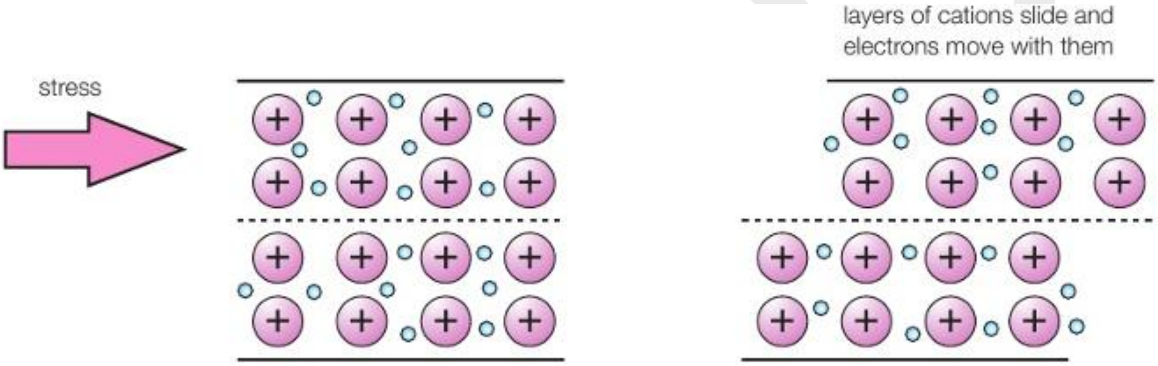
THERMAL CONDUCTIVITY

Two factors contribute to the ability of metals to transfer heat energy.
1 The free-moving delocalised electrons pass kinetic energy along the metal.
2 The cations are closely packed and pass kinetic energy from one cation to another.

The conduction by the delocalised electrons is by far the more significant of the two factors.

MALLEABILITY AND DUCTILITY

Metals can be hammered or pressed into different shapes (malleability). They can also be drawn into a wire (ductility). Both of these properties depend on the ability of the delocalised electrons and the cations to move throughout the structure of the metal.
When a stress is applied to a metal, the layers of cations may slide over one another (fig B).



▲ **fig B** The effect of stress on a metal.

SUBJECT VOCABULARY

delocalised electrons electrons that are not associated with any single atom or any single covalent bond
metallic bonding the electrostatic force of attraction between the metal cations and delocalised electrons

3E – 1 Introduction to sold lattices

METALLIC LATTICES

Metallic lattices are composed of a regular arrangement of positive metal ions (cations) surrounded by delocalised electrons.
Substances that have a giant metallic lattice typically have the following properties:

- high melting and boiling temperatures
- good electrical conductivity
- good thermal conductivity
- malleability
- ductility.

We explained these properties in Topic 3D.

GIANT IONIC LATTICES

Giant ionic lattices are composed of a regular arrangement of positive and negative ions. Substances that consist of giant ionic lattices typically have the following properties:

- fairly high melting temperatures
- brittleness
- poor electrical conductivity when solid but good when molten
- often soluble in water.

We explained these properties in Topic 3D.

GIANT COVALENT LATTICES

Giant covalent lattices are sometimes called network covalent lattices. They consist of a giant network of atoms linked to each other by covalent bonds.

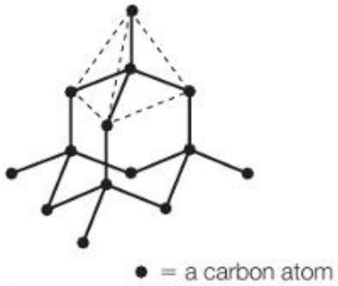
Four of the most common giant covalent substances are:

- diamond
- graphite
- graphene
- silicon (IV) oxide (not discussed below).

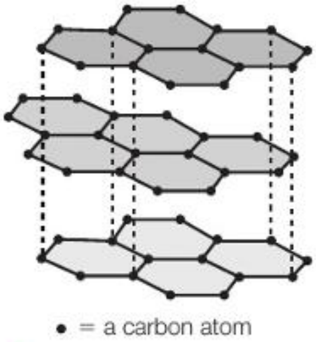
DIAMOND

In diamond, each carbon atom forms four sigma (δ) bonds to four other carbon atoms, in a giant three-dimensional tetrahedral arrangement (**fig A**). All bond angles are 109.5°.

Diamond is extremely hard because of the very strong C—C bonding throughout the structure. It also has a very high melting temperature because a great number of strong C—C bonds have to be broken in order to melt it. This requires a large amount of heat energy.



▲ **fig A** Structure of diamond.



▲ **fig B** Structure of graphite.

GRAPHITE

Graphite has a layered structure as shown in **fig B**.

Each carbon atom is bonded to three others by sigma bonds, forming interlocking hexagonal rings. The fourth electron on each carbon atom is in a p-orbital. The carbon atoms are close enough for the p-orbitals to overlap with one another to produce a cloud of delocalised electrons, both above and below the plane of the rings. We will compare this with the structure of benzene in **Topic 18 (Book 2: IAL)**.

GRAPHENE

Graphene is pure carbon in the form of a very thin sheet, one atom thick (fig C). The carbon atoms are bonded in exactly the same way as in graphite and it can, therefore, be described as a one-atom thick layer of graphite.

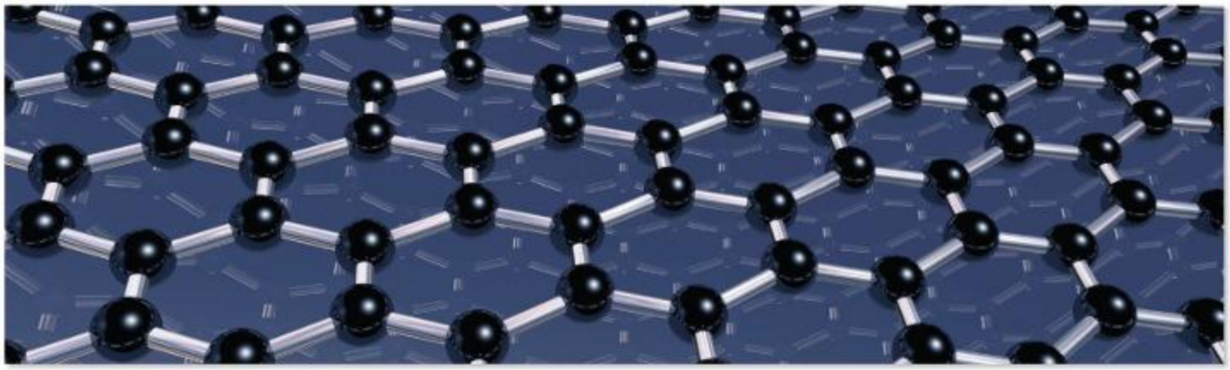


fig C Structure of graphene.

PHYSICAL PROPERTIES OF MOLECULAR SOLIDS

Molecular solids will, in general, have low melting and boiling temperatures. In order to melt a molecular solid, it is not necessary to break the covalent bonds within the molecule (the intramolecular bonds); it is only necessary to overcome the intermolecular forces of attraction.

Since intermolecular forces of attraction tend to be much weaker than covalent bonds, little energy is required to either break down the lattice structure of the solid and cause it to melt, or to separate the molecules and cause the liquid to boil and vaporise.

Intermolecular forces tend to increase with both an increase in the number of electrons per molecule and also with increasing length of molecule. This means that a macromolecular solid such as poly(ethene) will have a much higher melting temperature than its monomer, ethene.

ethene
melting point = −169°C

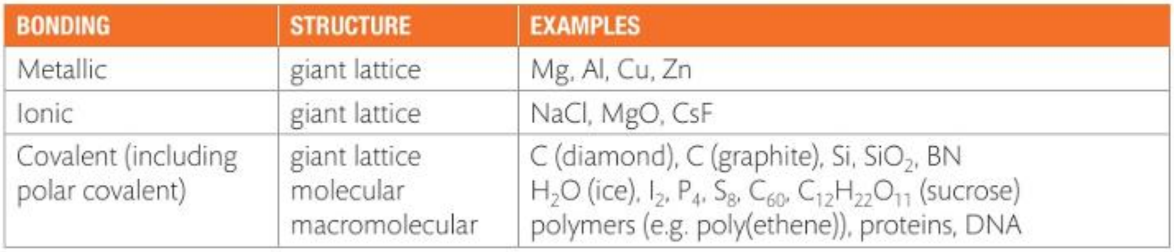
poly(ethene)
melting point typically
120 to 180°C

fig I Ethene and (poly)ethene.

3E – 2 Structure and properties

TYPES OF BONDING AND STRUCTURE

Table A shows the types of bonding and structure that exist in elements and compounds.

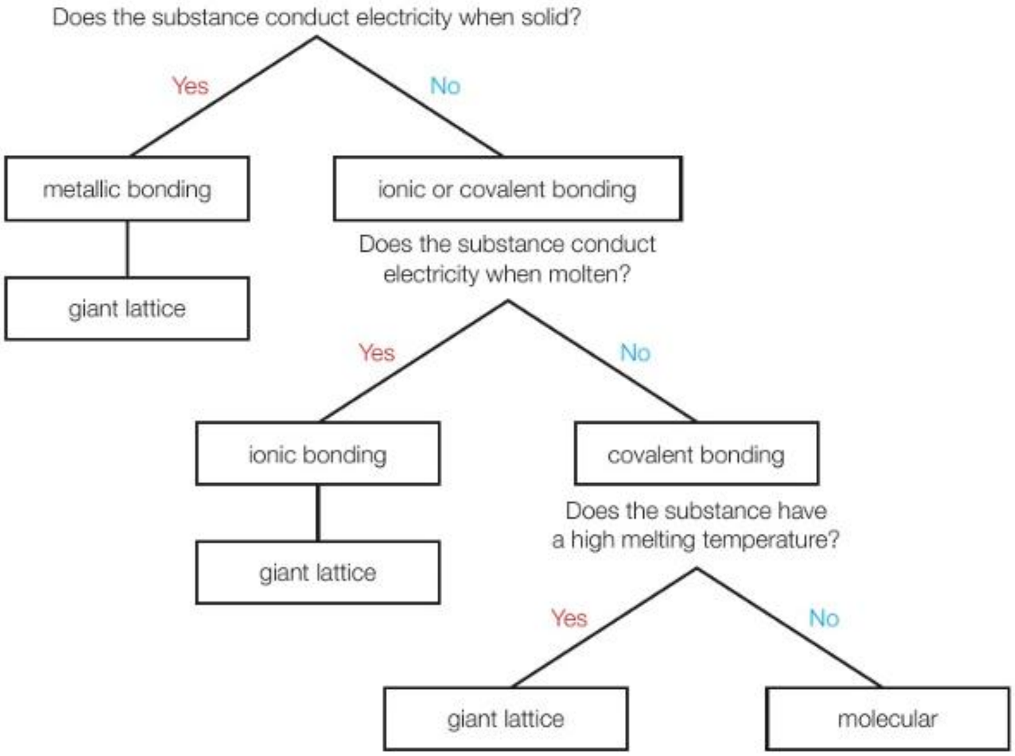


BONDING	STRUCTURE	EXAMPLES
Metallic	giant lattice	Mg, Al, Cu, Zn
Ionic	giant lattice	NaCl, MgO, CsF
Covalent (including polar covalent)	giant lattice molecular macromolecular	C (diamond), C (graphite), Si, SiO_2, BN H_2O (ice), I_2, P_4, S_8, C_{60}, $C_{12}H_{22}O_{11}$ (sucrose) polymers (e.g. poly(ethene)), proteins, DNA

table A Types of bonding and structure.

PREDICTING PHYSICAL PROPERTIES

The physical properties of a substance are determined by the type of bonding and structure it has.
Fig A allows you to determine the type of bonding and structure in a substance by considering some of its properties.



▲ **fig A** Flow chart for determining bonding and structure.

There will, of course, always be exceptions. For example, graphite has a giant covalent structure and yet it is a relatively good conductor of electricity when solid.

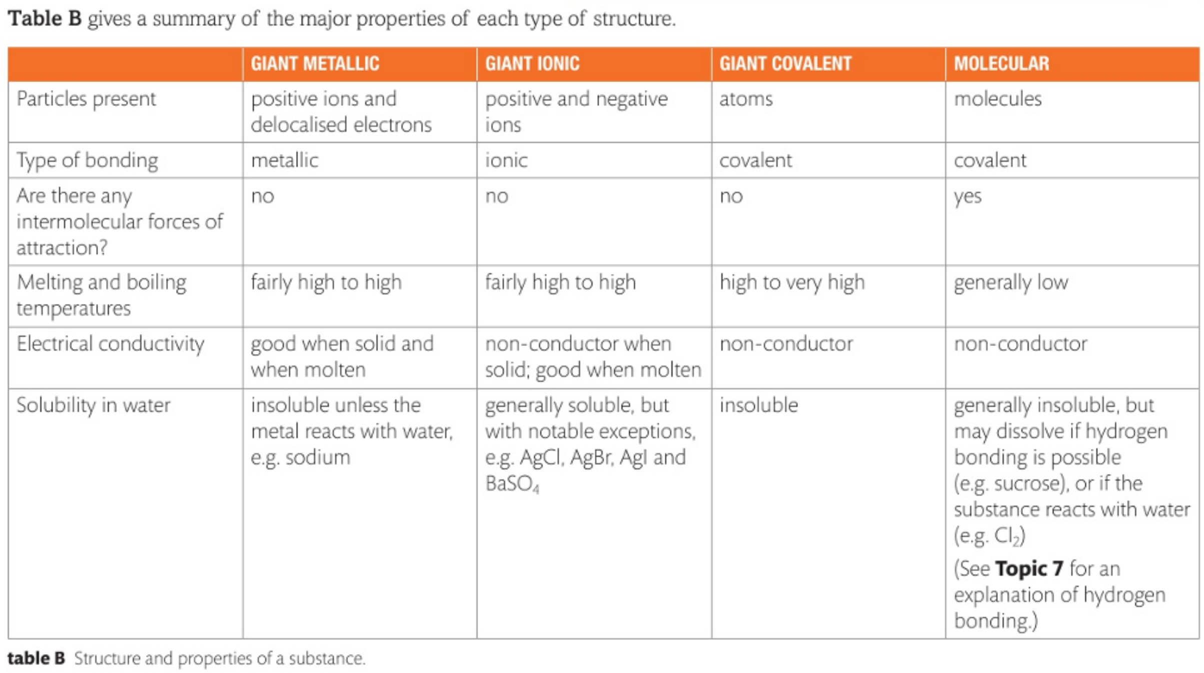


Table B gives a summary of the major properties of each type of structure.

	GIANT METALLIC	GIANT IONIC	GIANT COVALENT	MOLECULAR
Particles present	positive ions and delocalised electrons	positive and negative ions	atoms	molecules
Type of bonding	metallic	ionic	covalent	covalent
Are there any intermolecular forces of attraction?	no	no	no	yes
Melting and boiling temperatures	fairly high to high	fairly high to high	high to very high	generally low
Electrical conductivity	good when solid and when molten	non-conductor when solid; good when molten	non-conductor	non-conductor
Solubility in water	insoluble unless the metal reacts with water, e.g. sodium	generally soluble, but with notable exceptions, e.g. AgCl, AgBr, AgI and $BaSO_4$	insoluble	generally insoluble, but may dissolve if hydrogen bonding is possible (e.g. sucrose), or if the substance reacts with water (e.g. Cl_2) (See **Topic 7** for an explanation of hydrogen bonding.)

table B Structure and properties of a substance.

Revision questions

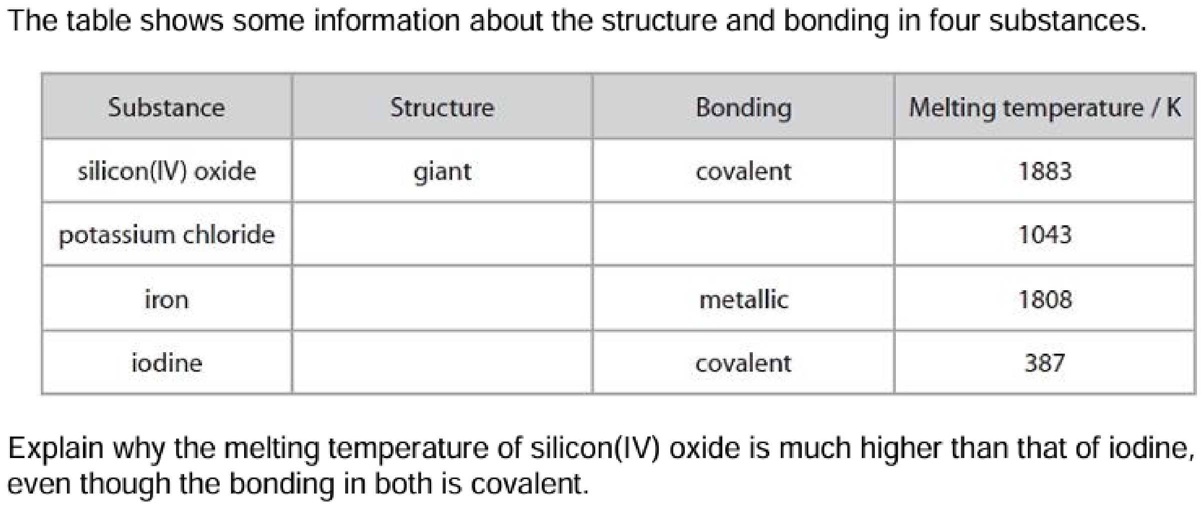
1. This question is about covalent bonds. State what is meant by the term covalent bond.

2. This question is about aluminium chloride. Aluminium chloride exists as a dimer, Al2Cl6, just above its boiling temperature.

(i) Draw a diagram to show how two AlCl3 molecules are joined together in the dimer.
ii) State the type of bond that joins the two AlCl3 molecules together.

3. State what is meant by the term electronegativity and hence explain the polarity, if any, of the bonds in chlorine trifluoride, ClF3.

4.



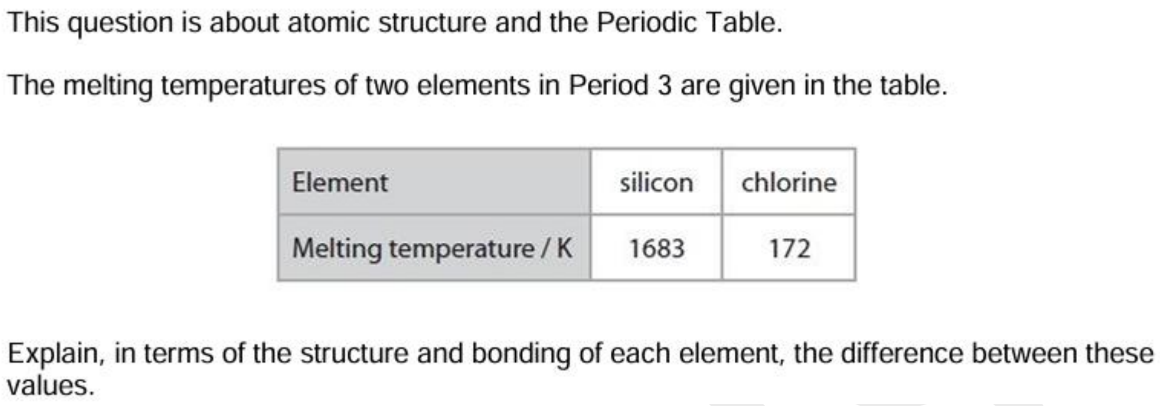
The table shows some information about the structure and bonding in four substances.

Substance	Structure	Bonding	Melting temperature / K
silicon(IV) oxide	giant	covalent	1883
potassium chloride			1043
iron		metallic	1808
iodine		covalent	387

Explain why the melting temperature of silicon(IV) oxide is much higher than that of iodine, even though the bonding in both is covalent.

5. This is a question about water. Explain why both water and carbon dioxide molecules have polar bonds but only water is a polar molecule.

6.



This question is about atomic structure and the Periodic Table.

The melting temperatures of two elements in Period 3 are given in the table.

Element	silicon	chlorine
Melting temperature / K	1683	172

Explain, in terms of the structure and bonding of each element, the difference between these values.

7. This question is about crystalline solids. Iodine and diamond are crystalline solids at room temperature. Explain why diamond has a much higher melting temperature than iodine.

8. This question is about the thermal stability of Group 1 and Group 2 nitrates and carbonates. Calcium carbonate is thermally decomposed during the manufacture of cement.

(i) Write an equation, including state symbols, for the thermal decomposition of calcium carbonate.

(ii) Name all the types of bond present in calcium carbonate.

(iii) Give a reason, in terms of the bonding, why a high decomposition temperature is required.

9. Boron and aluminium are in the same group of the Periodic Table. Both form compounds with chlorine and with fluorine.

Aluminium fluoride and aluminium chloride are both crystalline solids at room temperature. Aluminium fluoride sublimes to form a gas at 1291°C (1564 K), whilst aluminium chloride sublimes at 178°C (451 K). Use the Pauling electronegativity values in the Data Booklet to explain these differences in sublimation temperature.

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