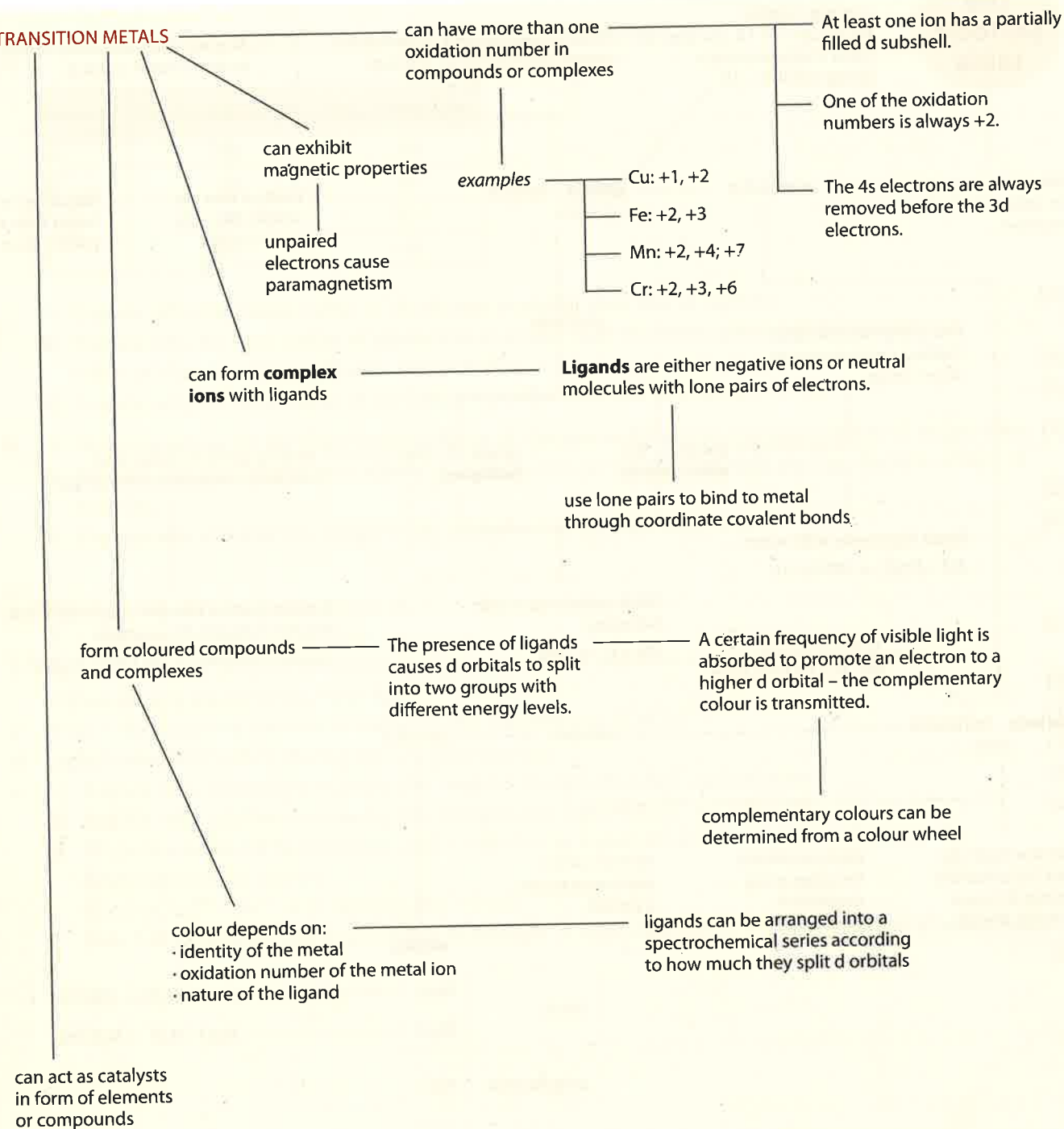


Summary – continued

HL

TRANSITION METALS



Chemical bonding and structure 4

Bonding

Compounds can be divided into two main classes according to the bonding in them – they are either **ionic** or **covalent**. The type of bonding present can usually be deduced by looking at the formula of the compound. Covalent compounds are those formed between two or more non-metallic elements, whereas ionic compounds are usually formed between a metallic element and a non-metallic one. For example, NaCl is an ionic compound but CH₄ is covalent.

There are some compounds for which the distinction is not so clear. For instance, ammonium chloride does not contain any metallic elements but has ionic bonding between the ammonium ions (NH₄⁺) and the chloride ions (Cl⁻). In addition to this, within the NH₄⁺ ion there is covalent bonding.

Generally, as a rough rule of thumb, elements that are close together in the periodic table form covalent compounds but elements that are far apart in the periodic table form ionic compounds. Thus elements from groups 1 and 17 combine to form ionic compounds (CsF being the most ionic) but elements from groups 14, 15, 16 and 17 combine to form covalent compounds. This is discussed in terms of electronegativity on page 129.

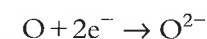
Ionic compound: metal and non-metal
Covalent compound: two or more non-metals

4.1 Ionic bonding and structure

Positive ions are usually formed by metallic elements by the loss of valence (outer shell) electrons. For example, magnesium loses the two electrons in its highest energy level (outer shell) to form a 2+ ion:



Negative ions are usually formed by non-metallic elements by the gain of electrons. For example, oxygen gains two electrons to fill up its outer shell (highest occupied energy level):



At the simplest level, when elements in the main groups of the periodic table (groups 1, 2, 13 (to a certain extent), 15, 16 and 17) form ions, electrons are gained or lost to achieve the electron configuration of the nearest **noble gas**. That is, electrons are gained or lost to make an ion that is **isoelectronic** (same number of electrons) with the nearest noble gas.

Another way of saying this is that electrons are lost or gained to achieve a full outer shell of electrons. Although this is true for the first 20 elements, it is not generally true after that because of the existence of transition metals (and d orbitals).

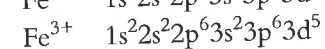
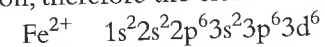
Learning objectives

- Recognise the formulas of ionic compounds
- Understand how ions are formed and recall the formulas of some common ions
- Work out the formulas of ionic compounds from the charges on the ions
- Describe the structure of sodium chloride as an example of an ionic lattice
- Explain the physical properties of ionic compounds in terms of structure and bonding

The transition metals can form more than one ion. For instance, iron can form iron(II), Fe^{2+} , and iron(III), Fe^{3+} .

An Fe^{2+} ion has 24 electrons, an Fe^{3+} ion has 23 electrons, and neither is isoelectronic with a noble gas.

The 4s electrons are lost first when a transition metal atom forms an ion; therefore the electron configurations of Fe^{2+} and Fe^{3+} are:



The number of electrons lost or gained is determined by the electron configuration of an atom.

The number of electrons lost by elements in groups 1 and 2 when they form ions is given by the group number. For instance, magnesium, in group 2 of the periodic table, has two outer shell electrons, and therefore forms a $2+$ ion (Figure 4.1). The number of electrons lost by elements in group 13 is given by the group number -10 . For example, aluminium forms a $3+$ ion.

The number of electrons gained by elements in groups 15 to 17 when they form ions is given by 18 minus the group number. For instance oxygen, in group 16 of the periodic table, has six outer shell electrons and gains $(18 - 16) = 2$ electrons to form a $2-$ ion (Figure 4.2).

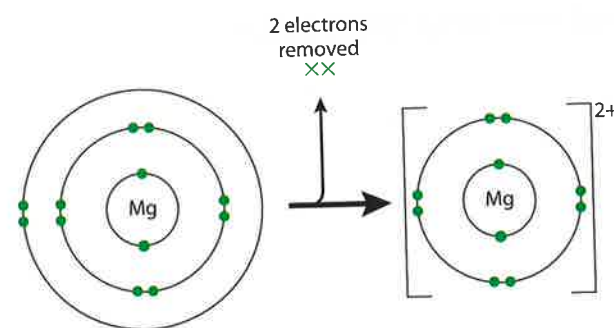


Figure 4.1 The Mg^{2+} ion is isoelectronic with the noble gas atom neon.

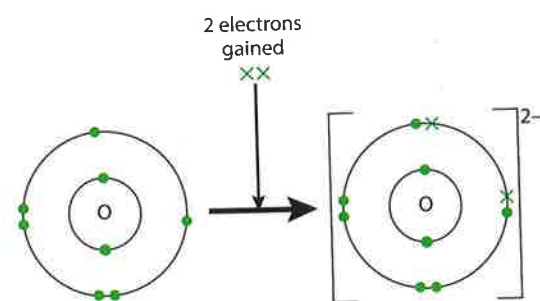


Figure 4.2 The O^{2-} ion is isoelectronic with the noble gas atom neon.

These do not have noble gas electron configurations.

Note: metal atoms do not 'want' to form ions with noble gas electron configurations – for instance, it takes the input of over 2000 kJ mol^{-1} of energy to remove two electrons from a magnesium atom to form an Mg^{2+} ion.

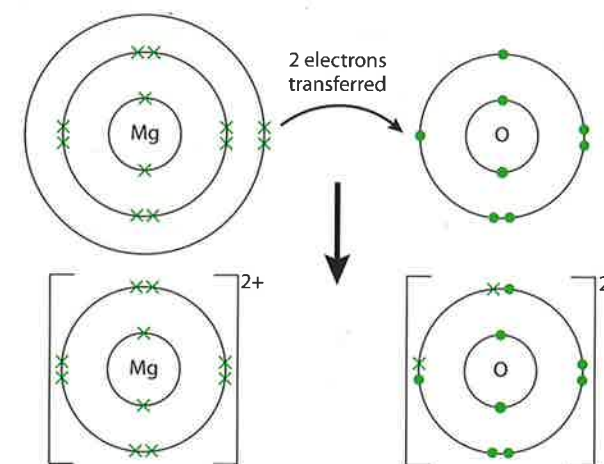


Figure 4.3 Electron transfer in ionic bonding.

When an ionic compound is formed, electrons are transferred from one atom to another to form positive and negative ions. Electrons cannot be created or destroyed; therefore, the total number of electrons lost must always equal the total number gained. You can see this in Figure 4.3.

In the formation of magnesium fluoride (Figure 4.4), one magnesium atom must combine with two fluorine atoms, because magnesium loses two electrons when it forms an ion but each fluorine atom can gain only one electron. So the formula of magnesium fluoride is MgF_2 (Figure 4.4).

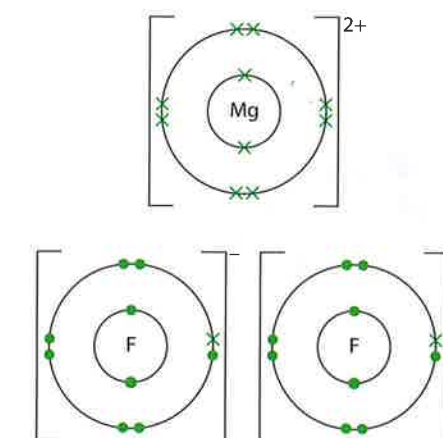


Figure 4.4 The ions in magnesium fluoride.

The formulas of ions

The formulas of commonly encountered positive ions are given in Table 4.1 and of some negative ions in Table 4.2.

Ion	Symbol	Ion	Symbol	Ion	Symbol
lithium	Li^+	magnesium	Mg^{2+}	iron(III)	Fe^{3+}
sodium	Na^+	calcium	Ca^{2+}	aluminium	Al^{3+}
potassium	K^+	barium	Ba^{2+}		
rubidium	Rb^+	iron(II)	Fe^{2+}		
caesium	Cs^+	copper(II)	Cu^{2+}		
silver	Ag^+	zinc	Zn^{2+}		
ammonium	NH_4^+	nickel(II)	Ni^{2+}		
hydrogen	H^+				

Table 4.1 Positive ions.

Ion	Symbol	Ion	Symbol	Ion	Symbol
fluoride	F ⁻	oxide	O ²⁻	nitride	N ³⁻
chloride	Cl ⁻	sulfide	S ²⁻	phosphate(V)	PO ₄ ³⁻
bromide	Br ⁻	carbonate	CO ₃ ²⁻		
iodide	I ⁻	sulfate(VI)	SO ₄ ²⁻		
hydroxide	OH ⁻				
hydrogencarbonate	HCO ₃ ⁻				
nitrate(V)	NO ₃ ⁻				

Table 4.2 Negative ions. Ions such as NO₃⁻ are most properly named including the oxidation number (i.e. nitrate(V)) but this is often omitted.

Exam tip

The formulas and charges of ions such as sulfate and nitrate must be learnt, but the formulas of ions formed by elements in groups 1, 2, 13, 15, 16 and 17 can be worked out.

The brackets around the OH are essential because, otherwise the formula would read MgOH₂, and would indicate the presence of only one oxygen atom.

Rubies and sapphires are mainly aluminium oxide.



Transition metal ions can form more than one ion, so the oxidation number of the ion is usually given with the name. For example, iron can form iron(II) sulfate or iron(III) sulfate. The Roman numeral in brackets indicates the oxidation number of the ion, which is the same as its charge. Iron(III) sulfate, therefore, contains the Fe³⁺ ion and has the formula Fe₂(SO₄)₃. Iron(II) sulfate contains the Fe²⁺ ion and has the formula FeSO₄.

The ionic bond and ionic crystals

An ionic bond is an **electrostatic** attraction between oppositely charged ions.

A crystal of sodium chloride consists of a giant lattice of Na⁺ and Cl⁻ ions (Figure 4.5). All the Na⁺ ions in the crystal attract all the Cl⁻ ions,

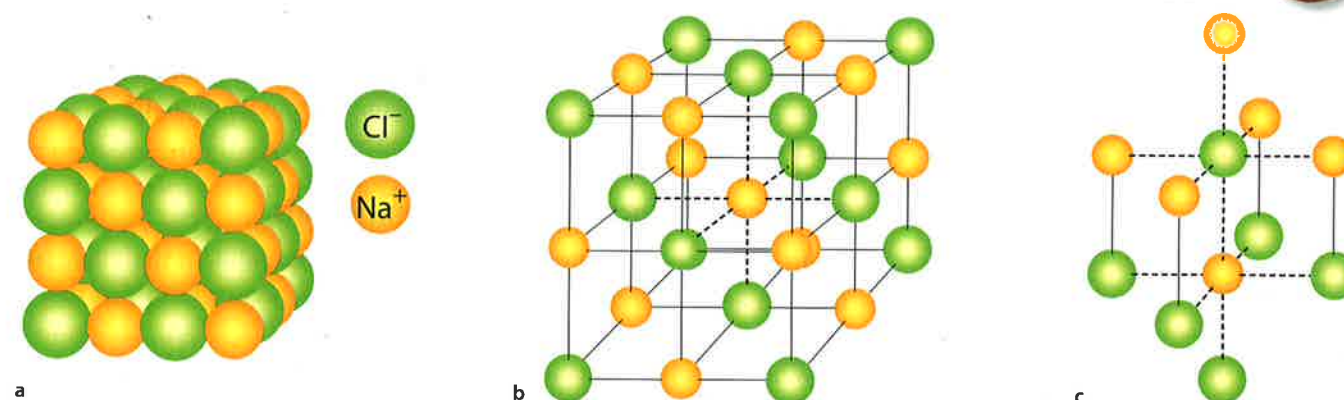


Figure 4.5 **a** A space-filling diagram of the NaCl lattice. The lattice keeps on going in three dimensions – only a tiny part of the structure is shown. **b** An expanded view of the NaCl lattice. **c** Each Na⁺ ion is surrounded by six Cl⁻ ions in an octahedral array and vice versa. The coordination number (number of nearest neighbours) of each ion is 6.

and vice versa, and it is this attraction between oppositely charged ions that holds the crystal together. These electrostatic forces are strong, so it is difficult to break apart the **lattice structure**.

This is a **giant structure** – there are no individual molecules of sodium chloride. Instead, the bonding extends fairly uniformly throughout the whole structure.

It is often better to avoid the term ‘ionic bond’ and talk about ‘ionic bonding’ as a whole – the dotted lines in the diagrams of the lattice structures are **not** ionic bonds, they are simply there to give a better idea of the shape. Ionic bonding (electrostatic attractions between oppositely charged ions) extends throughout the whole structure in all directions – there are no individual ionic bonds.

Physical properties of ionic compounds

Melting points and boiling points

Ionic compounds usually have high melting points and boiling points. For instance, sodium chloride has a melting point of 801 °C and a boiling point of over 1400 °C, while magnesium oxide has a melting point of over 2800 °C and a boiling point of about 3600 °C. This means that ionic substances are usually solids at room temperature.

The high melting and boiling points of ionic solids are due to the strong electrostatic forces between the oppositely charged ions. When an ionic solid is melted, the electrostatic forces throughout the giant lattice must be broken and, because these are so strong, a lot of energy is required.

Magnesium oxide has a much higher melting point than sodium chloride because the electrostatic attractions between the 2+ and 2- ions in the magnesium oxide lattice are much stronger than those between the 1+ and 1- ions in sodium chloride. A higher temperature is required to provide sufficient energy to separate the ions in magnesium oxide. The force between ions is proportional to the product of the charges (all other things being equal).

Extension

This is only one possible lattice for ionic crystals. The type of lattice adopted depends on the formula of the crystal and the ratio of the radii of the positive and negative ions.

Examples of physical properties are melting point, solubility, electrical conductivity, etc. Chemical properties are how a substance reacts.

The word ‘usually’ is used in the sentence ‘ionic substances are usually solids at room temperature’ because there are some low-melting-point ionic compounds, such as ethylammonium nitrate, that are liquids at room temperature (ionic liquids).

Extension

Coulomb’s law – the force between two charges – is given by:

$$F = \frac{1}{4\pi\epsilon_0} \times \frac{Q_1 Q_2}{r^2}$$

where Q_1 and Q_2 are charges, r is the distance between the charges and ϵ_0 is the electric permittivity of a vacuum.

Exam tip

It is important to be clear that ions are moving, not electrons, when an ionic substance conducts electricity.

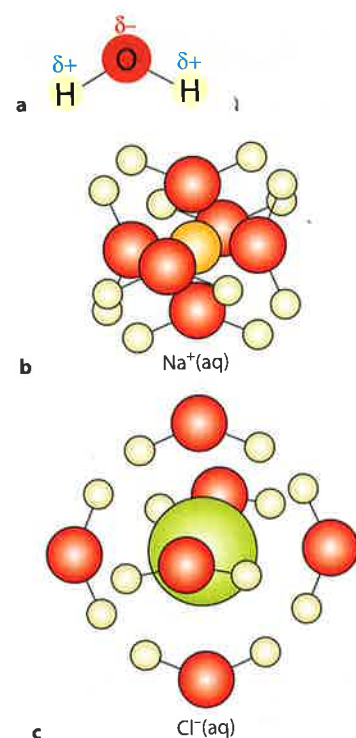


Figure 4.6 a A water molecule is polar.
b A hydrated sodium ion.
c A hydrated chloride ion.

Volatility

Ionic solids have low **volatility** (refers to how readily a substance evaporates). The volatility of ionic substances is low because the electrostatic forces between the ions are strong.

Electrical conductivity of ionic compounds

Ionic substances do not conduct electricity when solid. In the solid state, the ions are held tightly in position in the lattice structure so that they are not free to move around (other than vibrate).

When an ionic substance is melted the ions are able to move freely throughout the liquid. Positive ions can move towards a negative electrode and negative ions towards a positive electrode, so allowing the conduction of electricity.

Solubility in water

Ionic substances are often soluble in water. Water is a polar solvent, and energy is released when the ions are hydrated by being surrounded (ion-dipole attractions) by water molecules (Figure 4.6). This energy pays back the energy required to break apart the ionic lattice.

Electrical conductivity in ionic solutions

Aqueous solutions (solutions made with water) of ionic substances conduct electricity. This is because the ions are free to move around (Figure 4.7).

Solubility in non-polar solvents

Ionic solids are not usually soluble in non-polar solvents such as hexane. This is because a great deal of energy is required to break apart the ionic lattice and this is not paid back by the energy released when the non-polar solvent forms interactions with the ions (London forces). This will be considered in more detail on page 157.

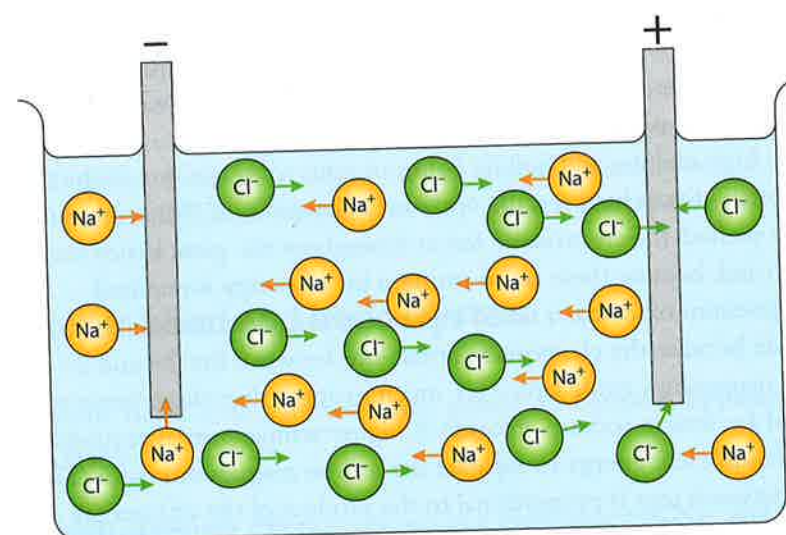


Figure 4.7 Ions move towards the oppositely charged electrode.

Nature of science

Scientists use theories to explain and predict the properties of substances. We can use our theories of the bonding in ionic compounds to explain their properties, for instance, the facts that they have high melting points, conduct electricity when molten etc.

Our theory of bonding in ionic substances predicts that all ionic substances have a common set of properties. Therefore we can predict the properties of any new ionic compound and use experimental observations to test the theory.

? Test yourself

1 State whether the following compounds have ionic or covalent bonding:

a LiF b CF₄ c CaO d NH₃ e PCl₃ f CuCl₂

2 Write the formulas of the following compounds:

a magnesium oxide
b barium sulfate
c calcium hydroxide
d sodium oxide
e strontium sulfide
f aluminium oxide

g lithium nitride
h magnesium phosphate
i magnesium fluoride
j potassium sulfate
k ammonium carbonate

l silver sulfide
m silver nitrate
n ammonium chloride
o copper(II) nitrate
p rubidium carbonate

4.2 Covalent bonding

Single covalent bonds

Covalent bonding occurs when atoms share electrons, and a covalent bond is the electrostatic attraction between a shared pair of electrons and the nuclei of the atoms that are bonded.

At the simplest level, electrons are shared to allow the atoms being bonded to achieve a full outer shell of electrons (noble gas electron configuration). One example is the formation of methane (CH₄).

A carbon atom has four electrons in its outer shell (highest occupied energy level) (Figure 4.8). It will share four electrons so that the number of electrons in its outer shell is eight.

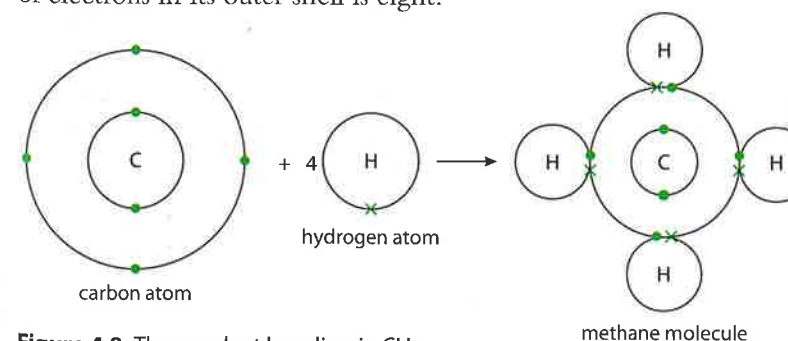


Figure 4.8 The covalent bonding in CH₄.

Learning objectives

- Understand that a covalent bond is formed when electrons are shared
- Understand the relationship between bond strength and bond length
- Understand what is meant by electronegativity
- Predict whether a bond will be polar or not

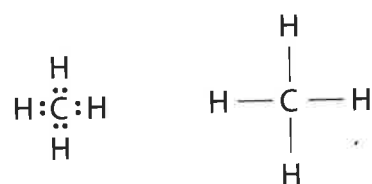


Figure 4.9 Two different types of Lewis structure for methane. In the second one, the line between the atoms represents a shared pair of electrons: that is, a covalent bond.



Figure 4.11 Lewis structures for water.

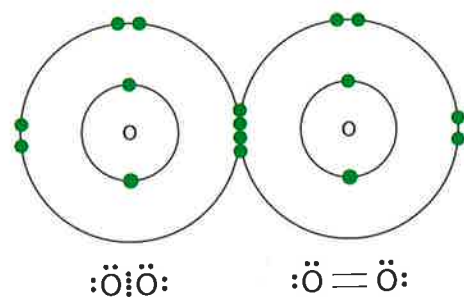


Figure 4.12 Representations of the covalent bonding in O_2 .

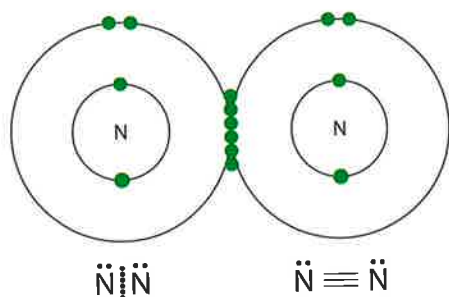


Figure 4.13 Representations of the covalent bonding in N_2 .

A hydrogen atom has one electron in its outer shell and will share one electron with another atom (carbon in this case) to generate an outer shell containing two electrons, i.e. a full outer shell (the same number of electrons as helium).

In methane, the shared electrons are in the outer shell of both atoms making up the bond and so each atom has a full outer shell of electrons (Figure 4.8).

Two alternative ways of representing the covalent bonding in methane are shown in Figure 4.9. These are **Lewis structures**.

Consider the bonding in water (H_2O) – an oxygen atom has six electrons in its outer shell and so will share two electrons to generate a full outer shell (eight electrons) or an octet of electrons. The covalent bonding in water is shown in Figure 4.10.

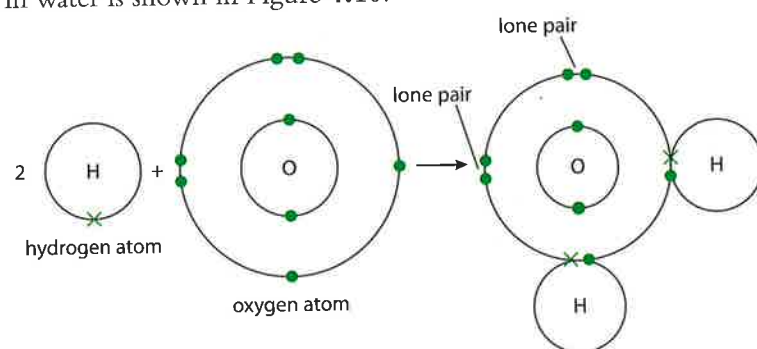


Figure 4.10 Covalent bonding in water. All atoms have full outer shells of electrons.

The pairs of electrons in the outer shell of atoms that are not involved in the covalent bonds are called **lone pairs** of electrons. There are two lone pairs in the outer shell of the oxygen atom in a molecule of water. Alternative representations of the covalent bonding in water are shown in Figure 4.11.

Multiple covalent bonds

It is possible for more than one pair of electrons to be shared between two atoms. A double bond results from the sharing of two pairs of electrons, and a triple bond arises when three pairs of electrons are shared. For example, the covalent bonding in an oxygen molecule, O_2 , is shown in Figure 4.12. Four electrons – that is, two pairs – are shared and so there is a double bond between oxygen atoms.

The covalent bonding in the nitrogen molecule, N_2 , is shown in Figure 4.13. A nitrogen atom shares three electrons to generate a full outer shell, so six electrons are shared when two nitrogen atoms combine to form N_2 . Three shared pairs of electrons between two atoms form a triple bond. More examples of molecules with multiple bonding are shown in Figure 4.14.

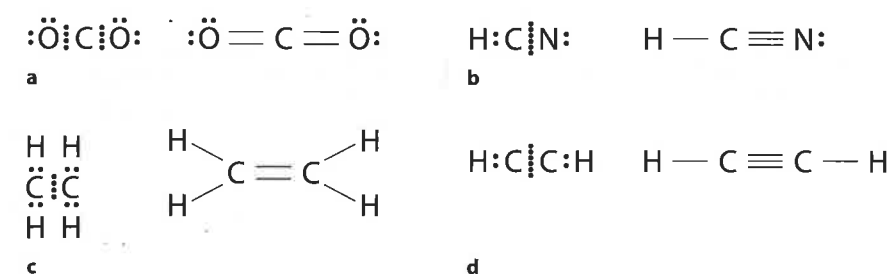


Figure 4.14 Covalent bonding in **a** CO_2 , **b** HCN , **c** C_2H_4 (ethene) and **d** C_2H_2 (ethyne).

What holds the atoms together in a covalent bond?

A covalent bond is the electrostatic interaction between the positively charged nuclei of both atoms and the shared pair of electrons.

The electrons are negatively charged and because the shared electrons are attracted to the nuclei (positively charged) of both atoms simultaneously, this holds the atoms together (Figure 4.15).

As can be seen from Table 4.3, triple bonds are stronger than double bonds, which are stronger than a single bond. This is because the attraction of the two nuclei for three electron pairs (six electrons) in a triple bond is greater than the attraction for two electron pairs (four electrons) in a double bond, which is greater than the attraction for one electron pair (two electrons) in a single bond (Figure 4.16).

It should also be noted that triple bonds are shorter than double bonds, which are shorter than single bonds. This is, again, due to stronger attraction between the bonding electrons and the nuclei when there are more electrons in the bond.

Bond	Length/nm	Bond energy/ kJ mol^{-1}
C–C	0.154	348
C=C	0.134	612
C≡C	0.120	837
C–O	0.143	360
C=O	0.122	743

Table 4.3 The relationship between number of bonds and bond length/strength.

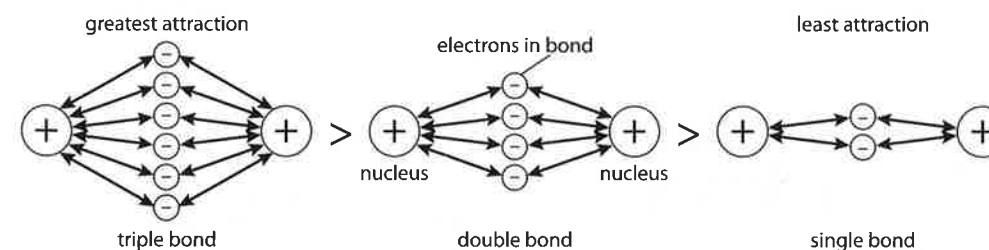


Figure 4.16 The more electrons that make up a covalent bond, the greater the attraction between the electrons and the nuclei, and therefore the stronger the bond.

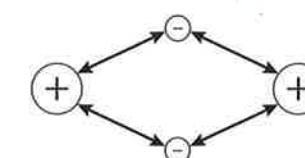


Figure 4.15 The positively charged nuclei attract the negatively charged electrons in the bond.

Strength
single bonds
double bonds
triple bonds
↓
increasing strength

Trends should really only be compared down a group because elements in the same group have the same number of outer shell electrons and therefore any effects due to effective nuclear charge or shielding are most similar. In general, comparisons such as this are most useful and valid when similar molecules, bonds or compounds are considered.

Group 14			Group 17		
Bond	Length / nm	Energy / kJ mol^{-1}	Bond	Length / nm	Energy / kJ mol^{-1}
C-C	0.154	348	Cl-Cl	0.199	242
Si-Si	0.235	226	Br-Br	0.228	193
Ge-Ge	0.241	188	I-I	0.267	151

Table 4.4 The relationship between length of bonds and bond strength.

In general, when we are comparing just single bonds, the longer the bond the weaker it is. Data for two groups in the periodic table are shown in Table 4.4.

If we consider the data for group 14, it can be seen that the single bond between the elements gets weaker as the bond gets longer. This is because, as the atoms get bigger, the electron pair in the covalent bond is further away from the nuclei of the atoms making up the bond. If the electron pair is further away from the nuclei, it is less strongly attracted and the covalent bond is weaker (Figure 4.17). A similar trend can be seen down group 17.

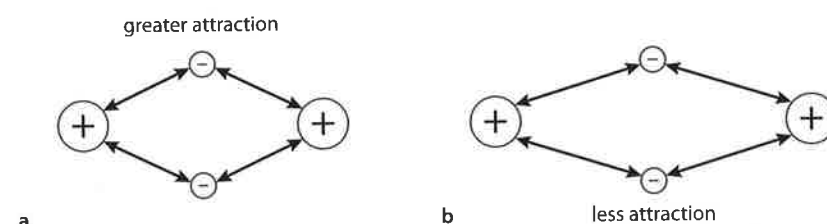


Figure 4.17 The bond in **a** is a shorter bond in which the bonding electrons are closer to the nuclei than in **b**.

Polarity

Electronegativity

In a covalent bond between two different atoms, the atoms do not attract the electron pair in the bond equally. How strongly the electrons are attracted depends on the size of the individual atoms and their nuclear charge.

In an F_2 molecule, the two fluorine atoms attract the electrons in the bond equally and so the electrons lie symmetrically (Figure 4.18). This molecule is non-polar.



Figure 4.18 **a** The electron density in F_2 ; **b** F_2 is a non-polar molecule.

Electronegativity is a measure of the attraction of an atom in a molecule for the electron pair in the covalent bond of which it is a part.

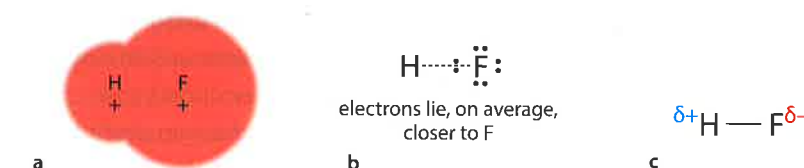


Figure 4.19 **a** The electron density in HF; **b** HF is a polar molecule; **c** usually represented like this

However, in HF, fluorine is more electronegative than hydrogen and attracts the electrons in the H-F bond more strongly than the hydrogen atom does. The electrons in the bond lie closer to the fluorine than to the hydrogen (Figure 4.19) – H-F is a polar molecule. The unsymmetrical distribution of electron density results in small charges on the atoms. Fluorine is δ^- because the electrons in the bond lie closer to F, whereas electron density has been pulled away from hydrogen, so it is δ^+ .

Pauling electronegativities

There are various scales of electronegativity and it is important to realise that, although they are derived from physical quantities (such as bond energies), the numbers themselves are not physical quantities – they have no units and must only be used in a comparative way. The most commonly used scale of electronegativity is that developed by Linus Pauling. The electronegativity values for some elements, worked out using the Pauling method, are shown in Table 4.5.

Noble gases do not have electronegativity values because they do not form compounds.

H 2.1							
Li 1.0	Be 1.5		B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2		Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0		Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0		In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5

Table 4.5 Pauling electronegativities for some elements.

Electronegativity generally decreases down a group and increases across a period. Trends in electronegativity were explained in Topic 3.

Atoms with similar electronegativities will form covalent bonds. Atoms with widely different electronegativities will form ionic bonds. The difference in electronegativity can be taken as a guide to how ionic or how covalent the bond between two atoms is likely to be.

δ^- indicates a small negative charge.

Non-metals have higher electronegativities than metals.

Exam tip

You do not need to learn these electronegativity values, but you should be aware of trends and recognise highly electronegative atoms such as N, Cl, O and F.

Exam tip

To remember the trends in electronegativity, just remember that fluorine is the atom with the highest electronegativity. Electronegativity must then increase across a period towards fluorine and decrease down a group from fluorine.

Exam tip

If asked about this, assume that the bonding between two elements is ionic if the difference is more than 1.7, and covalent if the difference is less than 1.7.

Linus Pauling related the electronegativity difference between two atoms to the ionic character of a bond. He suggested that an electronegativity difference of 1.7 corresponded to 50% ionic character in a bond and reasoned that a higher electronegativity difference than this corresponded to a structure that was more ionic than covalent, whereas if the difference is less than 1.7, the bonding is more covalent than ionic. This is a useful idea, but it must be used with great caution. For instance, KI (electronegativity difference 1.7) would come out of this discussion as having 50% ionic and 50% covalent character, and NaI (difference of 1.6) would appear to be mostly covalent, whereas both behave as predominantly ionic compounds. Pauling, in his original discussion of this, was actually referring to diatomic molecules and not to macroscopic compounds.

? Test yourself

- 3 Arrange the following atoms in order of electronegativity (lowest first):

Cl O H Br Na

Learning objectives

- Understand what is meant by a coordinate covalent bond
- Work out Lewis structures for molecules and ions
- Work out the shapes of molecules and ions with up to four electron domains
- Predict bond angles in molecules and ions
- Predict whether a molecule will be polar or non-polar
- Describe the structures and bonding of giant covalent substances
- Explain the physical properties of giant covalent substances in terms of structure and bonding

4.3 Covalent structures

The octet rule

In Subtopic 4.2 you met the concept that atoms in covalent bonds have a tendency to have a full valence shell with a total of eight electrons (or two in the case of hydrogen). This is known as the **octet rule**. In most covalent molecules and polyatomic ions (for example, NH_4^+ or CO_3^{2-}), each atom has an octet in its outer shell.

It is not, however, always the case that the formation of covalent bonds results in each atom attaining an octet of electrons. In BF_3 (Figure 4.20), boron has only six electrons in its outer shell. This is because a boron atom has only three electrons in its outer shell and can therefore share a maximum of three electrons. Similarly, in BeCl_2 the beryllium atom only has a total of 4 electrons in its outer shell.

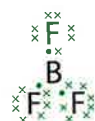


Figure 4.20 Covalent bonding in BF_3 .



Figure 4.21 Covalent bonding in SF_6 .

It is also possible for atoms to have more than eight electrons in their outer shell. For instance, in SF_6 (Figure 4.21) the sulfur atom has 12 electrons in its outer shell, and this is described as sulfur having expanded its octet. Only elements in period 3 and beyond (periods 4, 5 ...) can expand their octet. Expansion of the octet will be discussed in more detail in the Higher Level section later (see Subtopic 4.6).

Coordinate covalent bonds (dative covalent bonds)

A coordinate covalent bond is a type of covalent bond in which both electrons come from the same atom.

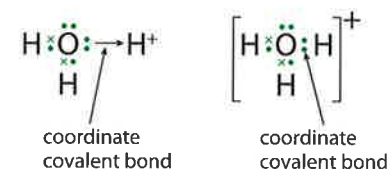
Once a coordinate covalent bond has been formed, it is identical to an 'ordinary' covalent bond. For example, NH_4^+ can be formed when H^+ becomes bonded to NH_3 :



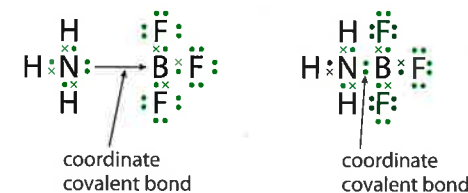
H^+ does not have any electrons with which to form a covalent bond, but NH_3 has a lone pair of electrons that can be used to form a covalent bond (Figure 4.22).

A coordinate covalent bond is sometimes shown as an arrow (Figure 4.23a). Once it has been formed, a coordinate bond is, however, the same as any other covalent bond. The ammonium ion can be represented as shown in Figure 4.23b, in which no distinction is made between the individual bonds.

H_3O^+ is formed when a lone pair of electrons is donated from the O in H_2O to the H^+ :



NH_3 and BF_3 can combine to form an **adduct** (two molecules bonded together):



In BF_3 there are only six electrons in the outer shell of the boron atom – so there is space for the boron to accept a pair of electrons.

Carbon monoxide

Normally carbon shares four electrons to form four covalent bonds, and oxygen shares two to form two covalent bonds. If a carbon atom combines with an oxygen atom with the formation of two covalent

Exam tip

Expansion of the octet is very rarely encountered at Standard Level.

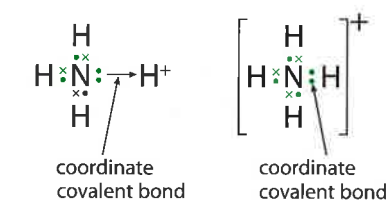


Figure 4.22 Coordinate covalent bonding in NH_4^+ .

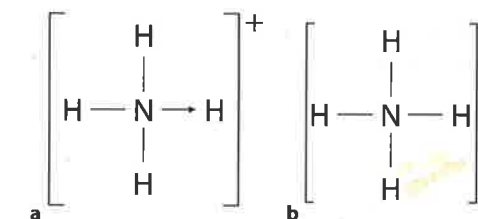




Figure 4.23 The ammonium ion, **a** with the coordinate bond shown and **b** with no distinction between the types of bonds.

This is an example of a Lewis acid-base reaction (see Subtopic 8.2).


Figure 4.24 The structure of carbon monoxide if two 'ordinary' covalent bonds were formed.


Figure 4.25 The structure of carbon monoxide if two 'ordinary' covalent bonds and one coordinate covalent bond were formed.

$\text{:C} \equiv \text{O:}$ or $\text{:C} \equiv \text{O:}$ or $\text{IC} \equiv \text{OI}$

Figure 4.26 Other ways of showing the bonding in carbon monoxide.

bonds, we get the structure shown in Figure 4.24. However, in this structure, although the oxygen atom has a full outer shell (octet), the carbon atom has only six electrons in its outer shell.

Both atoms can attain an octet if the oxygen atom donates a pair of electrons to carbon in the formation of a coordinate covalent bond. There is now a triple bond between the two atoms, made up of two 'ordinary' covalent bonds and one coordinate covalent bond (Figure 4.25). Both atoms have a lone pair of electrons.

Other ways of representing the bonding in carbon monoxide are shown in Figure 4.26.

Coordinate covalent bonds are important in the formation of transition metal complexes.

Lewis (electron dot) structures

Lewis structures are diagrams showing all the valence (outer shell) electrons in a molecule (or ion). Examples of Lewis structures are shown in Figure 4.27. Electrons may be shown individually as dots or crosses, or a line may be used to represent a pair of electrons, as in the Lewis structure of CO shown in Figure 4.27.

Rules for working out Lewis structures:

- 1 Make sure that the *outer* atoms have eight electrons in their outer shell (except, of course, hydrogen which should have two). This is done by using single bonds, double bonds, triple bonds and + or – charges.
- 2 If the central atom is from period 2 it should have no more than eight electrons in its outer shell. It should generally (but not always) have a noble gas electron configuration.
- 3 If the central atom is from period 3 it may have up to 18 electrons in its outer shell.

Let us consider a few examples and go through the steps for drawing the Lewis structures.

NF₃

The central atom is nitrogen and the three outer atoms are fluorine. A fluorine atom has seven electrons in its outer shell and therefore only needs to form one single bond to have a full outer shell.

Therefore, in order for each F atom to have eight electrons in its outer shell, three single bonds between the nitrogen and the fluorine must be formed.

Figure 4.28 shows the Lewis structure for NF₃. Each outer atom has eight electrons in the outer shell and the central atom also has eight electrons in its outer shell. All valence electrons are shown.



CO₃²⁻

Carbon is the central atom and the oxygens are the outer atoms. An oxygen atom has six electrons in its outer shell and therefore needs two more for a full octet. Oxygen can attain a full outer shell by forming a double bond or by forming a single bond and gaining another electron as a negative charge (Figure 4.29a).

Because the carbon atom has only four electrons in its outer shell, it does not have enough electrons to form three double bonds with the oxygens, but it does have enough electrons to form one double bond and two single bonds (Figure 4.29b).

The overall charge on the ion must be included and square brackets drawn around the ion. The Lewis structure for CO₃²⁻ is shown in Figure 4.30.

As a final check, you should make sure that the central atom has no more than eight electrons in its outer shell, because it is from period 2.

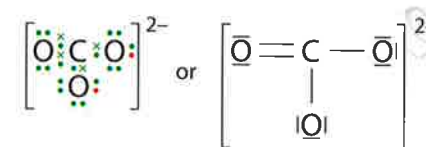


Figure 4.30 The Lewis structure for CO₃²⁻.

Resonance structures

There is more than one way of drawing the structure of the CO₃²⁻ ion (Figure 4.31) depending on where we put the C=O (and lone pairs).

There are many other molecules/ions in which it is possible to draw more than one Lewis structure which differ only in the position of double bonds (and lone pairs). Consider ozone O₃ (Figure 4.32).

Similarly, in the structure of benzene, C₆H₆, the double bonds can be drawn in two ways as shown in Figure 4.33.

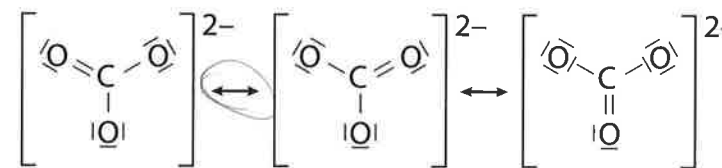


Figure 4.31 Resonance structures of the carbonate ion.

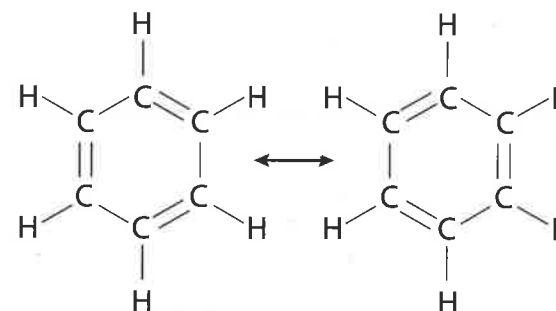


Figure 4.33 Resonance structures of benzene.

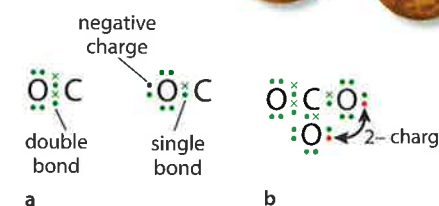


Figure 4.29 a Carbon and oxygen can bond in two different ways. b The resultant structure of the CO₃²⁻ ion.

The electron for the negative charge will come from sodium, calcium, etc. – the CO₃²⁻ ion cannot be formed in isolation – a metal atom must lose electrons at the same time to form the 2– charge.

Exam tip

You must remember to show lone pairs. A very common mistake is to forget to show the lone pairs on the outer atoms. The brackets and the charge are also essential.

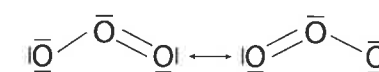


Figure 4.32 Resonance structures of ozone.

These individual structures differ only in the position of the double bond and are called **resonance structures**. In CO_3^{2-} , the carbon–oxygen bonds are equal in length, in O_3 the oxygen–oxygen bond lengths are equal and in benzene the carbon–carbon bonds are all identical. This cannot be explained by looking at just one of the structures (in which double bonds would be shorter than single bonds). The actual structure is described as a hybrid of the individual resonance structures. This is shown by the double headed arrow and is considered more fully in the Higher Level section below.

Two possible Lewis structures for the same molecule

SO_2

Two different Lewis structures are possible for SO_2 depending on whether the octet on S is expanded or not.

Approach 1:

Sulfur does not expand its octet

Sulfur has six electrons in its outer shell and can, therefore, form a maximum of two normal covalent bonds. If these are both formed to the same oxygen atom, we get the structure shown in Figure 4.34a. However, in this structure there is no bond between the sulfur and the right-hand oxygen atom. The structure can be completed by a coordinate bond between the sulfur and the second oxygen, so that all atoms have eight electrons in their outer shell (Figure 4.34b).

Approach 2:

S expands its octet

Each oxygen atom can achieve an octet by forming a double bond.

A sulfur atom has six electrons in its outer shell and when it forms two double bonds it will have ten electrons in its outer shell and is said to have expanded its octet (Figure 4.34c).

This is possible for elements in period 3 and beyond because they have d orbitals available for bonding – the maximum number of electrons in the third shell (the outer shell in sulfur) is 18.

Both approaches to working out Lewis structures are valid, although more detailed considerations which involve working out the formal charge on each atom suggest that the second structure is a better representation of the bonding in the molecule (see the Higher Level section later). The bond lengths in SO_2 also suggest the presence of two double bonds in the molecule.

Alternative method for working out Lewis structures

This approach is useful for working out the Lewis structures of molecules/ions just containing period 2 atoms.

- 1 Add up the total number of valence electrons of all the atoms in the molecule/ion.
- 2 Divide by two to get the total number of valence electron pairs.
- 3 Each pair of electrons is represented by a line.

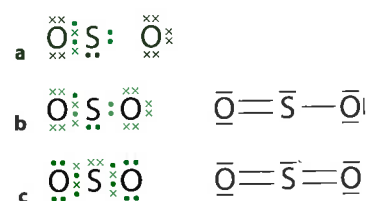


Figure 4.34 Two possible Lewis structures for SO_2 . **a** Sulfur forms two covalent bonds with one oxygen atom. **b** In the first approach, the structure is completed with a coordinate bond between sulfur and the second oxygen atom. **c** In the second approach, sulfur expands its octet, forming a double bond with the second oxygen atom.

- 4 Arrange the lines (electron pairs) so that all the atoms are joined together by at least single bonds and the outer atoms have full outer shells, i.e. are connected to four lines.
- 5 Rearrange the lines (electron pairs) so that every period 2 atom has four pairs of electrons. The outer atoms already have four pairs, so this should normally involve moving only lone pairs so that they become bonding pairs of electrons.

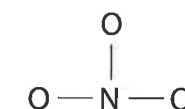
NO_3^-

$$\begin{array}{ccccccc} \text{total no. electrons} & = & 5 & + & 3 \times 6 & + & 1 & = & 24e^- \\ & & \text{N} & & 3 \times \text{O} & & \text{negative charge} & & \end{array}$$

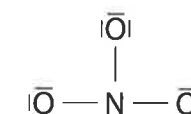
There are therefore $\frac{24}{2} = 12$ pairs of electrons, shown here by 12 lines.



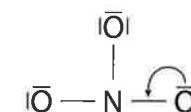
Three must be now used to join all the atoms together:



This leaves nine lines (electron pairs) that will be distributed as lone pairs of electrons on the O atoms (as O is the outer atom) to give each an octet.



Now each O is 'attached to four lines' (has four pairs of electrons in its outer shell) and all the electrons have been used. The nitrogen, however, has only three pairs of electrons in its outer shell, and one of the lines needs to be moved from being a lone pair on the O to make a double bond between the N and an O. This does not change the number of electrons in the outer shell of the O but will increase the number of electrons in the outer shell of the N to eight.



The final Lewis structure for the NO_3^- ion is shown in Figure 4.35. As with CO_3^{2-} earlier (with which it is isoelectronic), more than one resonance structure can be drawn with the double bond in different positions.

This is a purely mechanical technique for working out the Lewis structure and does not really involve any understanding of the bonding in the ion. The Lewis structure showing the electrons as dots and crosses is probably clearer (Figure 4.36).

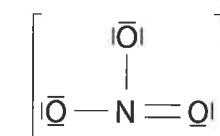


Figure 4.35 The Lewis structure for NO_3^- .



Figure 4.36 The Lewis structure of NO_3^- with the electrons shown individually.

Exam tip

NO₂ has been asked about in examinations. It has an odd number of electrons and therefore an unpaired electron. The Lewis structure can be shown with an N=O double bond and an N → O coordinate bond. The unpaired electron would then be on the N.

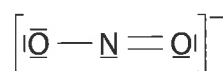


Figure 4.37 The Lewis structure for NO₂⁻.

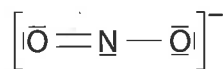


Figure 4.38 An alternative resonance structure for NO₂⁻.

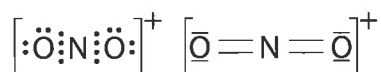


Figure 4.39 The Lewis structures for NO₂⁺.



Figure 4.40 The Lewis structures for CO₂.

NO₂⁻

$$\text{total no. electrons} = 5 + 2 \times 6 + 1 = 18e^-$$

N 2 × O negative charge

There are therefore $\frac{18}{2} = 9$ pairs of electrons



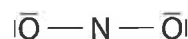
The atoms are joined together using two lines:



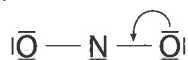
More lines are added to the outer atoms to give each an octet:



So far, only eight lines (electron pairs) have been used and the last line must be put as a lone pair on the N. It cannot be put anywhere else, as the Os already have four electron pairs each.



N only has three electron pairs and so a lone pair is moved from an O to form a double bond:

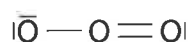


This results in the Lewis structure for NO₂⁻ shown in Figure 4.37.

It is important to note that the Lewis structure could be drawn the other way round and that this is entirely equivalent (Figure 4.38).

O₃

Ozone is isoelectronic with NO₂⁻ and has the same Lewis structure:



NO₂⁺ and CO₂

NO₂⁺ and CO₂ are isoelectronic and have the same Lewis structures (Figures 4.39 and 4.40).

This technique for drawing Lewis structures is useful for molecules/ions involving just period 2 elements, but it also works for compounds involving period 3 elements (and below) if the idea that the atoms do not expand their octet (approach 1, above) is adopted.

Nature of science

Scientists often make careful observations and look for patterns and trends in data, however, noticing discrepancies in these trends can lead to advances in knowledge. For instance, the observation that compounds containing metallic elements had different properties to those containing just non-metallic elements led to the idea of different types of structure and bonding.

Lewis introduced the idea of atoms sharing electrons and distinguished between compounds with ionic and covalent bonding (although he did not originally call them that). He also considered the unequal sharing of electrons and polar compounds. Linus Pauling built on this work by developing the concept of electronegativity to quantify, to a certain extent, the unequal sharing of electrons.

? Test yourself

4 Work out Lewis structures for the following:

- a H₂S d COF₂ g FNO j PCl₄⁺
b PCl₃ e HCN h N₂H₄ k NO⁺
c CCl₄ f CS₂ i H₂O₂ l OCN⁻

5 Some harder ones – these are likely only to be encountered at Higher Level:

- a XeF₄ c BrF₅ e N₂O g I₃⁻
b PCl₆⁻ d ClF₃ f SF₄ h N₃⁻

Shapes of molecules: valence shell electron pair repulsion theory

We can predict the shapes of molecules using the **valence shell electron pair repulsion (VSEPR) theory**.

Pairs of electrons (electron domains) in the valence (outer) shell of an atom repel each other and will therefore take up positions in space to minimise these repulsions – to be as far apart in space as possible.

The pairs of electrons may be either non-bonding pairs (lone pairs) or bonding pairs (pairs of electrons involved in covalent bonds).

Basic shapes

The shape of a molecule depends on the number of electron pairs in the outer shell of the central atom. There are five basic shapes (for two to six electron pairs), which are derived from the idea of how a number of things, joined to a central point, can be arranged in space to be as far apart from each other as possible. However, first of all we will just consider molecules with up to four pairs of electrons around the central atom. The basic shapes and bond angles are shown in Table 4.6.

No. electron domains	Shape	Diagram	Bond angle	Example
2	linear	$\text{Y} - \text{X} - \text{Y}$	180°	BeCl ₂ (g)
3	trigonal planar	$\begin{array}{c} \text{Y} \quad \text{Y} \\ \quad \diagdown \quad \diagup \\ \quad \text{X} \\ \quad \diagup \quad \diagdown \\ \text{Y} \end{array}$	120°	BF ₃
4	tetrahedral	$\begin{array}{c} \text{Y} \\ \diagdown \\ \text{Y} \quad \text{X} \quad \text{Y} \\ \diagup \\ \text{Y} \end{array}$	109.5°	CH ₄

Table 4.6 Basic molecule shapes and bond angles.

More precisely, it is a question of how points can be arranged on the surface of a sphere to be as far away from each other as possible.

A double bond is made up of two pairs of electrons, but these electron pairs are constrained to occupy the same region of space. A double bond (or a triple bond) therefore behaves, in terms of repulsion, as if it were just one electron pair and so it is better to talk about the number of **electron domains** – where an electron domain is either a lone pair, the electron pair that makes up a single bond or the electrons pairs that together make up a multiple bond.

How to predict the shapes of molecules

- 1 Draw a Lewis structure for the molecule or ion.
- 2 Count up the number of electron pairs (bonding pairs and lone pairs) in the outer shell of the central atom. A multiple bond counts as a single electron pair, because the electrons are constrained to occupy the same region of space. This gives the total number of electron domains.
- 3 Look at Table 4.7 to get the basic shape (spatial arrangement of the electron domains).
- 4 A lone pair is just an electron pair in the outer shell of an atom and, as such, it contributes to the overall shape of the molecule but cannot itself be 'seen'.
- 5 State the actual shape of the molecule. See Figure 4.41 for how to draw 3D shapes.

CH₄

The Lewis structure for CH₄ is shown in Figure 4.42. The number of electron pairs in the outer shell of the central atom (C) is four, i.e. there are four electron domains. These four electron domains repel each other and take up positions in space as far away from each other as possible. The shape that allows four things to be as far away from each other as possible is **tetrahedral**. Therefore, the four electron pairs (electron domains) are arranged tetrahedrally around the C atom. The shape of the methane molecule is tetrahedral and the H–C–H bond angle is 109.5° (Figure 4.43).

NH₃

The Lewis structure for NH₃ is shown in Figure 4.44.

Bonding pairs of electrons: 3 (in three single bonds)
Non-bonding pairs of electrons: 1 (in one lone pair)
Electron domains: 4

Because these four electron domains repel each other and take up positions in space to be as far apart as possible, the electron pairs are distributed in a tetrahedral arrangement. The basic shape is tetrahedral – but a lone pair is just a pair of electrons in the outer shell of the central atom and, although it repels the other pairs of electrons and influences the shape, it cannot be 'seen'. The shape adopted by the atoms is therefore **trigonal pyramidal** (a pyramid with a triangular base) (Figure 4.45).

The H–N–H bond angle here is smaller than in a perfect tetrahedron, because the lone pair repels the bonding pairs of electrons more than they repel each other. This will be considered in more detail later.

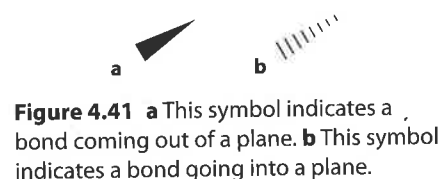


Figure 4.41 a This symbol indicates a bond coming out of a plane. b This symbol indicates a bond going into a plane.

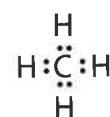


Figure 4.42 The Lewis structure for CH₄.

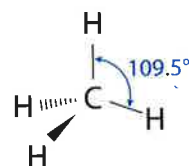


Figure 4.43 CH₄ is tetrahedral.

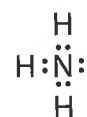


Figure 4.44 The Lewis structure for NH₃.



Figure 4.45 The shape of the NH₃ molecule is based on a tetrahedron, but the actual shape is trigonal pyramidal.



Here, we talk about it not being possible to 'see' a lone pair of electrons, but of course it is not possible to see **any** of these molecules.

There are various techniques for determining the shapes of molecules experimentally. Probably the most important of these is X-ray crystallography, in which a crystal of the substance is placed in an X-ray diffractometer and, from the position and intensity of diffracted X-ray beams, the shape of the molecules, all the angles and bond lengths can be calculated. The lone

pairs of electrons cannot be detected by this technique. Do we know or believe the shapes of molecules stated here? Which ways of knowing do we use to interact with this microscopic world? In biology, microscopes are used to 'view' things that are too small to be seen with the naked eye. Is there a difference between the use of a microscope to interact with this invisible world and the use of an X-ray diffractometer? What about the use of electron microscopes?

CO₂

The Lewis structure for CO₂ is shown in Figure 4.46.

Bonding pairs of electrons: 4 (in two double bonds)
Non-bonding pairs of electrons: 0
Electron domains: 2 (because a double bond counts as one electron domain – the four electrons that make up the double bond are constrained to occupy the same region of space)

Because these two electron domains repel each other and take up positions in space to be as far apart as possible, the electron domains are distributed in a linear arrangement (Figure 4.47), and the shape adopted by the atoms is **linear**.

SO₂

The Lewis structure for SO₂ is shown in Figure 4.48.

Bonding pairs of electrons: 4 (in two double bonds)
Non-bonding pairs of electrons: 1 (one lone pair on S)
Electron domains: 3 (because a double bond counts as one electron domain)

Because these three electron domains repel each other and take up positions in space to be as far apart as possible, the electron domains are distributed in a trigonal planar (flat triangle) arrangement (Figure 4.49a). The lone pair on sulfur is just a pair of electrons in its outer shell and cannot be 'seen'. The shape adopted by the atoms is therefore **bent** (also called 'angular', or 'V-shaped').

Again the bond angle is slightly less than the ideal angle in a trigonal planar structure (120°), and this results from the extra repulsion of a lone pair, so that the bonding pairs are pushed closer together and the bond angle is reduced.

If the Lewis structure had been drawn differently (Figure 4.49b), with sulfur not expanding its octet, this would have made no difference to the predicted shape.



Figure 4.46 The Lewis structure for CO₂.

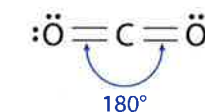


Figure 4.47 The linear CO₂ molecule.



Figure 4.48 The Lewis structure for SO₂.

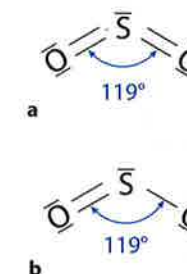


Figure 4.49 a The bent SO₂ molecule
b alternative model for SO₂.

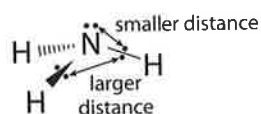


Figure 4.50 Lone pairs lie closer to the central nucleus than bonding pairs.

Exam tip

A general rule of thumb, if you are asked to predict a bond angle in a particular molecule, just take two or three degrees off the basic angle (the bond angle in the basic shape) for each lone pair present on the central atom. For example, a bent molecule based on a trigonal planar structure (one lone pair on the central atom) could have a bond angle of $120 - 3 = 117^\circ$. There is no scientific basis for doing this, but it is useful for answering examination questions.

Note: both SO_2 and H_2O have bent structures, but the SO_2 structure is based on trigonal planar whereas the H_2O structure is based on tetrahedral. This means that the bond angle is larger in SO_2 .

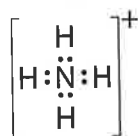


Figure 4.51 The Lewis structure for NH_4^+ .

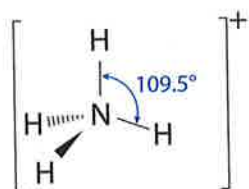


Figure 4.52 Tetrahedral NH_4^+ .

Lone pairs and bond angles

The order of repulsion strength for pairs of electrons is:

lone pair–lone pair > lone pair–bonding pair > bonding pair–bonding pair

This is because lone pairs are held closer (Figure 4.50) to the central nucleus than are bonding pairs (lone pairs are in the outer shell of the central atom, whereas a bonding pair can be imagined as being, on average, halfway between the bonded atoms). The lone pairs are thus closer to the bonding pairs of electrons than the bonding pairs are to each other and repel them more strongly. This means that the repulsion due to lone pairs causes other bond angles to become smaller.

Consider CH_4 , NH_3 and H_2O , each of which has four electron pairs in the outer shell of the central atom (Table 4.7). The basic shape is the arrangement of the electron pairs in the outer shell of the central atom. The more lone pairs present, the smaller the H-X-H bond angle. This is due to greater repulsion from lone pairs than from bonding pairs of electrons. Two lone pairs cause greater repulsion than one, so the bond angle gets smaller as the number of lone pairs increases.

Molecule	Lewis structure	Bonding pairs	Lone pairs	Basic shape	Actual shape	H-X-H bond angle
CH_4		4	0	tetrahedral	tetrahedral	109.5°
NH_3		3	1		trigonal pyramidal	107.3°
H_2O		2	2		bent	104.5°

Table 4.7 Structural characteristics of CH_4 , NH_3 and H_2O .

Predicting the shapes of ions

The approach to predicting the shapes of ions is exactly the same as for neutral molecules.

NH_4^+

The Lewis structure for NH_4^+ is shown in Figure 4.51.

Bonding pairs of electrons: 4
Non-bonding pairs of electrons: 0
Electron domains: 4

Because these four electron domains repel each other and take up positions in space to be as far apart as possible (Figure 4.52), the electron pairs are distributed in a tetrahedral arrangement.

H_3O^+

The Lewis structure for H_3O^+ is shown in Figure 4.53.

Bonding pairs of electrons: 3
Non-bonding pairs of electrons: 1
Electron domains: 4

Because these four electron domains repel each other and take up positions in space to be as far apart as possible, the electron pairs are distributed in a tetrahedral arrangement. One of the electron pairs is a lone pair, so the actual shape of the ion is trigonal pyramidal (Figure 4.54). This structure is based on tetrahedral (bond angle 109.5°) with one lone pair, so a bond angle of about 107° for the H-O-H bond could be predicted (the molecule is isoelectronic with ammonia).

NO_2^-

The Lewis structure for NO_2^- is shown in Figure 4.55.

Bonding pairs of electrons: 3 (one single bond and one double bond)
Non-bonding pairs of electrons: 1
Electron domains: 3 (because a double bond counts as one electron domain)

Because these three electron domains repel each other and take up positions in space to be as far apart as possible, the electrons pairs are distributed in a trigonal planar arrangement. One of the electron pairs is a lone pair, so the actual shape of the ion is bent (Figure 4.56). This structure is based on trigonal planar (bond angle 120°) with one lone pair, so a bond angle of about 117° could be predicted.

Molecules with more than one central atom

The approach to predicting the shapes of molecules with more than one central atom is the same as for other molecules, except that each 'central atom' must be considered separately.

N_2H_4

The Lewis structure for N_2H_4 is shown in Figure 4.57. In this molecule, the two N atoms are 'central atoms' and each one must be considered separately (Table 4.8).

Left-hand nitrogen	Right-hand nitrogen
bonding pairs of electrons: 3	bonding pairs of electrons: 3
non-bonding pairs of electrons: 1	non-bonding pairs of electrons: 1
electron domains: 4	electron domains: 4

Table 4.8 Counting electron domains around the nitrogen atoms in N_2H_4 .

It can be seen (Figure 4.58) that the arrangement of electron pairs around each nitrogen is tetrahedral and, with one lone pair on each nitrogen, the shape about each N atom is trigonal pyramidal.

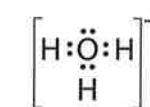


Figure 4.53 The Lewis structure for H_3O^+ .

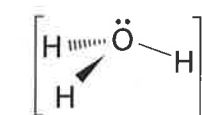


Figure 4.54 Trigonal pyramidal H_3O^+ .

No definitive value for the bond angle in H_3O^+ exists. Values have been measured, but they depend on the actual compound i.e. the negative ion present.



Figure 4.55 The Lewis structure for NO_2^- .

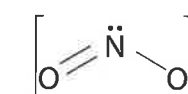


Figure 4.56 NO_2^- is bent.

No definitive value for the bond angle in NO_2^- exists. Values have been measured, but they depend on the actual compound.

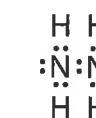


Figure 4.57 The Lewis structure for N_2H_4 .

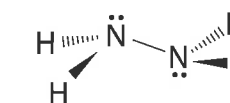


Figure 4.58 The structure of N_2H_4 .

Figure 4.59 The Lewis structure for C_2H_2 .

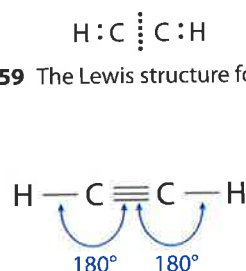
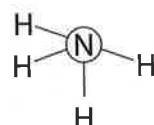


Figure 4.60 Linear C_2H_2 .

'Basic shape' is the arrangement of the electron pairs around the central atom.

Extension

VSEPR gives us no information about how the two NH_2 groups in hydrazine are twisted relative to each other, and in the gas phase hydrazine adopts the conformation with the two NH_2 groups staggered relative to each other.



view of a hydrazine molecule looking down the N—N bond

Total electron domains	Bonding pairs	Lone pairs	Basic shape	Actual shape	Example
2	2	0	linear	linear	CO_2 , NO_2^+ , HCN , $BeCl_2$
3	3	0	trigonal planar	trigonal planar	BF_3 , SO_3 , NO_3^- , CO_3^{2-}
3	2	1	trigonal planar	bent, V-shaped, angular	SO_2 , O_3 , NO_2^-
4	4	0	tetrahedral	tetrahedral	CCl_4 , XeO_4 , NH_4^+ , BCl_4^- , SO_4^{2-} , PO_4^{3-}
4	3	1	tetrahedral	trigonal pyramidal	NH_3 , PCl_3 , XeO_3 , H_3O^+ , ClO_3^- , $SOCl_2$
4	2	2	tetrahedral	bent, V-shaped, angular	H_2O , SCl_2 , ClF_2^+ , I_3^+

Table 4.9 The basic and actual shapes of some specific molecules – see Subtopic 4.6 for information about atoms with more than four electron domains.

C_2H_2

The Lewis structure for C_2H_2 is shown in Figure 4.59. In ethyne, each C is considered separately, but each one is identical. For each C:

Bonding pairs of electrons: 4 (one single bond and one triple bond)
Non-bonding pairs of electrons: 0
Electron domains: 2

The triple bond counts as one electron domain, so, with two electron domains around each C, the shape is linear (Figure 4.60) about each C and therefore linear overall.

VSEPR summary

The shapes taken up by molecules depend on the number of **pairs** of electrons in the outer shell of the central atom. To take account of molecules containing multiple bonds, this is often expressed in terms of electron domains, where one multiple bond counts as one electron domain.

Pairs of electrons in the outer shell of an atom repel each other. The pairs of electrons may be either bonding pairs or lone pairs. The pairs of electrons take up positions in space to minimise repulsions in a molecule, i.e. to be as far apart from each other as possible. The basic shapes adopted are shown in Table 4.9.

Lone pairs influence the shapes of molecules but cannot actually be 'seen'. The shapes of some specific molecules are also shown in Table 4.9.

Lone pairs repel bonding pairs of electrons more than the bonding pairs repel each other. Therefore the presence of lone pairs results in a closing up of bond angles.

Polar molecules

The electronegativity difference between two atoms covalently bonded together results in the electrons lying more towards one atom than the other. We call such a bond **polar**. However, whether an overall molecule is polar also depends on the shape of the molecule.

For a molecule to be polar it must have a positive end to the molecule and a negative end. For instance HCl , NH_3 and H_2O are all polar (Figure 4.61). These molecules all have an overall **dipole moment**, and the arrow indicates the direction of the moment.

Although individual bonds may be polar, a molecule may be non-polar overall if, because of the symmetry of the molecule, the dipole moments of the individual bonds cancel out.

CO_2 is a non-polar molecule (Figure 4.62). Each $C=O$ bond is polar, because oxygen is more electronegative than carbon, but overall the dipoles cancel so that there is no overall dipole moment and the molecule is non-polar.

BF_3 is also non-polar. Again, each individual bond is polar but the dipoles cancel.

CCl_4 is non-polar, but $CHCl_3$ is polar (Figure 4.63).

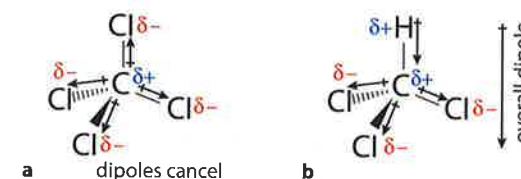


Figure 4.63 a CCl_4 is non-polar because the individual dipoles cancel. b $CHCl_3$ is polar because the dipoles do not cancel out; there is a positive end to the molecule and a negative end. Although the C in $CHCl_3$ is shown as δ^+ , it is not as positive as the H (C is more electronegative than H); therefore, the C is slightly negative compared with the H, although it is positive overall in the molecule.

Some polar and non-polar molecules are shown in Table 4.10.

Polar	Non-polar
HCl , H_2O , NH_3 , SO_2 , $CHCl_3$, CH_2Cl_2 , CH_3Cl , SCl_2 , XeO_3 , PCl_3 , $SOCl_2$, $POCl_3$	CO_2 , C_2H_2 , C_2Cl_4 , BF_3 , XeF_2 , XeF_4 , SF_6 , PF_5 , XeO_4 , SO_3
	These molecules are non-polar, because the symmetry of the molecules causes the individual dipole moments of the bonds to cancel out.

Table 4.10 Some polar and non-polar molecules.

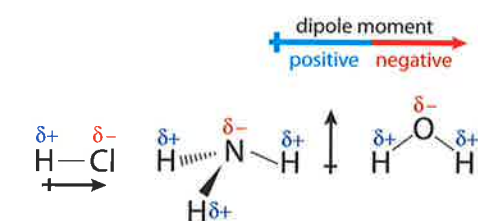


Figure 4.61 These molecules are all polar – one end of the molecule is slightly positive compared with the other end. The arrow indicates the dipole moment direction.

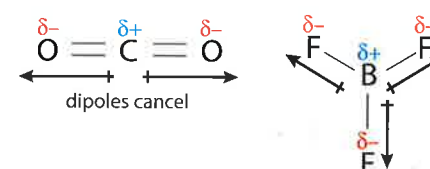


Figure 4.62 Bond polarities can cancel out.

Exam tip

The examination answer as to why CCl_4 is non-polar is 'although each individual bond is polar due to the difference in electronegativity of the atoms, because of the symmetry of the molecule, the dipoles cancel'.

Extension

Dipole moment is the product of the charge and the distance between the charges. The unit is the debye (D).



Many people talk about the scientific method and the idea of testing theories against experimental data – if the experimental results do not agree with the theory then the theory should be discounted. However, scientists do not dismiss theories so easily. The bond angle in an H_2Te molecule is 90° , which is a lot smaller than we would predict, but this does not mean that we dismiss VSEPR completely – rather, theories are modified and improved. It is rare that a theory is completely discounted – this would constitute a paradigm shift and an awful lot of evidence would have to build up to warrant such a radical change.

Nature of science

Scientists often use simplified models as a representation of the real world. A simple picture of balls (atoms) joined together by sticks (covalent bonds) allows us to visualise the molecular world. The VSEPR theory allows us to rationalise and predict the shapes of molecules. Using these fairly simple models we can explain observed properties and make predictions, however, when the models prove inadequate, more sophisticated ones must be developed.

? Test yourself

- 6 Work out the shapes of the following molecules or ions and predict their bond angles:
- | | | |
|------------------------|--------------------|--------------------------|
| a H_2S | e COF_2 | i OCN^- |
| b PCl_3 | f CS_2 | j O_3 |
| c CF_4 | g FNO | k C_2F_4 |
| d HCN | h PCl_4^+ | l NO_2^+ |
- 7 Select the polar molecules from the following list. For the polar molecules, draw diagrams showing the dipoles.
- | | | | | |
|--------------------------|----------------|----------------|-------------------------|----------------------|
| HBr | HCN | PH_3 | SCl_2 | CF_4 |
| N_2 | OCl_2 | BCl_3 | C_2Cl_2 | H_2S |
| CH_2Cl_2 | | | | |

Giant covalent structures

Allotropes of carbon

Allotropes are different forms of the same element. For instance, diamond, graphite, graphene and fullerenes are all allotropes of carbon. They all contain only carbon atoms, but these atoms are joined together differently in each structure.

Diamond

Diamond has a giant covalent (macromolecular) structure. There are no individual molecules – the whole structure, continuing in three dimensions, represents one giant molecule (Figure 4.64). Each carbon atom is joined to four others, in a **tetrahedral** array, by covalent bonds.

Diamond has a very high melting point and boiling point (about 4000°C) because a lot of energy must be supplied to break covalent bonds (very strong) when diamond is melted/boiled. Diamond is very hard for the same reason.

Diamond does not conduct electricity, because all the electrons are held strongly in covalent bonds and are therefore not free to move around in the structure.

Diamond is not soluble in water or organic solvents because the forces between the atoms are too strong. The energy to break these covalent bonds would not be paid back when the C atoms were solvated.

Graphite

Like diamond, graphite has a giant covalent structure. Unlike diamond, however, it has a layer structure (Figure 4.65). Each C is covalently bonded to three others in a trigonal planar array.

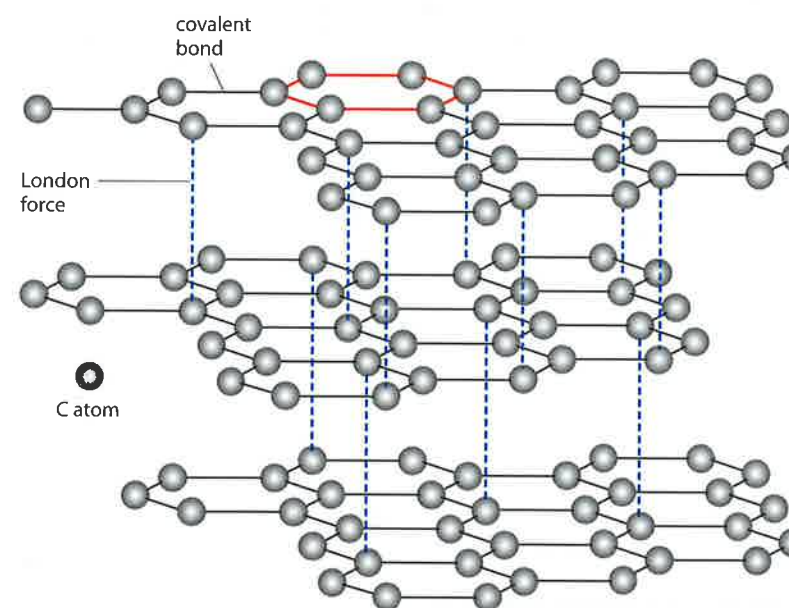


Figure 4.65 Part of the structure of graphite, which is based on planar hexagonal rings. One hexagon is highlighted in red.

There are covalent bonds between the C atoms within a layer but only London forces between the layers (some of these are shown in blue in Figure 4.65). The presence of weak forces between the layers is usually given as the explanation that graphite is a good lubricant (used in pencils, for example) – not much force is required to separate the layers. However, it has a very high melting/boiling point because covalent bonds within the layers must be broken when it is melted/boiled.

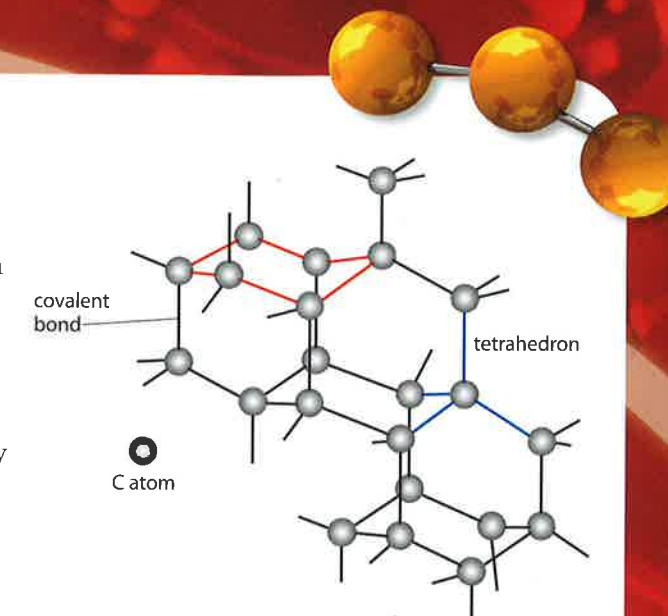


Figure 4.64 Part of the diamond structure, which is based on puckered hexagonal rings. One hexagon is highlighted in red.

Diamond is the hardest naturally occurring substance. It also has the highest thermal conductivity of any substance – more than five times that of copper. Both these properties make it suitable for use on drill bits. Diamond-encrusted drills can be used to drill through rock.

Substances with giant structures are sometimes called network solids.

Extension

The lubricant properties of graphite are usually explained as being due to the weak forces between layers of carbon atoms. However, graphite is a poor lubricant in a vacuum and it is now believed that the lubricant properties come from adsorbed water molecules.

Because of the strong covalent bonds between atoms, graphite is not soluble in water or non-polar solvents.

Graphite conducts electricity because each C atom forms only three covalent bonds – the extra electrons not used in these bonds (carbon has four outer shell electrons) are able to move within the layers.

Because only three covalent bonds are formed by each carbon atom in the layers, each C atom possesses one p orbital, containing one electron (Figure 4.66), perpendicular to the plane of the layers. These p orbitals can overlap side-on to give a π **delocalised system** (see Higher Level material on page 170) extending over the whole layer. Movement of electrons within this system allows the conduction of electricity within layers. Graphite is, however, an electrical insulator perpendicular to the plane of the layers.

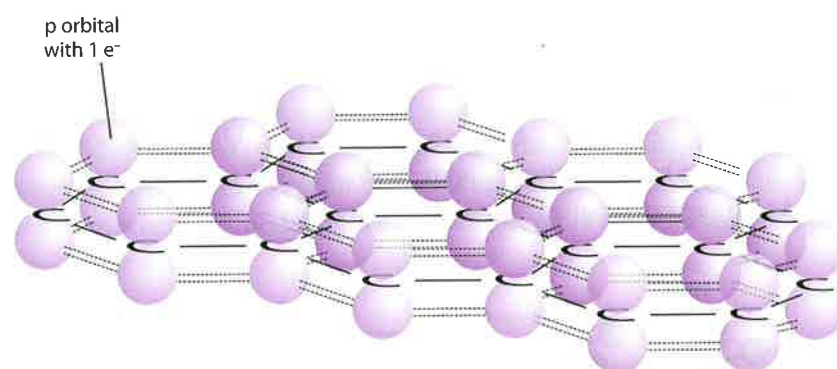


Figure 4.66 Delocalisation in graphite.

Graphene

Graphene is a relatively new form of carbon that consists of a single layer of graphite. Only very small pieces have been formed so far but it has some interesting properties that could make it very important in the near future as a new material.

Graphene has a very high tensile strength and would be expected to have a very high melting point because covalent bonds need to be broken to break the sheet. It is also a very good electrical (C forms only three bonds) and thermal conductor.

C₆₀ fullerene (buckminsterfullerene)

The fourth allotrope of carbon that will be considered here is a molecular rather than a giant structure. It consists of individual C₆₀ molecules, with covalent bonds within the molecule and London forces between the molecules (Figure 4.67).

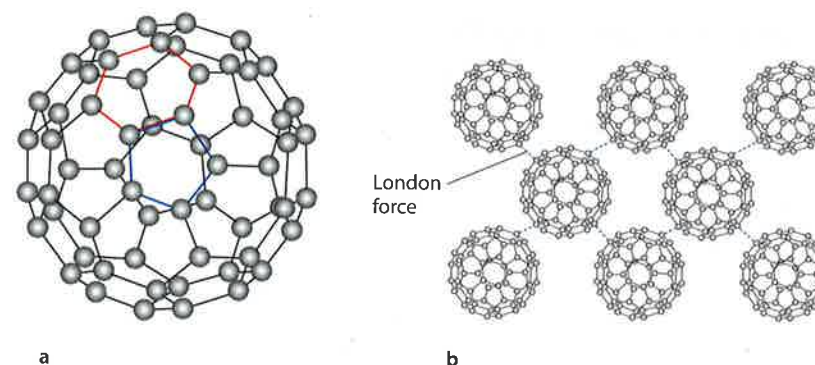


Figure 4.67 **a** One molecule of C₆₀. The structure is based on hexagons (one highlighted in red) and pentagons (one highlighted in blue); **b** London forces exist between C₆₀ molecules in the solid state.

C₆₀ is insoluble in water but soluble in some organic solvents such as benzene. The energy to overcome the London forces between the C₆₀ molecules is paid back by the energy released when London forces are formed between the C₆₀ molecules and the solvent.

C₆₀ does not conduct electricity. Although each C forms three bonds in the C₆₀ molecule, so that there is delocalisation of electrons over the molecule, the molecular structure means that electrons are not able to move from one molecule to the next.

Silicon dioxide

SiO₂ (quartz) has a giant covalent structure (Figure 4.68). Each silicon atom is bonded to four oxygen atoms in a tetrahedral array. Each oxygen atom is bonded to two silicon atoms. Due to two lone pairs on each oxygen atom, the basic shape about each Si–O–Si unit is bent (based on a tetrahedron).

The formula is SiO₂ because each Si has a half share of four O atoms, i.e. $\text{Si}(\text{O}\frac{1}{2})_4 = \text{SiO}_2$. The oxide has high melting and boiling points, because covalent bonds between atoms must be broken in order to melt/boil it and this requires a lot of energy.

Nature of science

Science is a highly collaborative subject. The study of graphene lies on the boundary between chemistry and physics. The isolation of graphene was the result of collaboration between scientists of different nationalities and at universities in different countries. Scientists publish work in peer-reviewed journals, which make the knowledge available to other scientists.

Diamond and graphite are **giant** structures but fullerene is a **molecular** structure. The melting points of diamond and graphite are therefore substantially higher than that of fullerene, because covalent bonds must be broken when diamond and graphite are melted but only intermolecular forces (London forces) must be overcome when fullerene melts (it actually undergoes sublimation at about 530 °C).

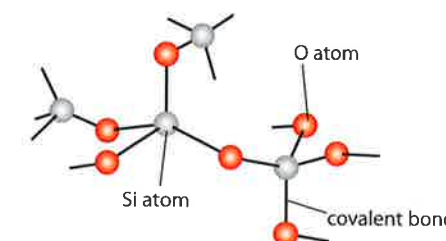


Figure 4.68 Silicon dioxide structure.

Quartz is a piezoelectric material and is used in clocks and watches.

Learning objectives

- Understand how intermolecular forces arise
- Understand how physical properties of covalent molecular substances depend on the intermolecular forces
- Predict relative boiling points of substances

Van der Waals' forces is the collective name given to the forces between molecules and includes London (dispersion) forces, dipole–dipole interactions and dipole–induced dipole interactions.

Intramolecular forces are forces within a molecule.

Intermolecular forces are forces between molecules.

Intermolecular forces are much weaker than covalent bonds.

London forces are present between all molecules in solid and liquid states.

4.4 Intermolecular forces

The nature of intermolecular forces

Br_2 is a liquid at room temperature. It consists of discrete molecules in which the two Br atoms are joined by a covalent bond (an **intramolecular** force). But if Br_2 is to be a liquid, there must be some forces between molecules holding them in the liquid state (otherwise it would be a gas). These forces are **intermolecular** forces (Figure 4.69).

There are various types of intermolecular forces. The main type between non-polar atoms/molecules is the **London (dispersion) force**. London forces are much weaker than covalent bonds. Therefore, when bromine is heated to form a gas, the Br_2 molecules (held together by covalent bonds) remain intact and it is the London forces that are overcome (Figure 4.70).

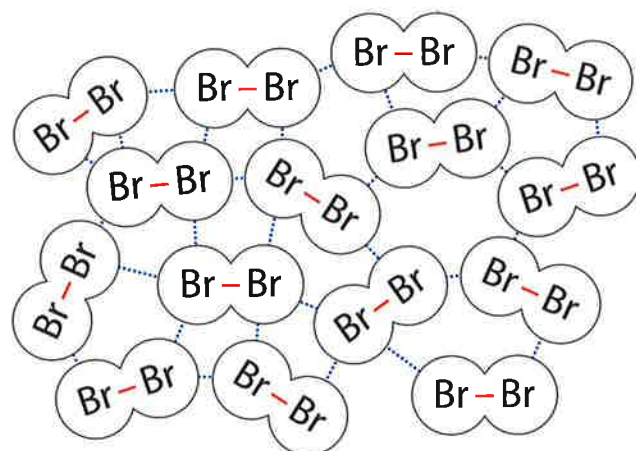


Figure 4.69 Intermolecular and intramolecular forces in liquid bromine. Intramolecular forces are shown in red and intermolecular forces are the dashed lines in blue.

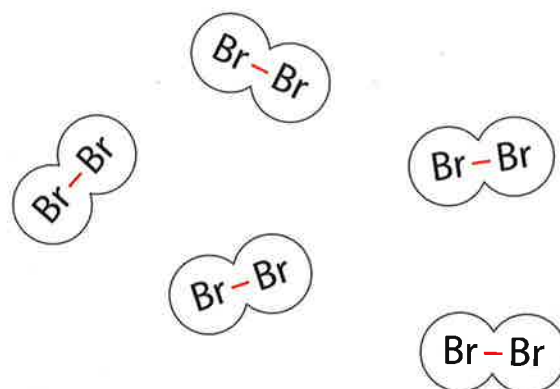


Figure 4.70 Gaseous bromine. Intramolecular forces (covalent bonds) are still present, but the intermolecular forces have been overcome.

How London forces arise

London forces are temporary (instantaneous) dipole–induced dipole interactions.

Consider liquid argon. The electrons in an atom are in constant motion, and at any one time they will not be symmetrically distributed about the nucleus. This results in a temporary (instantaneous) dipole in the atom, which will induce an opposite dipole in a neighbouring atom. These dipoles will attract each other so that there is an attractive force between atoms (Figure 4.71). Although the dipoles are constantly disappearing and reappearing, the overall force between the argon atoms is always attractive because a dipole always induces an opposite one.

In general, London forces get stronger as the number of electrons in molecules increases. As the number of electrons increases, the relative molecular mass also increases, and we normally talk about 'an increase in the strength of London forces as the relative molecular mass increases'.

A clear correlation between boiling point and relative molecular/atomic mass can be seen down group 17 (blue line) and down group 18 (red line) in Figure 4.72.

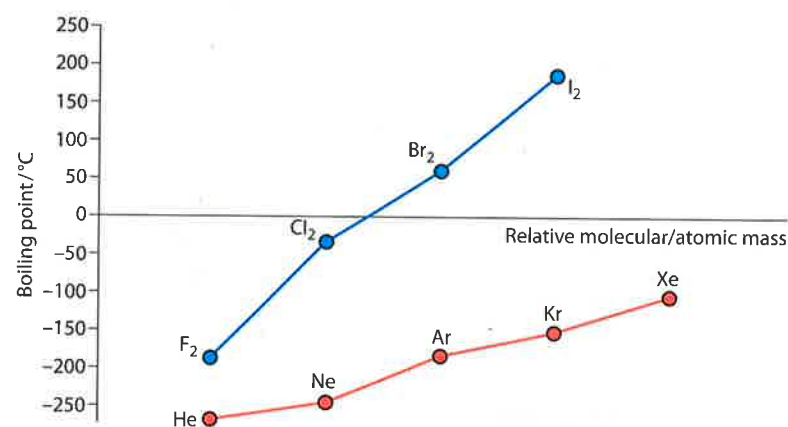


Figure 4.72 Variation in boiling points of elements in groups 17 and 18.

Consider group 17: fluorine (M_r 38.00) is a gas at room temperature, but iodine (M_r 253.80) is a solid. This is because there are more electrons in an iodine molecule, and the atoms making up the molecule are larger. More electrons means that the temporary dipoles will be larger with more electrons moving around. The larger atoms in the molecule means that the outer electrons will be less strongly held, so the molecule is more polarisable, and therefore the induced dipoles will be larger.

Care must be exercised when using this rule of thumb. If the above data for group 17 and group 18 are plotted together against relative molecular mass (relative atomic mass for group 18) we get the graph shown in Figure 4.73, which does not show a clear correlation.

As the length (and so the relative molecular mass) of a hydrocarbon chain increases, so do the boiling points – butane (C_4H_{10}) has a higher boiling point than ethane (C_2H_6) (Figure 4.74). A higher boiling point

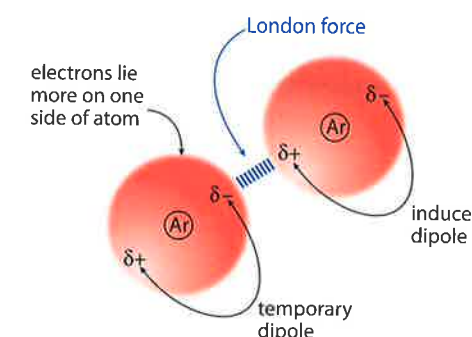


Figure 4.71 The origin of London forces.

In general, London forces get stronger as the relative molecular mass increases.

Comparisons are most useful when comparing similar substances – for instance, the elements within a group or a series of similar compounds.

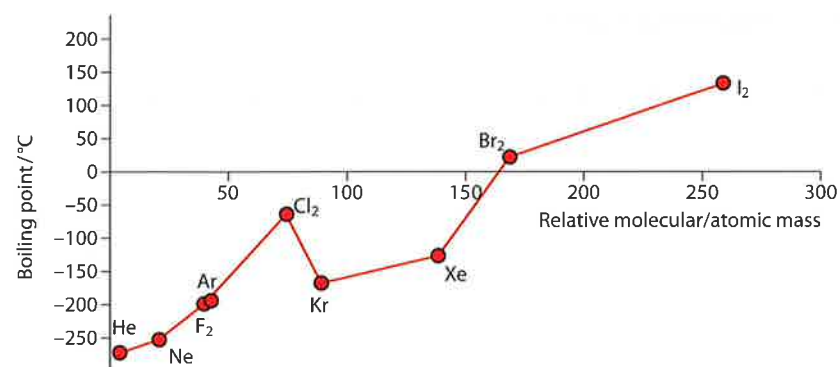


Figure 4.73 Variation in boiling point in groups 17 and 18 with M_r/A_r .

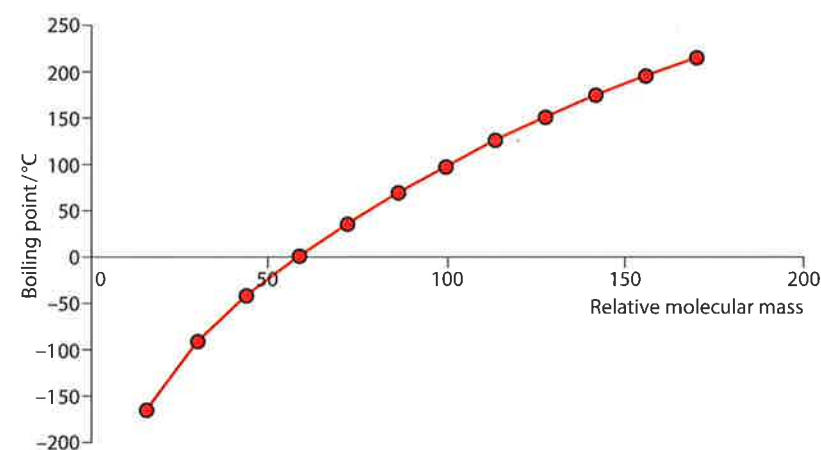


Figure 4.74 Boiling points of alkanes.

means that the London forces between molecules are stronger. The forces between the molecules are stronger because there are more atoms, and therefore more electrons, present in butane than in ethane and also more points of contact between the chains.

The effect of polar molecules

Because of the electronegativity difference between H and Cl, H-Cl molecules are polar.

London forces are present between the molecules in HCl(l) but, because of the polarity of the molecules, there are also other intermolecular forces present (Figure 4.75). These are called **permanent dipole-permanent dipole** interactions, or usually just **dipole-dipole** attractions.

The intermolecular forces between molecules which are polar (permanent dipole-permanent dipole interactions as well as London forces) are stronger than those between non-polar molecules (only London forces), all other things being equal.

In general, all other things being equal, these permanent dipole interactions would be expected to cause melting points and boiling points to be higher for polar molecules.

If we compare propane and ethanal (Table 4.11), both have a relative molecular mass of 44 and therefore the strength of London forces should

be similar. However, ethanal is a polar molecule and has dipole-dipole interactions as well as London forces. The intermolecular forces between molecules of ethanal are stronger than those between propane molecules and ethanal has a significantly higher boiling point (more energy must be supplied to overcome the forces between molecules).

Molecule	Lewis structure	M_r	Boiling point / °C
propane	$\begin{array}{c} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & \\ \text{H} & \text{H} & \text{H} \end{array}$	44	-42
ethanal	$\begin{array}{c} \text{H} & & \text{O} \\ & & // \\ \text{H}-\text{C}-\text{C} \\ & & \backslash \\ \text{H} & & \text{H} \end{array}$	44	21

Table 4.11 Comparing ethanal and propane.

A similar situation is seen when we compare Br₂ with ICl (Table 4.12).

Compound	M_r	Boiling point / °C
Br ₂	159.80	59
ICl	162.35	100

Table 4.12 Comparing bromine and iodine(I) chloride.

The relative molecular masses of these two compounds are very similar, and so the strengths of the London forces are similar. However, ICl is polar (Cl is more electronegative than I), whereas Br₂ is non-polar. The intermolecular forces are stronger in ICl because of the permanent dipole-permanent dipole interactions. Stronger intermolecular forces means that the boiling point of ICl is higher than that of Br₂.

That we simply cannot say that polar molecules have stronger intermolecular forces and higher boiling points than non-polar molecules can be seen if we compare Br₂ with three other interhalogen compounds (Table 4.13).

Compound	M_r	Boiling point / °C	Polar / non-polar?
Br ₂	159.80	59	non-polar
ClF	54.45	-100	polar
BrF	98.90	20	polar
ClBr	115.35	5	polar

Table 4.13 Comparing bromine with interhalogen compounds.

Br₂ is the only molecule here that is non-polar, but it has the highest boiling point as a result of its highest relative molecular mass and, therefore, strongest London forces.

If molecules with similar relative molecular masses are compared, polar molecules have higher melting and boiling points than non-polar molecules.

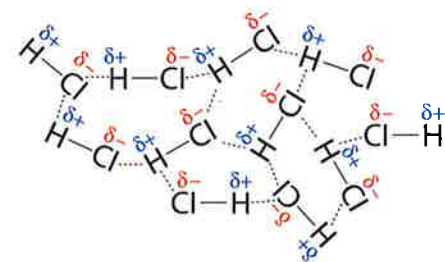


Figure 4.75 Permanent dipole-permanent dipole interactions exist between molecules. These are shown in purple.

All other things being equal – this basically means that we should compare compounds with relative molecular masses as similar as possible.

Extension

Explain why BrF has a higher boiling point than ClBr, despite ClBr having the higher relative molecular mass.

Extension

Comparison of *cis*- and *trans*-1,2-dichloroethene

Cis-1,2-dichloroethene and *trans*-1,2-dichloroethene are *cis-trans* isomers – they differ only in the orientation of the Cl atoms about the C=C (Figure 4.76). (This will be discussed in Topic 10.)

Both molecules have the same relative molecular mass and are identical, except that one is polar and the other is not. The difference between the boiling points is then solely due to the permanent dipole–dipole interactions in the *cis* form.

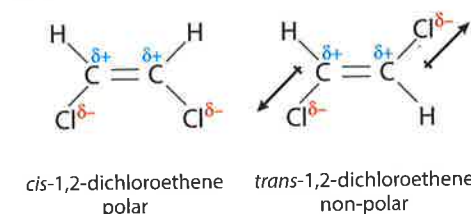


Figure 4.76 *Cis*- and *trans*-1,2-dichloroethene.

Hydrogen bonding

The third type of intermolecular force that we will examine is hydrogen bonding. **Hydrogen bonding** influences many properties of substances – it is responsible for ice floating on water, it is the force between strands of DNA, it helps maintain the 3D structure of proteins, it is the reason that ethanol is soluble in water. It could be argued that hydrogen bonding is the reason why life on Earth exists as we know it!

The origin of hydrogen bonding

Table 4.14 and Figure 4.77 compare the boiling points of the hydrides of group 16 elements.

Group 16 hydride	Boiling point/°C
H ₂ O	100
H ₂ S	–60
H ₂ Se	–41
H ₂ Te	–4

Table 4.14 Boiling points of some hydrides.

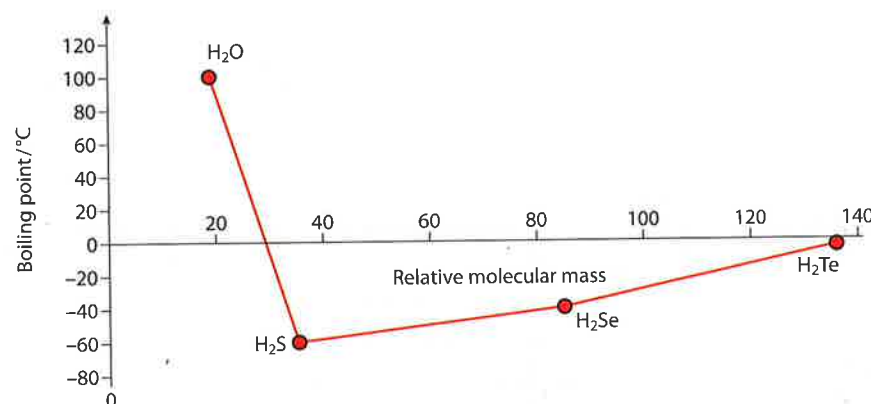


Figure 4.77 Boiling points of group 16 hydrides.

The boiling point increases from H₂S to H₂Te, as would be expected from the increase in the strength of London forces as the relative molecular mass increases.

H₂O has, however, a much higher boiling point than would be expected from its relative molecular mass. This suggests that there must be intermolecular forces other than London forces between H₂O molecules and that these intermolecular forces are stronger than the London forces. These extra intermolecular forces between H₂O molecules are called **hydrogen bonds**. A hydrogen bond between two water molecules is shown in Figure 4.78.

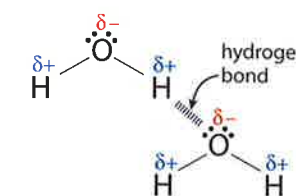


Figure 4.78 A hydrogen bond between two water molecules. The hydrogen bond is the dashed purple line between the lone pair of a δ^- oxygen on one molecule and the δ^+ hydrogen on the other molecule.

It is important to realise that, although hydrogen bonding is the strongest of the intermolecular forces, it is much weaker than covalent bonding.

Hydrogen bonding occurs between molecules when a very electronegative atom (N, O, F) is joined to a hydrogen atom in the molecule. The electronegative atom withdraws electron density from the hydrogen, polarising the bond such that there is a strong interaction between the δ^+ hydrogen and the δ^- atom (N, O, F) on the other molecule.

The hydrogen bonding between ammonia molecules and hydrogen fluoride molecules is shown in Figure 4.79.

We can work out whether there will be hydrogen bonding between molecules simply by looking at whether the molecule contains N/O/F joined directly to a hydrogen atom (Table 4.15).

Hydrogen bonding between molecules	No hydrogen bonding between molecules
HF	HCl
H ₂ O	H ₂ S
NH ₃	PH ₃
CH ₃ CH ₂ OH	CH ₃ OCH ₃
CH ₃ CH ₂ NH ₂	CH ₃ CH ₂ F
Hydrogen bonding between molecules, because there is an H joined directly to an N, O or F atom	No hydrogen bonding between molecules, because H is not joined to N, O or F

Table 4.15 Hydrogen bonding or no hydrogen bonding?

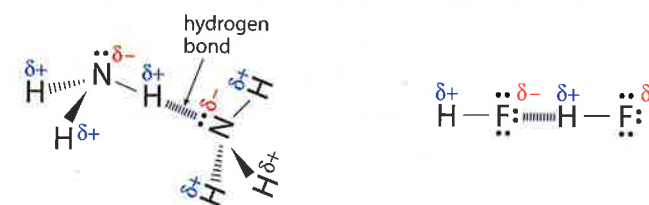


Figure 4.79 Hydrogen bonding between ammonia and hydrogen fluoride molecules.

Extension

There is more to hydrogen bonding than just an electrostatic interaction between dipoles. When H is attached to a very electronegative atom, the electron density is pulled away strongly from the H. There is then an interaction between the electron density of the lone pair on N, O or F in one molecule and the H nucleus in a different molecule. There is thus a directional component to hydrogen bonds. If the interaction were purely dipole–dipole then Cl, with the same electronegativity as N, would also be expected to participate in hydrogen bonding – but it does not. This could be explained by the higher energy and more diffuse lone pair on the Cl not interacting effectively with the H.

The requirements for hydrogen bonding are that the H atom is attached to a very electronegative atom – N, O or F – which possesses at least one lone pair of electrons.

Hydrogen bonding can influence the solubility of substances in water, and often molecules that are able to hydrogen bond are soluble in water – this will be discussed later.

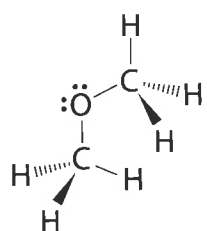


Figure 4.80 The structure of CH_3OCH_3 .

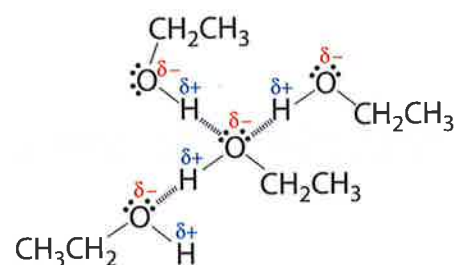


Figure 4.81 Hydrogen bonding in ethanol.

cis-trans isomerism is discussed in Topic 10.

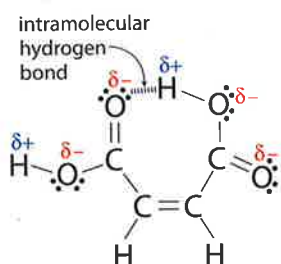
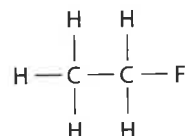


Figure 4.82 Intramolecular hydrogen bonding in *cis*-but-2-ene-1,4-dioic acid.

There is no hydrogen bonding between molecules of $\text{CH}_3\text{CH}_2\text{F}$ because the H is not joined directly to an F atom:



CH_3OCH_3 is an ether with the structure shown in Figure 4.80. It is a polar molecule, but there is no hydrogen bonding between molecules.

The hydrogen bonding between some molecules of ethanol is shown in Figure 4.81.

Hydrogen bonding within molecules

Consider the *cis* and *trans* forms of butenedioic acid shown in Table 4.16.

<i>cis</i> -but-2-ene-1,4-dioic acid (maleic acid)	<i>trans</i> -but-2-ene-1,4-dioic acid (fumaric acid)
melting point: 130°C	melting point: 287°C

Table 4.16 The influence of intramolecular hydrogen bonding within molecules.

The *cis* form has a lower melting point because as well as intermolecular hydrogen bonding (Figure 4.82). This means that there is less hydrogen bonding between molecules and that the intermolecular forces are weaker than in the *trans* form. The *trans* form participates in only intermolecular hydrogen bonding, because the COOH groups are further away from each other – the intermolecular forces are therefore stronger in the *trans* form.

Melting points and boiling points

Only intermolecular forces are broken when covalent molecular substances are melted or boiled – covalent bonds are **not** broken.

We have looked at several factors that influence the strength of intermolecular forces, and hence the melting and boiling points of covalent substances. Now let us consider all the above points together with some examples.

The stronger the intermolecular forces, the more energy must be supplied to break them and the higher the boiling point. Differences in melting and boiling points are sometimes explained using this idea about intermolecular forces of attraction:

London < permanent dipole–dipole < hydrogen bonding
WEAKEST → STRONGEST

However, London forces are present between all molecules and, in some substances, can provide a higher contribution to the intermolecular forces than dipole–dipole interactions – it is therefore important to consider substances with similar relative molecular masses. Table 4.17 summarises the influence of the type of intermolecular force on the boiling point of substances.

Type of substance	Intermolecular forces
substances containing H bonded to N, O or F	hydrogen bonding permanent dipole–dipole London forces
polar substances	permanent dipole–dipole London forces
non-polar substances	London forces

Table 4.17 If relative molecular masses are approximately equal, then the boiling points usually change in the order shown.

Worked examples

4.1 Arrange sulfur, chlorine and argon in order of increasing boiling point and explain your order.

Sulfur, chlorine and argon are all non-polar substances and therefore the only intermolecular forces are London forces. Any difference between these substances is due to the strength of London forces, which is affected by relative molecular mass (relative atomic mass for argon). Sulfur forms S_8 molecules with a relative molecular mass of 256.56; Cl_2 has a relative molecular mass of 70.90; and Ar has a relative atomic mass of 39.95. Therefore the boiling point of sulfur would be expected to be highest because S_8 has a higher relative molecular mass and therefore stronger London forces than Cl_2 and Ar. More energy is required to overcome the intermolecular forces in sulfur than the intermolecular forces in chlorine and the interatomic forces in Ar. Chlorine would be expected to have a higher boiling point than Ar, again due to the greater mass and the stronger London forces. So, the order of increasing boiling points is argon < chlorine < sulfur.

The actual boiling points for these substances are:

Sulfur: 445°C Chlorine: –34°C Argon: –186°C

4.2 Compare the boiling points of propane ($\text{CH}_3\text{CH}_2\text{CH}_3$), methoxymethane (CH_3OCH_3) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$).

Let us compare the relative molecular masses of these substances:

$\text{CH}_3\text{CH}_2\text{CH}_3$: 44.11 CH_3OCH_3 : 46.08 $\text{CH}_3\text{CH}_2\text{OH}$: 46.08

The relative molecular masses are all very similar and therefore the strengths of the London forces are going to be similar.

The next thing we can look at is whether any of the molecules are polar:

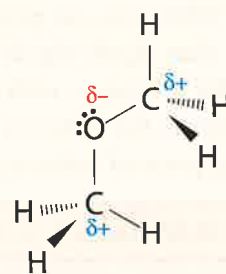
$\text{CH}_3\text{CH}_2\text{CH}_3$: non-polar CH_3OCH_3 : polar $\text{CH}_3\text{CH}_2\text{OH}$: polar

Relative molecular mass – generally substances with higher relative molecular masses have higher melting points and boiling points due to stronger London forces.

The presence of the very electronegative O atom in CH_3OCH_3 and $\text{CH}_3\text{CH}_2\text{OH}$ means that these substances are polar. $\text{CH}_3\text{CH}_2\text{CH}_3$ is the only non-polar molecule and will have the lowest boiling point because the only forces between molecules are London forces.

CH_3OCH_3 and $\text{CH}_3\text{CH}_2\text{OH}$ are both polar and have the same relative molecular mass, but $\text{CH}_3\text{CH}_2\text{OH}$ has the higher boiling point because it has an H joined to an O, and therefore there is also hydrogen bonding between molecules.

Hydrogen bonding in $\text{CH}_3\text{CH}_2\text{OH}$ is a stronger intermolecular force than the permanent dipole interactions in CH_3OCH_3 ; therefore the intermolecular forces are stronger between molecules of $\text{CH}_3\text{CH}_2\text{OH}$ than between molecules of CH_3OCH_3 .



The boiling points of these compounds are:

$\text{CH}_3\text{CH}_2\text{CH}_3$: -42°C CH_3OCH_3 : -25°C $\text{CH}_3\text{CH}_2\text{OH}$: 78°C

? Test yourself

8 Arrange the following sets of molecules in order of increasing boiling point (lowest first):

- | | | |
|---|---|---|
| a CH_4 | CCl_4 | CF_4 |
| b NH_3 | PH_3 | AsH_3 |
| c NH_3 | N_2H_4 | CH_4 |
| d CH_3OH | CH_3F | C_2H_4 |
| e H_2O | H_2S | H_2O_2 |
| f $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ | $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ |
| g N_2 | F_2 | HF Ne |

9 Arrange the following sets of substances in order of increasing boiling point:

- | | | | |
|-----------------------------|---------------------------------|------------------------|---|
| a NaCl | SiCl_4 | CCl_4 | HCl |
| b Br_2 | HBr | CaBr_2 | PBr_3 |
| c C_4H_{10} | $\text{C}_3\text{H}_7\text{OH}$ | C_3H_8 | $\text{CH}_3\text{CH}_2\text{COOH}$ $\text{C}_4\text{H}_9\text{OH}$ |
| d SO_2 | SiO_2 | CO_2 | |

Solubility

It is often said, when referring to solubility, that 'like dissolves like'. What this means is that:

generally a substance will dissolve in a solvent if the intermolecular forces in the solute and solvent are similar.

Solubility is discussed here from the point of view of energy, but entropy changes (discussed in Topic 5) must also will be considered.

Whether or not a substance dissolves depends (in part) on how much energy is needed to overcome intermolecular forces in the solvent and solute and then how much energy is released, to pay back this energy, when intermolecular forces are formed between solvent and solute molecules in the solution.

Pentane is readily soluble in hexane but insoluble in water

The amount of energy required to overcome the London forces in pure hexane and pure pentane is paid back when London forces are formed between the molecules of hexane and pentane (Figure 4.83). Pentane does not dissolve in water because there is hydrogen bonding between water molecules. If pentane were to dissolve in water there would be London forces between water molecules and pentane. The energy released if London forces were to form between water molecules and pentane molecules would not pay back the energy required to break the hydrogen bonds between water molecules, because hydrogen bonds are stronger than London forces (Figure 4.84).

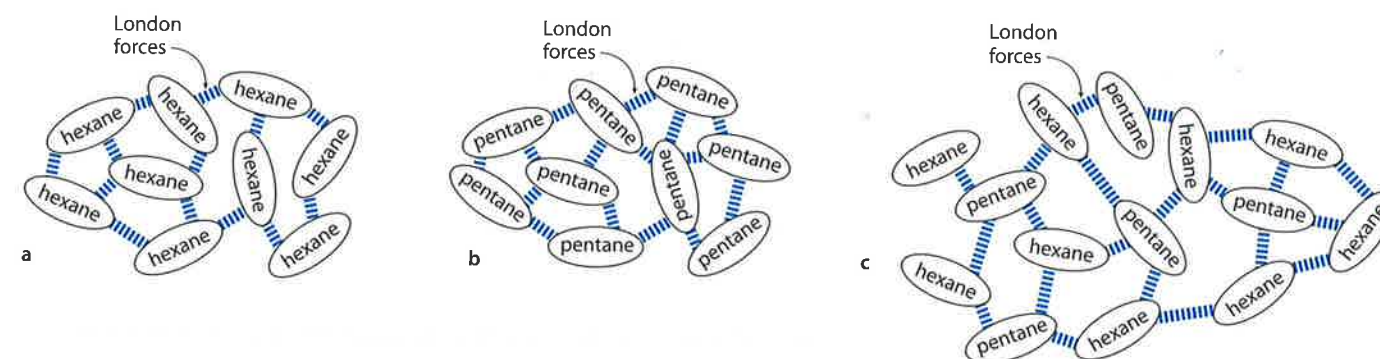


Figure 4.83 a There are London forces between hexane molecules; b there are London forces between pentane molecules; c there are London forces between hexane and pentane molecules when pentane dissolves in hexane.

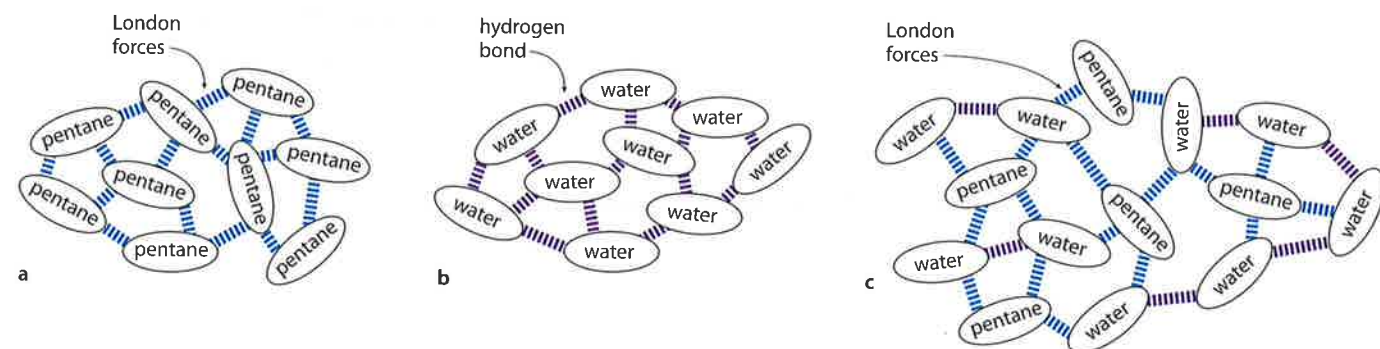


Figure 4.84 a There are London forces between pentane molecules; b there are hydrogen bonds between water molecules; c pentane does not dissolve in water because only London forces would be formed between pentane and water molecules.

Substances that are able to participate in hydrogen bonding will generally be soluble in water, because they are able to hydrogen bond to the water.

Ethanol is soluble in water

Ethanol ($\text{C}_2\text{H}_5\text{OH}$) is very soluble in water, because ethanol is able to hydrogen bond to the water (Figure 4.85). The hydrogen bonding between water molecules and ethanol molecules in the solution releases energy and pays back the energy to break the hydrogen bonds in pure water and pure ethanol.

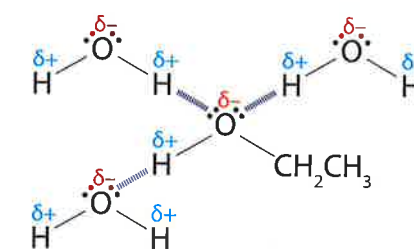


Figure 4.85 Hydrogen bonding between water and ethanol.

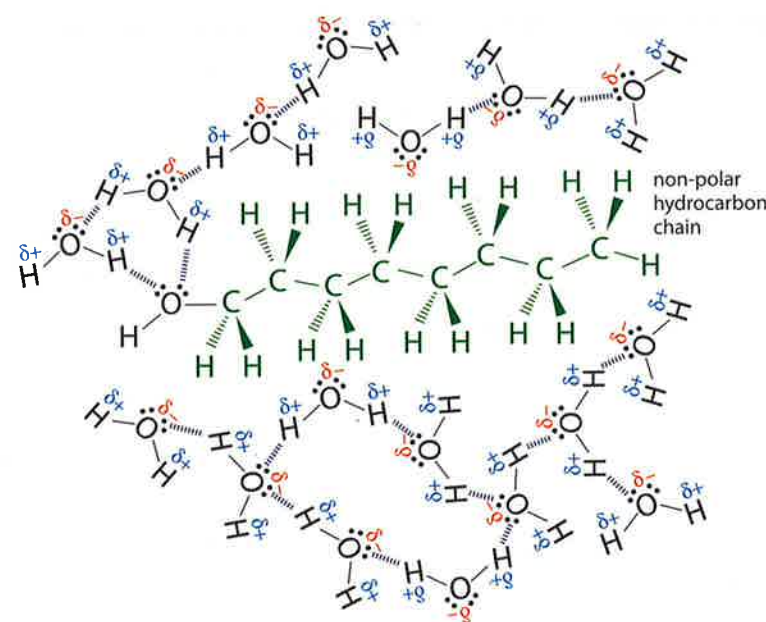


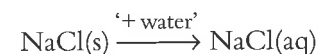
Figure 4.86 The hydrocarbon chain in octan-1-ol prevents hydrogen bonding between water molecules on either side.

Longer chain alcohols become progressively less soluble in water

Octan-1-ol is insoluble in water. Although there is some hydrogen bonding between the O-H group of the alcohol and water molecules, the long hydrocarbon chain prevents water molecules on either side from hydrogen bonding to each other (Figure 4.86). Energy is needed to break the hydrogen bonds between the water molecules, but this is not paid back as only London forces form between the water molecules and the hydrocarbon part of the molecule.

Dissolving ionic substances

Consider the dissolving of sodium chloride:



The aqueous solution contains aqueous ions ($\text{Na}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$). Ion-dipole interactions form between the water and the ions (Figure 4.87). Energy is required to overcome the electrostatic forces in the ionic lattice but energy is released when hydrated ions are formed. If the energy released when the hydrated ions are formed is comparable to the energy required to break apart an ionic lattice then the substance is generally soluble.

Ionic substances are not usually soluble in non-polar solvents such as hexane because the interactions between the ions and the hexane molecules would be weak London forces. Sodium chloride is insoluble in hexane because the energy released when a sodium ion or a chloride ion is surrounded by hexane molecules (solvated) is not enough to pay back the energy required to break apart the lattice.

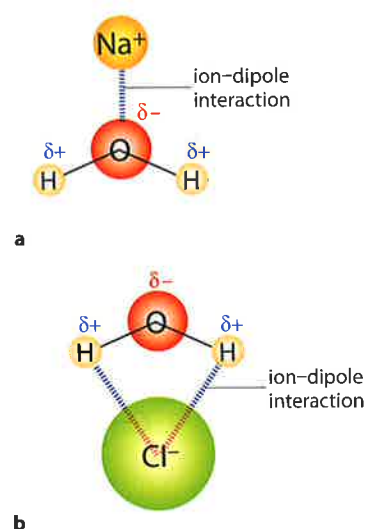


Figure 4.87 Ion-dipole interactions
a between water and sodium ions;
b between water and chloride ions.

Comparison of the physical properties of ionic and covalent molecular substances

Table 4.18 shows a comparison of the physical properties of ionic and covalent molecular substances.

Ionic	Covalent molecular
usually solids with high melting points	may be solid, liquid or gas at room temperature
strong electrostatic forces in the giant lattice structure must be overcome	only intermolecular forces are overcome when the substances are melted or boiled; intermolecular forces are weaker than the electrostatic forces in an ionic lattice; no covalent bonds are broken when covalent molecular substances are melted or boiled
non-volatile	many are volatile
strong electrostatic forces in the lattice	weak intermolecular forces
many are soluble in water and usually insoluble in organic solvents	not usually soluble in water but soluble in organic solvents
strong interactions between the ions and the polar water molecules provide the energy to break apart the lattice structure	substances dissolve when intermolecular forces in the solvent and solute are similar; molecules that are able to hydrogen bond to water are usually soluble in water
do not conduct electricity in the solid state but do conduct when molten or in aqueous solution, because of mobile ions	do not conduct electricity in any state
ions not free to move in solid state because they are held tightly in the lattice structure; ions free to move around when molten or dissolved in water	no ions or free electrons present; some substances, such as HCl, dissolve in water with ionisation – HCl(aq) conducts electricity

Table 4.18 The physical properties of ionic and covalent molecular substances compared.

Nature of science

Careful observation and collection of data are important in development of theories. Covalent molecular substances can be liquids or solids which indicates that there must be some force between molecules that holds them in the liquid/solid state (London forces, hydrogen bonds etc.). Calculation indicates that this attraction must be a lot stronger than the gravitational attraction between molecules.

Theories can be used to make predictions. An understanding of the structure and bonding of substances can be used to make predictions about the melting point and solubility of a new substance.

Patterns are important in science but exceptions (such as the boiling point of water) to these often lead to advances in our theoretical understanding. Careful observations from experimental work over many years eventually led to the idea of the hydrogen bond. More and more sophisticated models for the hydrogen bonding in substances are still being developed.

? Test yourself

10 Arrange the following sets in order of solubility in water (least soluble first):

- | | | |
|--------------------------|---------------------------|------------------------------------|
| a NaCl | C_6H_{12} | $\text{C}_5\text{H}_{11}\text{OH}$ |
| b CH_3Cl | CaCl_2 | CH_4 |

Learning objectives

- Describe the structure of, and bonding in, metals
- Explain some of the properties of metals in terms of structure and bonding
- Explain what is meant by an 'alloy' and how the properties of alloys are different from those of pure metallic elements

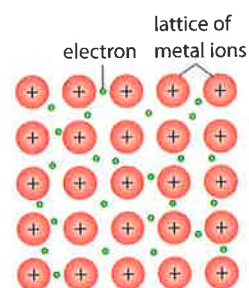


Figure 4.88 A metallic structure. This is a giant structure – there are no individual molecules.

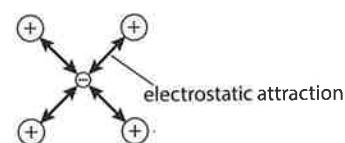
Metals contain a regular lattice arrangement of positive ions surrounded by a 'sea' of delocalised electrons.

Metallic elements have relatively low ionisation energies and so form positive ions more easily than non-metals.

Metallic bonding is the electrostatic attraction between the positive ions in the lattice and the delocalised electrons.

4.5 Metallic bonding

The structure of a typical metal is shown in Figure 4.88. The electrons are described as **delocalised** because they do not belong to any one metal atom but, rather, are able to move throughout the structure. The metallic bond is thus electrostatic in nature, resulting from the attraction between the positive metal ions and the negatively charged delocalised electrons:



Each electron is attracted by all the positive ions in the structure, so the whole lattice is held together.

The melting points of sodium and magnesium are 98°C and 649°C, respectively. There are several reasons why magnesium has a higher melting point than sodium. The first is that magnesium forms a 2+ ion compared with sodium, which forms a 1+ ion (Figure 4.89). This means that the electrostatic attraction between the ions and the delocalised electrons is stronger in magnesium.

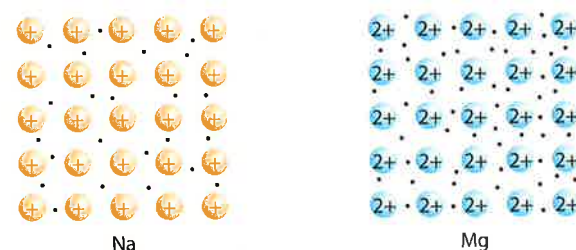


Figure 4.89 Metallic bonding in sodium and magnesium.

The second reason is that the Mg^{2+} ion (65 pm) is smaller than the Na^+ ion (98 pm), and therefore the delocalised electrons are closer to the nucleus of the positive ion in magnesium and are more strongly attracted.

A third reason why magnesium has a higher melting point than sodium is that there are two delocalised electrons per atom in magnesium. Therefore there will be stronger electrostatic attractions between the ions and the delocalised electrons.

Some other physical properties of metals are shown in Table 4.19.

Physical property	Comment
lustrous	shiny, when freshly scratched/cut
good conductors of electricity	e.g. copper is used in making electrical wires; conduction decreases as temperature increases
good conductors of heat	although the best conductor is diamond
ductile	may be drawn into wires
malleable	may be hammered into shape – many uses arise from the ability to easily shape metals, e.g. making car bodies

Table 4.19 Some physical properties of metals.

Metals conduct electricity because the delocalised electrons are free to move around.

Metals are **malleable/ductile** because of the non-directionality of the bonding. The metal ions in the lattice attract the delocalised electrons in all directions. So, when two layers slide over each other (Figure 4.90), the bonding in the resulting structure is exactly the same as in the original. This can be compared with ionic solids (Figure 4.91), which are brittle, as displacement of one layer relative to the other results in like charges repelling each other.



Metals such as iron have a wide range of uses, such as in construction (bridges, cars, etc.). Iron is usually used in the form of steel, an alloy of iron and carbon. The fact that mild steel is malleable makes it ideal for the construction of car bodies (and for crushing them afterwards!).

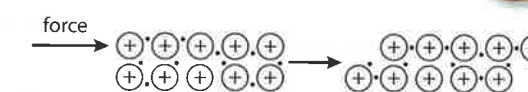


Figure 4.90 Ductility.

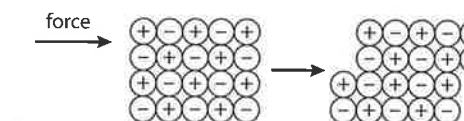


Figure 4.91 Brittleness.

Extension

Actually, metals are more ductile than this simple picture of planes sliding over each other would predict. Ductility is better explained by the movement of dislocations through the lattice.

Alloys are homogeneous mixtures of two or more metals, or of a metal with a non-metal.

Alloys

The majority of metals we come across in everyday life are alloys rather than pure metals. Steel, an alloy of iron and carbon, is used much more than pure iron. Other examples of alloys include brass (Cu and Zn), bronze (Cu and Sn) and pewter (Sn, Sb and Cu).

Alloys tend to be stronger and stiffer than pure metals and often combine the desirable properties of the different metals involved. So, aluminium is a light (low density) metal but it is not strong enough to be used in airplane manufacture until it is alloyed with copper (and smaller amounts of magnesium and manganese) to produce duralumin.

The reason why alloys are stronger than pure metals can be explained in terms of structure. At the simplest level, we can imagine that a differently sized atom will prevent planes of metal atoms sliding over each other (Figure 4.92).

Some properties of alloys are not desirable – e.g. aluminium alloys are more susceptible to corrosion than the pure metal, and the electrical conductivity of copper is reduced by alloying with other metals.

Nature of science

Scientific theories can be used to explain natural phenomena. Careful observation established that metals have different properties to ionic and covalent substances – these properties can be explained in terms of a simple model involving a sea of delocalised electrons and non-directional bonding.



Test yourself

11 Arrange the following sets in order of increasing melting point (lowest first):

- a Na Li K
b Al Mg Na

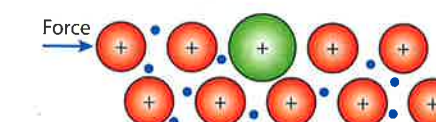


Figure 4.92 The introduction of a larger atom makes it more difficult for the planes of atom/ions to slide over each other – so alloys tend to be stronger and stiffer than pure metals.

Learning objectives

- Use the concept of formal charge to decide between alternative Lewis structures
- Understand that there are exceptions to the octet rule
- Use VSEPR to predict the shapes of molecules and ions with five or six electron domains
- Explain the formation of sigma and pi bonds in molecules
- Predict the number of sigma and pi bonds in molecules
- Use the concepts of resonance and delocalisation to explain the bonding in molecules and ions
- Explain the absorption of different frequencies of UV light by oxygen and ozone
- Describe the mechanism of CFC and NO_x catalysed ozone depletion

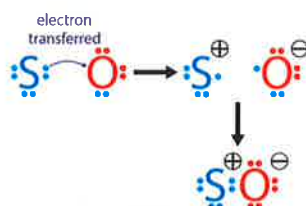


Figure 4.93 Formation of a coordinate covalent bond results in a formal charge on each atom.

Formal charge closest to zero means that there will be the most even distribution of charge in the molecule/ion.

Formal charges closest to zero will generally result in a more stable structure because the separation of charge in a structure requires energy.

4.6 Covalent bonding and electron domains and molecular geometries (HL)

Formal charge and alternative Lewis structures

We have already seen (page 134) that it is possible to draw more than one Lewis structure for compounds such as SO₂. In this section we will use the concept of **formal charge** to select the best Lewis structure when more than one is possible, that is, the one that provides the best representation of the structure of the actual molecule.

'Formal charge' is the charge that an atom in a molecule would have if we assume that the electrons in a covalent bond are equally shared between the atoms that are bonded – i.e. we assume that all atoms have the same electronegativity. Atoms in a molecule can gain a formal charge either if a coordinate covalent bond is formed or if the molecule has an overall charge (it is an ion).

A coordinate covalent bond is formed when both shared electrons come from the same atom. When the bond forms, it can be imagined that the donor atom gives an electron to the receiver atom, so that each now has one electron, which can be used to form a covalent bond. Because the donor atom has given away an electron, it now has a formal charge of 1+ and the receiver atom has a formal charge of 1– (Figure 4.93).

The formal charge (FC) on an atom can be worked out from the Lewis structure using the formula:

$$\text{FC} = (\text{number of valence electrons in the uncombined atom}) - \frac{1}{2} (\text{number of bonding electrons}) - (\text{number of non-bonding electrons})$$

In general, the preferred Lewis structure is the one in which the formal charges are closest to zero.

The calculations of the formal charges in the two possible structures for SO₂ are shown in Table 4.20.

Structure A (no expansion of octet)	Structure B (expansion of octet)
S FC = 6 – (½ × 6) – 2 = 1+	S FC = 6 – (½ × 8) – 2 = 0
O1 FC = 6 – (½ × 4) – 4 = 0	O1 FC = 6 – (½ × 4) – 4 = 0
O2 FC = 6 – (½ × 2) – 6 = 1–	O2 FC = 6 – (½ × 4) – 4 = 0

Table 4.20 Calculating formal charges in SO₂.

The formal charge on the sulfur atom in structure A was worked out as follows:

- An unbonded S atom has 6 electrons in its outer shell because it is in group 16; there are 6 electrons involved in covalent bonds (S forms three bonds); and there is one lone pair – two non-bonding electrons
- $\text{FC} = (\text{number of valence electrons in the uncombined atom}) - \frac{1}{2} (\text{number of bonding electrons}) - (\text{number of non-bonding electrons}) = 6 - (\frac{1}{2} \times 6) - 2 = 1+$
- The formal charges on the atoms in SO₂ are shown in Figure 4.94.

It can be seen that structure B is the preferred one because there are no formal charges on the atoms.

Consider the two alternative Lewis structures for the sulfate(VI) ion shown in Figure 4.95. The formal charges are worked out in Table 4.21. There are fewer atoms with a formal charge and the formal charges are closer to zero in structure D and this is the preferred structure. In both cases, the sum of the formal charges is 2–, which is the overall charge on the ion.

Structure C	Structure D
In the first structure, S has not expanded its octet and there are two coordinate covalent bonds. The formal charges are:	In the second structure the S has expanded its octet and there are no coordinate covalent bonds. The formal charges are:
S FC = 6 – ½ × 8 – 0 = 2+	S FC = 6 – ½ × 12 – 0 = 0
O1 FC = 6 – ½ × 2 – 6 = 1–	O1 FC = 6 – ½ × 2 – 6 = 1–
O2 FC = 6 – ½ × 2 – 6 = 1–	O2 FC = 6 – ½ × 4 – 4 = 0
O3 FC = 6 – ½ × 2 – 6 = 1–	O3 FC = 6 – ½ × 2 – 6 = 1–
O4 FC = 6 – ½ × 2 – 6 = 1–	O4 FC = 6 – ½ × 4 – 4 = 0

Table 4.21 Calculating formal charges in SO₄^{2–}.

A similar analysis can be carried out on the phosphate(V) ion, PO₄^{3–}. Two possible Lewis structures and formal charges are shown in Figure 4.96. The formal charges are closer to zero in structure E and this is the preferred structure.

? Test yourself

- 12 Draw alternative Lewis structures with and without an expanded octet on the central atom for each of the following molecules/ions. Then use the concept of formal charge to decide which structure is probably a better representation of the actual structure.

a POCl₃ b ClO₄[–] c XeO₄



Figure 4.94 Formal charges on the atoms in alternative Lewis structures for SO₂.

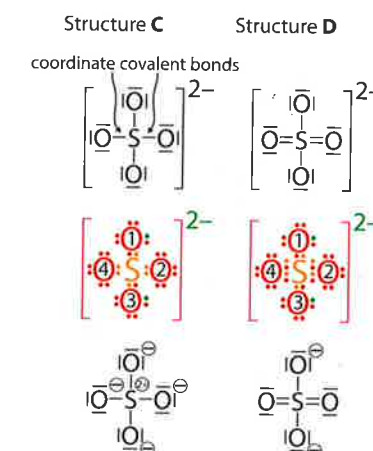


Figure 4.95 Formal charges for SO₄^{2–}.

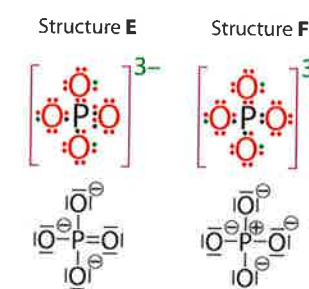


Figure 4.96 Formal charges for PO₄^{3–}.



The concept of formal charge assumes that the bonding in a molecule/ion is purely covalent. The concept of oxidation number, which will be introduced in Topic 9, assumes that the bonding in a molecule/ion is purely ionic. Neither provides a complete picture of the bonding; why do we use them?



Figure 4.97 The Lewis structure of SF_6 .

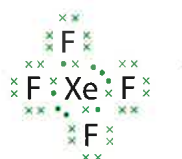


Figure 4.98 The Lewis structure for XeF_4 .

Exceptions to the octet rule

As mentioned previously (Subtopic 4.3), there are some molecules, such as BF_3 , BCl_3 and $\text{BeCl}_2(\text{g})$, in which the central atom has fewer than 8 electrons in its outer shell – and is said to have an **incomplete octet**. We have also met some molecules and ions, e.g. SO_4^{2-} , PO_4^{3-} and SO_2 , for which a structure could be drawn with the central atom having more than eight electrons in its outer shell, – it has **expanded its octet**.

However, for molecules and ions with expanded octets it was always possible to draw structures in which the central atom did not have more than eight electrons in its outer shell if coordinate covalent bonds were used in the Lewis structure instead of double bonds. We will now consider some species in which the central atom is joined to outer atoms with only single bonds – and so the central atom must have an expanded octet. The Lewis structure for sulfur(VI) fluoride, SF_6 , is shown in Figure 4.97. In this structure, the sulfur atom has twelve electrons in its outer shell.

Similarly, in noble gas compounds such as XeF_4 the central atom is usually described as having an expanded octet (Figure 4.98).

For an atom to be able to expand its octet, it must be in period 3 or beyond (periods 4, 5 ...). A period 2 atom cannot expand its octet because the maximum number of electrons in the second shell (main energy level) – the outer shell of a period 2 atom – is 8. For period 3 and beyond, the atoms have d subshells that are available for bonding – so a period 3 atom can have up to 18 electrons in its outer shell (8 + 10 in the 3d subshell). Hence, we can, for example, explain why PF_5 can exist but NF_5 cannot.

Shapes of molecules and ions with five or six electron domains around the central atom

We have already used valence shell electron pair repulsion to explain and predict the shapes of molecules and ions with up to four electron domains (page 138). Here we will extend the technique to include molecules and ions with five or six electron domains.

The basic shapes for five and six electron domains are shown in Table 4.22.

Electron domains	Shape	Diagram	Example
5	trigonal bipyramid		PF_5
6	octahedral		SF_6

Table 4.22 The basic shapes for molecules with five or six electron domains.

PF_5

The Lewis structure and molecular shape of phosphorus(V) fluoride are shown in Figure 4.99.

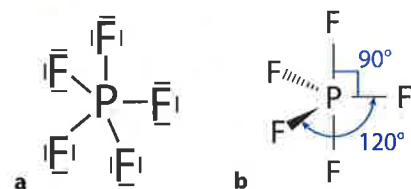


Figure 4.99 a) Lewis structure and b) molecular shape of PF_5 .

Bonding pairs of electrons: 5
Non-bonding pairs of electrons: 0
Electron domains = $5 + 0 = 5$

Because these five electron domains repel each other and take up positions in space to be as far apart as possible, the electrons pairs are distributed in a trigonal bipyramidal arrangement. The shape adopted by the atoms is also trigonal bipyramidal (two triangular-based pyramids on top of each other). It is not possible to arrange five things on the surface of a sphere such that they are evenly spaced from each other, so there are two different bond angles in a trigonal bipyramid.

The positions around the middle plane of a trigonal bipyramid are described as equatorial (Figure 4.100); the positions above and below the central triangle are described as axial.

In a trigonal bipyramid, the axial and equatorial positions are not equivalent. Lone pairs always go in an equatorial position. This applies only to trigonal bipyramidal structures.

SF_4

The Lewis structure and molecular shape of sulfur(IV) fluoride are shown in Figure 4.101.

Bonding pairs of electrons: 4
Non-bonding pairs of electrons: 1
Electron domains: 5

These five electron domains repel each other and take up positions in space to be as far apart as possible – again, the electron pairs are distributed in a trigonal bipyramidal arrangement. One of these electron pairs is a lone pair, and this adopts an equatorial position in a trigonal bipyramid (Figure 4.101b). The molecule is often described as having a 'see-saw' shape. The lone pair causes the other bonding pairs to bend away from it, and a better representation of the shape is shown in Figure 4.101c. It can be seen that the lone pair has a very large influence on the bond angles – more than just a couple of degrees.

Extension

The lone pairs always going in an equatorial position is often discussed in terms of the repulsion between the pairs of electrons. The repulsion between electron pairs at 90° to each other is greater than between pairs at 120° to each other. Having the lone pairs (which cause greater repulsion than bonding pairs of electrons) in equatorial positions limits the number of 90° repulsions to two. Having the lone pairs in axial positions would mean that there would be three 90° repulsions – i.e. greater repulsion overall and a less stable molecule.

An alternative explanation is in terms of the hybridisation of the central atom (see Subtopic 4.7). A trigonal bipyramid involves two different hybridisation schemes – sp^2 for the equatorial positions and pd for the axial positions. An s orbital has lower energy than a p orbital or a d orbital, and therefore if a lone pair occupies an sp^2 orbital it is lower in energy than if it were in a pd orbital. Because a lone pair exists solely on the central atom, this should be in the orbital with the lowest available energy – an sp^2 orbital – in the equatorial position.

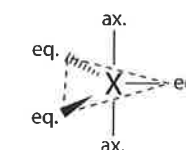


Figure 4.100 Axial and equatorial positions.

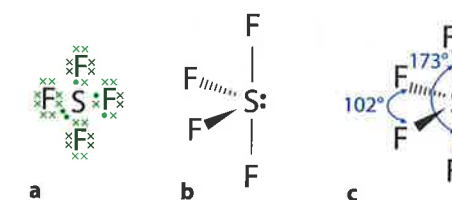


Figure 4.101 Structure of SF_4 : a) Lewis structure; b) the see-saw shape; c) F atoms bend back away from the lone pair.

Exam tip

Care must be exercised here – if you write the angle 102° for the bond angle in your answer it could be marked incorrect, even though it is the correct answer, because it is quite a bit less than 120° .

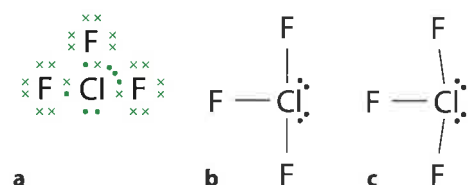


Figure 4.102 Structure of ClF_3 : **a** Lewis structure; **b** T-shaped molecule; **c** F atoms bend back away from the lone pairs.

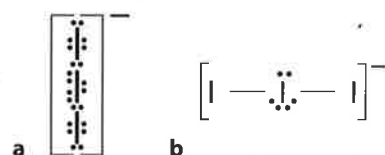


Figure 4.103 Structure of I_3^- : **a** Lewis structure; **b** linear ion.

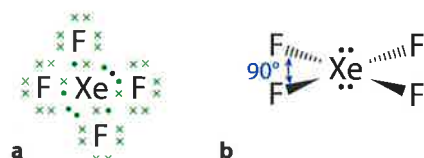


Figure 4.104 Structure of XeF_4 : **a** Lewis structure; **b** square planar molecule.

XeF_4 can be prepared by heating xenon with excess fluorine at high temperature and pressure in a nickel container. It is a white, crystalline solid at room temperature.

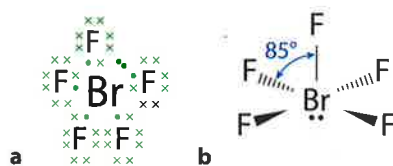


Figure 4.105 Structure of BrF_5 : **a** Lewis structure; **b** slightly distorted square pyramidal molecule.

Electron domains	Bonding pairs	Lone pairs	Basic shape	Actual shape	Examples
5	5	0	trigonal bipyramidal	trigonal bipyramidal	PF_5 , XeO_3F_2
5	4	1	trigonal bipyramidal	see-saw	SF_4 , XeO_2F_2
5	3	2	trigonal bipyramidal	T-shape	BrF_3 , XeOF_2
5	2	3	trigonal bipyramidal	linear	I_3^- , XeF_2
6	6	0	octahedral	octahedral	SF_6 , PF_6^- , XeO_6^{4-} , IO_6^{5-}
6	5	1	octahedral	square pyramidal	SF_5^- , BrF_5 , XeF_5^+ , XeOF_4
6	4	2	octahedral	square planar	XeF_4 , SF_4^{2-}

Table 4.23 The shapes of molecules and ions with more than four electron domains.

ClF_3

The Lewis structure and molecular shape of chlorine(III) fluoride are shown in Figure 4.102.

Bonding pairs of electrons: 3
Non-bonding pairs of electrons: 2
Electron domains: 5

Two of the electron pairs are lone pairs and take up equatorial positions in the trigonal bipyramid (Figure 4.102b). The actual shape adopted by the molecule is usually described as 'T-shaped' (Figure 4.102c). The lone pairs cause the other bonding pairs to bend away from them, therefore a better description of the structure might be 'arrow-shaped'

I_3^-

The Lewis structure and molecular shape of the triiodide ion are shown in Figure 4.103. The ion has three lone pairs and two bonding pairs around the central atom, so the electron pairs are distributed in a trigonal bipyramidal arrangement. The shape is linear, with three lone pairs around the middle of the trigonal bipyramid.

XeF_4

Xenon(IV) fluoride has four bonding pairs and two lone pairs around the central atom. Its Lewis structure and molecular shape are shown in Figure 4.104. The arrangement of electron pairs is octahedral and the two lone pairs take up positions opposite each other to minimise repulsion. The shape adopted by the molecule is described as square planar.

BrF_5

Bromine(V) fluoride has five bonding pairs and one lone pair around the central atom. Its Lewis structure and molecular shape are shown in Figure 4.105. The arrangement of the electron pairs is octahedral and the shape of the molecule is square pyramidal. The lone pair causes the four fluorine atoms on the base of the pyramid to bend away from it slightly due to greater repulsion between a lone pair and a bonding pair than between two bonding pairs (Figure 4.105b).

Table 4.23 summarises the shapes of molecules and ions with five and six electron domains.

? Test yourself

13 Work out the shapes of the following molecules and ions and predict their bond angles:

- | | |
|---|--|
| a BrF_3 | f AsF_6^- |
| b ClF_5 | g TeF_5^- |
| c SO_2Cl_2 (S central atom) | h F_2ClO_2^- (Cl central atom) |
| d SeF_4 | i I_3^+ |
| e XeF_2 | j ICl_2^- |

14 Sort the following molecules into polar and non-polar molecules. For the polar molecules, draw diagrams showing the dipoles.

XeF_6 XeF_4 SF_4 PCl_5 SF_2 SF_6 ClF_5 BrF_3 SOCl_2

Sigma and pi bonds

A covalent bond is formed when two atomic orbitals, each containing one electron, overlap. When these orbitals overlap **head-on**, the bond formed is a normal single bond and is called a **sigma (σ) bond** (Figure 4.106). Another way of describing the formation of the sigma bond is that two s atomic orbitals combine to form a σ molecular orbital (Figure 4.107). Atomic orbitals are found in atoms, but electrons occupy molecular orbitals in molecules. Molecular orbitals, like atomic orbitals, can hold a maximum of two electrons.

The term 'linear combination of atomic orbitals' (LCAO) is used in the syllabus. LCAO is a mathematical approximation that assumes that molecular orbitals can be described as linear combinations (adding or subtracting the wave functions) of the original atomic orbitals. In the context here, the molecular orbitals (sigma and pi bonding orbitals) are formed by adding s and/or p orbitals.

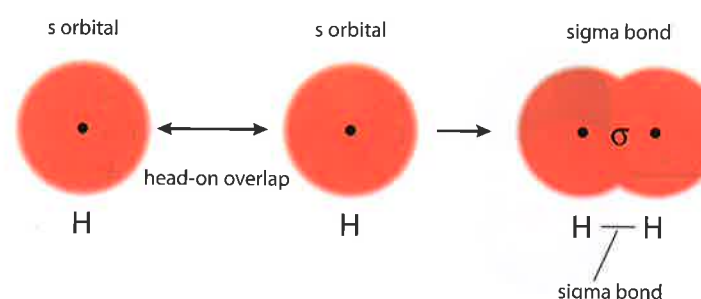


Figure 4.106 The overlap of two s orbitals to form a σ bond.

Extension

When two atomic orbitals combine, two molecular orbitals are formed – one 'bonding' and the other 'antibonding'.

A covalent bond can also be formed when an atomic orbital containing two electrons overlaps with an empty orbital. This is a coordinate covalent bond.

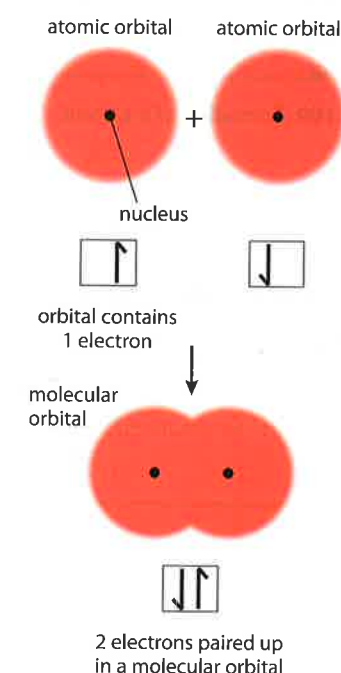


Figure 4.107 The overlap of two s orbitals to form a covalent bond.

'Axial' here refers to the orbitals overlapping head-on, i.e. along an axis.

Sigma bonds result from the axial (head-on) overlap of atomic orbitals. The electron distribution in a sigma bond lies mostly along the axis joining the two nuclei.

Sigma bonds can be formed by the axial overlap of any two orbitals – it can be two p orbitals; an s orbital and a p orbital; an sp^3 hybrid orbital (see Subtopic 4.7) and an s orbital; a d orbital and a p orbital, and so on. Figure 4.108 shows a sigma bond formed from overlap of two p orbitals.

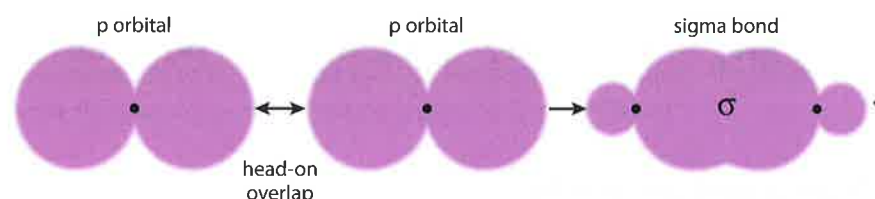


Figure 4.108 Sigma bond formed by head-on overlap of p orbitals.

All covalent bonds (single, double and triple) contain 1 σ bond.

A **pi (π) bond** is formed when two parallel p orbitals overlap side-on (Figure 4.109).

A π bond is formed by the sideways overlap of parallel p orbitals. The electron density in the π bond lies above and below the internuclear axis.

If there are two p orbitals available for bonding on each atom then a triple bond can be formed (Figure 4.110). A triple bond consists of one σ bond and two π bonds.

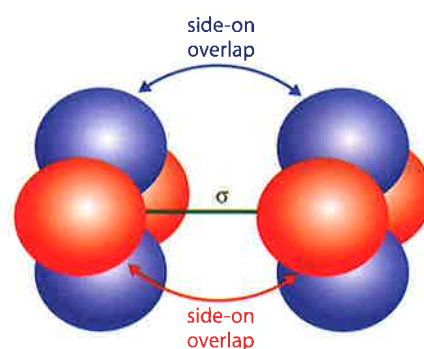


Figure 4.110 A triple bond.

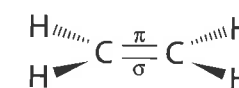
To summarise:

- a single bond consists of a σ bond
- a double bond consists of a σ bond and a π bond
- a triple bond consists of a σ bond and two π bonds.

The bonding in ethene, C_2H_4

When carbon atoms and hydrogen atoms come together to form ethene, sigma bonds are formed between the carbon and hydrogen atoms as shown in Figure 4.111. There are four orbitals (one s and three p) in the outer shell of each carbon atom. Only three orbitals are used in bonding to the other carbon atom and to two hydrogen atoms, so there is a p orbital (containing 1 electron) remaining on each C atom. These p orbitals can overlap **side-on** to form a **pi (π)** bond (Figure 4.112).

A double bond has two components:



That these components are different can be seen from the bond energies in Table 4.24. A C=C bond has less than twice the strength of a C–C single bond, meaning that the π bond in ethene is not as strong as the C–C σ bond. Side-on overlap (π bond) is not as effective as head-on overlap – there is a more direct attraction between the electron pair and the nuclei in a σ bond.

	Bond energy / kJ mol^{-1}
C–C	348
C=C	612

Table 4.24 Bond energies in single and double bonds.

? Test yourself

15 Work out the number of sigma and pi bonds in each of the following:

- | | |
|-----------|----------------|
| a O_2 | g N_2F_2 |
| b N_2 | h CO |
| c BCl_3 | i CH_3CHCH_2 |
| d CO_2 | j $SOCl_2$ |
| e H_2CO | k $HCCCH_3$ |
| f HCN | l H_2SO_4 |

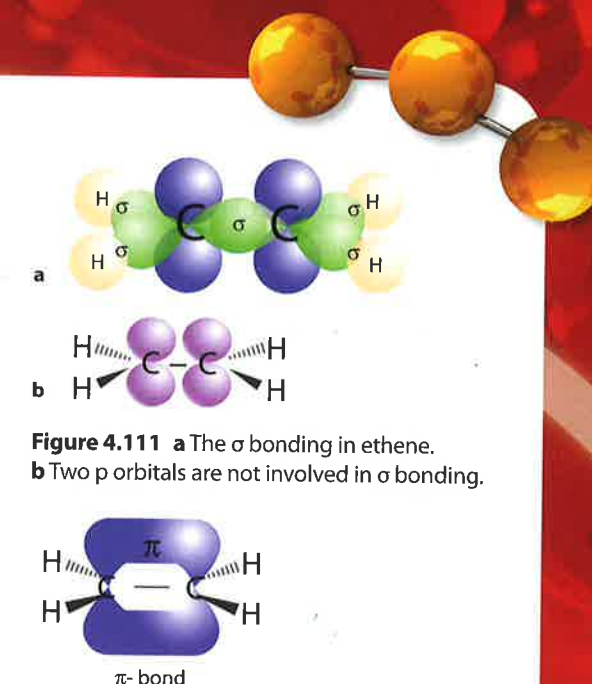


Figure 4.111 a The σ bonding in ethene.
b Two p orbitals are not involved in σ bonding.

Figure 4.112 Bonding in ethene.

Extension

Life is never that simple in chemistry – compare the strength of single and double bonds for O–O and N–N bonds.

Extension

There is one isomer of C_3H_4 that contains two C=C double bonds. Determine the shape of this molecule. Is it planar?

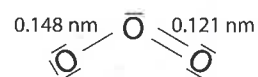


Figure 4.113 The Lewis structure for O_3 with expected bond lengths.



Figure 4.114 Resonance structures for O_3 .

Resonance and delocalisation

The Lewis structure of ozone, O_3 , is shown in Figure 4.113. It would be expected from this structure that there would be one short ($\text{O}=\text{O}$) and one long ($\text{O}-\text{O}$) bond. However, both bond lengths are equal at 0.128 nm. This can be compared with an $\text{O}=\text{O}$ bond length of 0.121 nm and an $\text{O}-\text{O}$ bond length of 0.148 nm. The first attempt at explaining the equality of bond lengths in molecules such as O_3 involved the idea of **resonance structures** and **resonance hybrids**. As discussed on page 134, it is possible to draw an alternative Lewis (resonance) structure for O_3 with the double bond between the other two atoms (Figure 4.114).

Neither of these structures alone can explain the equal $\text{O}-\text{O}$ bond lengths, and so the idea of a resonance hybrid is used. This is a hybrid of these two structures – a form that is neither one structure nor the other, but somewhere in between. In this case, with equal contributions from both resonance forms, the bond lengths in the resonance hybrid would be expected to be equal. The double-headed arrow between the resonance structures indicates that the actual structure is a resonance hybrid of the two resonance structures.

The term ‘resonance’ is an unfortunate one because it is used in other contexts in conjunction with vibrations. It is important to note that the structure is not constantly flipping between the different resonance forms but is a mixture of them – rather like a mule is a hybrid of a donkey and a horse; it is not a horse one second and a donkey the next.

A more satisfying explanation of the equal bond lengths in O_3 comes from the idea of **delocalisation** of electrons.

Delocalisation is the sharing of a pair of electrons between three or more atoms.

If the sigma framework (single bonds) of the O_3 molecule is examined (Figure 4.115) it can be seen that there is a p orbital on each oxygen atom that is perpendicular to the plane of the molecule. The p orbital on oxygen atom 1 can overlap with the p orbital on oxygen atom 2, which is part of the π bond. In this way, the electron pair of the π bond is spread (delocalised) over all three oxygen atoms (Figure 4.116).

The delocalised system can be shown using dashed lines between atoms (Figure 4.117).

A single bond is said to have a bond order of 1, a double bond has bond order 2 and a triple bond has bond order 3.

Because the π bond in ozone is shared between two $\text{O}-\text{O}$ bonds rather than just one, we consider that each bond has a half share of it, and we talk about ozone having a bond order of 1.5. So, the $\text{O}-\text{O}$ bonds are identical and somewhere between a single bond and a double bond.

We can recognise molecules and ions that are likely to have a delocalised π system by drawing resonance structures. If it is possible to draw more than one resonance structure, where the only difference between them is the position of a double bond (and a lone pair if there is one) then it is likely that this molecule/ion will have a delocalised structure. The delocalisation can be shown using curly arrows, as in Figure 4.118.

NO_2^- is isoelectronic with O_3 and the bonding can be described in the same way. The two resonance structures for NO_2^- are shown in Figure 4.118. In each structure, all atoms have a complete octet. The nitrogen–oxygen bonds are equal in length (0.118 nm) in the NO_2^- ions and are between the length of an $\text{N}-\text{O}$ single bond (0.140 nm) and an $\text{N}=\text{O}$ double bond (0.114 nm). The two resonance structures are identical except for the position of the double bond (and a lone pair) and, therefore, a delocalised structure is predicted. The arrows show the delocalisation of the π bond between the two $\text{N}-\text{O}$ bonds. The π bond (shown in orange in Figure 4.118) is shared between two bonds, therefore the nitrogen–oxygen bond order is 1.5. The delocalised structure of NO_2^- can be represented as shown in Figure 4.119.

CO_3^{2-} and NO_3^- , which are isoelectronic ions, also have delocalised electrons. Three resonance structures can be drawn for each and these differ only in the position of a double bond (and a lone pair). Figure 4.120 shows the resonance structures of CO_3^{2-} .

All the carbon–oxygen bonds have the same length and are between the length of a single bond and a double bond. This can be explained by the ion having a π delocalised system over the whole ion. The π bond (shown in orange in Figure 4.120) is shared over three $\text{C}-\text{O}$ bonds – so the carbon–oxygen bond order is $1 + \frac{1}{3}$ or $1\frac{1}{3}$.

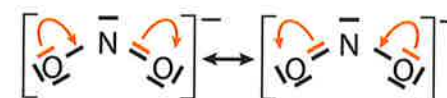


Figure 4.118 The two possible Lewis structures for NO_2^- . The curly arrows (showing movement of a pair of electrons) indicate the delocalisation of electrons.

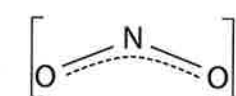


Figure 4.119 NO_2^- is isoelectronic with O_3 and adopts a similar structure.



Figure 4.120 Three possible Lewis structures for CO_3^{2-} .

Extension

There are four electrons in the π delocalised system in ozone. To understand why this does not result in two double bonds between the atoms, we have to use a more complex approach to bonding, called molecular orbital theory. Two of the electrons in the π system occupy a bonding molecular orbital and the other two occupy a molecular orbital that is non-bonding.

If asked for a Lewis structure or resonance structure of a species such as NO_2^- in an examination, you must show a structure with all its bonds and lone pairs – one of the structures shown in Figure 4.118. You must not show the delocalised structure unless specifically asked for this. If you are asked for the delocalised structure you should not include lone pairs of electrons.

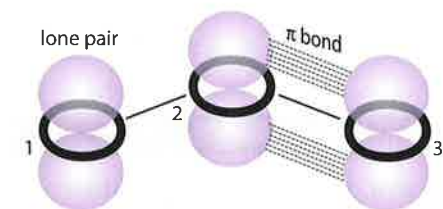


Figure 4.115 The sigma framework and p orbitals of O_3 .

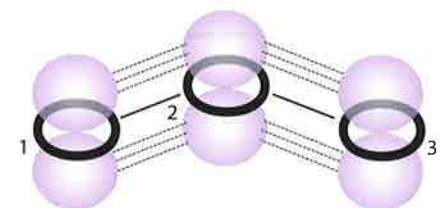


Figure 4.116 O_3 has a delocalised π system.

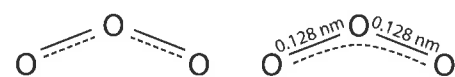


Figure 4.117 Two equivalent representations of the delocalisation in ozone. The dashed lines represent the delocalisation of electrons.

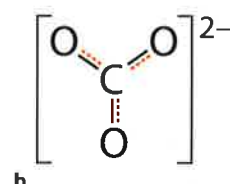
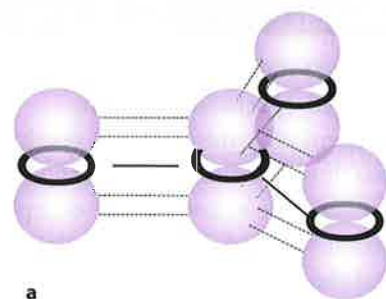


Figure 4.121 **a** Overlap of p orbitals in the carbonate ion. **b** Representation of the delocalisation in the carbonate ion.

There is a p orbital on each atom and these overlap side-on to form the π delocalised system. The electrons in this system do not belong to any one atom (Figure 4.121) but are delocalised over the whole ion (Figure 4.121a).

The nitrogen–oxygen bond length in the nitrate ion, NO_3^- , is 0.124 nm, which can be compared with the nitrogen–oxygen bond length of 0.118 nm in NO_2^- . The bond order of the nitrogen–oxygen bonds in NO_2^- is 1.5, whereas it is 1.33 in NO_3^- , so the bond lengths would be expected to be longer in NO_3^- .

Benzene

Benzene has the molecular formula C_6H_6 . A ring structure for this with alternating double and single bonds was originally proposed by Friedrich Auguste Kekulé (Figure 4.122). One piece of evidence against this being the best representation of the structure of benzene came when it became possible to measure bond lengths. All the carbon–carbon bond lengths in benzene are equal and, at 0.140 nm, are between the $\text{C}=\text{C}$ bond length of 0.134 nm and the single bond length of 0.154 nm. This was originally explained by a resonance hybrid with equal contributions from the two structures shown in Figure 4.122. However, it is explained much better by the idea of delocalisation. The sigma framework (without the double bonds) and p orbitals on each C atom are shown in Figure 4.123.

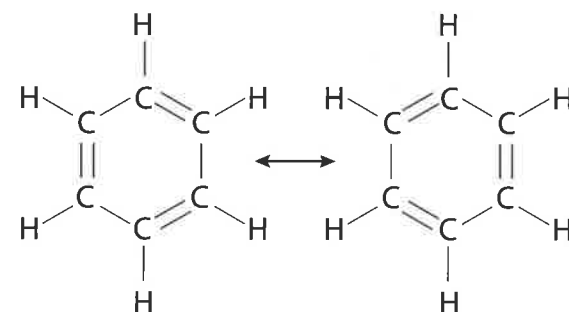


Figure 4.122 The benzene structure with alternating single and double bonds is still known as 'Kekulé benzene' – more systematic names for this would be cyclohexa-1,3,5-triene or 1,3,5-cyclohexatriene.

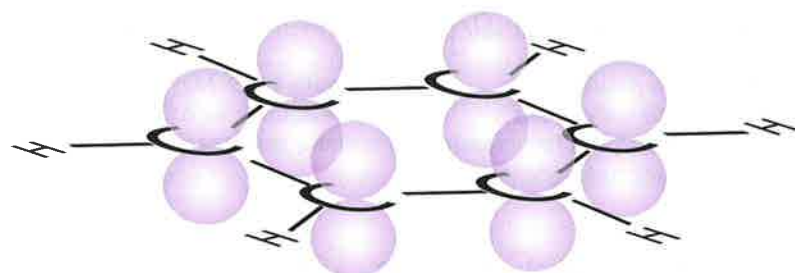


Figure 4.123 The sigma framework for C_6H_6 .

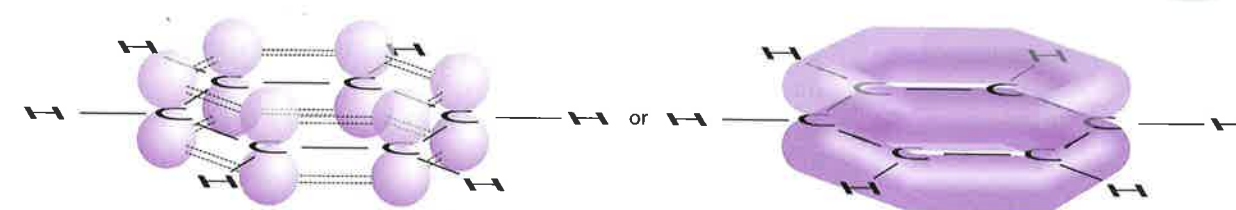


Figure 4.124 Delocalisation over the whole benzene molecule.

Figure 4.124 shows that, instead of the p orbitals just overlapping side-on between adjacent C atoms to give three π bonds, delocalisation can occur over the whole structure.

So benzene has a π delocalised ring of electrons that extends all around the ring of carbon atoms. The structure of benzene is usually drawn (Figure 4.125) as a hexagon with a ring in the middle indicating the π delocalised system.

Because the π component of each double bond is shared between two carbon–carbon bonds, the bond order in benzene is 1.5.

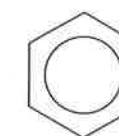


Figure 4.125 A common way of representing the benzene molecule.

Nature of science

Science is an ever-changing body of knowledge. When new and conflicting evidence comes to light, such as bond length data, theories must be modified. Theories can be superseded by new ones which provide a better explanation of experimental data. The theory of resonance has been largely replaced by the theory of delocalisation.

? Test yourself

16 Work out the X–O bond order in each of these delocalised structures:

- a** SO_4^{2-} **b** PO_4^{3-} **c** ClO_4^-

Absorption of ultraviolet light in the atmosphere

Ozone (O_3) and oxygen (O_2) are important in protecting the surface of the Earth from the damaging effects of ultraviolet radiation. The 'ozone layer' is a region in the stratosphere where there is a higher concentration of ozone. The maximum concentration occurs in the lower regions of the stratosphere between about 15 and 35 km above the Earth's surface. About 90% of the ozone in the atmosphere is found in this region. Even in the ozone layer, the concentration of ozone is very low and there is roughly only one ozone molecule for every 100 000 air molecules.

The atmosphere can be divided into different regions. The troposphere is the region closest to the Earth and the stratosphere is the region between about 12 and 50 km, on average, above the Earth's surface.

λ stands for wavelength

Free radicals are atoms or groups of atoms with unpaired electrons. An oxygen free radical is simply an oxygen atom and has two unpaired electrons.

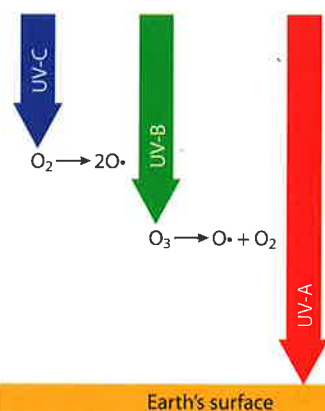


Figure 4.126 Absorption of UV radiation in the atmosphere.

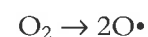
CFC stands for chlorofluorocarbon – a molecule containing carbon, chlorine and fluorine.

Homolytic fission – the covalent bond breaks so that one electron goes back to each atom making up the bond.

Ultraviolet (UV) light from the Sun reaching the Earth can be divided into three components:

- UV-C $\lambda < 280$ nm (highest energy)
- UV-B $\lambda = 280$ – 320 nm
- UV-A $\lambda = 320$ – 400 nm

UV radiation is absorbed by molecules of O_2 or O_3 as they undergo dissociation. The highest energy UV radiation is absorbed by O_2 molecules in the atmosphere, which causes them to undergo dissociation into oxygen free radicals:



The UV radiation required to do this is in the UV-C part of the spectrum and must have a wavelength shorter than 242 nm to provide sufficient energy to break the bond. The bond between the atoms in an O_2 molecule is a double bond (bond order 2), but O_3 has a delocalised structure where the bond order is 1.5. This means that the $O=O$ bond in O_3 is weaker than the $O=O$ in O_2 and so lower energy (longer wavelength) radiation (up to 330 nm) is absorbed by O_3 molecules to break the bond:



So, ozone molecules are particularly effective at absorbing lower energy UV-B radiation (and some UV-C). In the process the molecule is split apart into an oxygen molecule and an oxygen atom, as in the above equation.

All the UV-C and most of the UV-B reaching the Earth from the Sun is absorbed by oxygen (O_2) in the upper parts of the atmosphere and by ozone (O_3) in the stratosphere before it reaches the Earth's surface. Most of the UV radiation reaching the Earth's surface is the least harmful UV-A (Figure 4.126).

Catalysis of ozone depletion by CFCs and NO_x

Ozone molecules are easily destroyed by free radicals. These are present in the stratosphere as nitrogen oxides or are produced when CFCs are broken down by UV light.

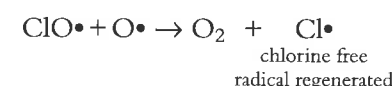
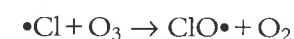
Chlorofluorocarbons

CFCs such as CCl_2F_2 are very stable compounds at ground level but they are broken down by absorbing UV radiation in the upper atmosphere:

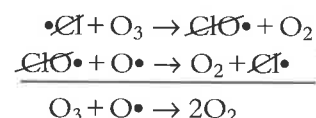


A C–Cl bond is weaker than a C–F bond and undergoes homolytic fission more readily. The chlorine free radical released in this process

can take part in a chain reaction, which uses up ozone and regenerates chlorine free radicals, $Cl\cdot$ to react with more ozone:

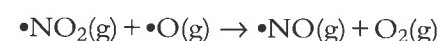
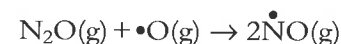


The net effect of these reactions can be seen if the intermediate and the catalyst are cancelled:

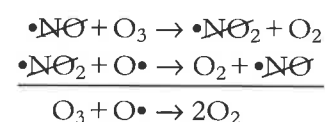


Nitrogen oxides, NO_x

NO can be formed at high altitudes by aircraft and from the reaction of N_2O or NO_2 with atomic oxygen:

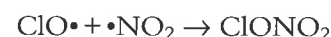


Similar types of reactions to those discussed above for CFCs occur with nitrogen oxides. Both NO and NO_2 have unpaired electrons – their total numbers of electrons are odd numbers. The destruction of ozone catalysed by NO can be represented as:



NO is a catalyst in this reaction – it is used up in the first step but regenerated in the second step – overall it is not used up.

The cycles involved in the destruction of ozone can stop when the free radicals involved collide:



Nature of science

Despite the fact that all scientists have the same data available to them, they do not always agree about the interpretation of this data. For example, scientists do not agree about the extent of d orbital involvement in pi bonding ($d_{\pi}-p_{\pi}$ interactions), for instance in the compound $N(Si(CH_3)_3)_3$ the planar structure can be explained by $d_{\pi}-p_{\pi}$ or by steric effects.

All reactions occur in the gaseous phase.

Oxygen atoms, O , are available from the dissociation of oxygen or ozone.

The chlorine free radical is a catalyst in these reactions because it is not used up. One $Cl\cdot$ free radical can destroy many thousands of ozone molecules.

Extension

The bond order in NO is 2.5. A simple approach to bonding does not explain this – NO has one electron in a π^* antibonding molecular orbital.

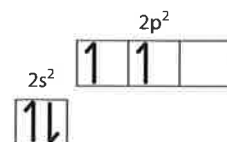
Learning objectives

- Understand what is meant by hybridisation
- Predict the hybridisation of atoms in a molecule

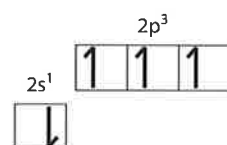
4.7 Hybridisation (HL)

Forming a covalent bond

To form a covalent bond, two orbitals each containing one electron are required. These orbitals overlap to form a covalent bond. Carbon has the outer shell electronic configuration $2s^2 2p^2$:



Because it has only two unpaired electrons, carbon should form two covalent bonds. However, it is well known that carbon virtually always forms four covalent bonds. One of the electrons in the 2s orbital must be promoted to the 2p subshell to give four unpaired electrons.



This requires energy. However, bond formation releases energy and the subsequent formation of four bonds instead of two more than pays back the energy needed to promote an electron to a higher subshell.

Carbon now has four unpaired electrons and can form four covalent bonds, but the atomic orbitals do not point in the correct directions for bonding. CH_4 is tetrahedral with bond angles of 109.5° , but the p orbitals are at 90° to each other (Figure 4.127).

In order to form methane, the four atomic orbitals on carbon (one s and three p) mix to give four sp^3 hybrid orbitals, which point to the vertices of a tetrahedron. This is the process of **hybridisation** (Figure 4.128).

Hybridisation is the mixing of atomic orbitals in a particular atom to produce a new set of orbitals (the same number as originally) that have characteristics of the original orbitals and are better arranged in space for covalent bonding.

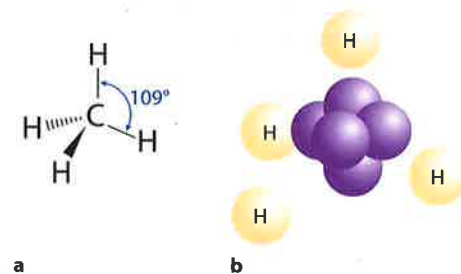


Figure 4.127 a The bond angles in CH_4 ; b the p orbitals on C are at 90° to each other.

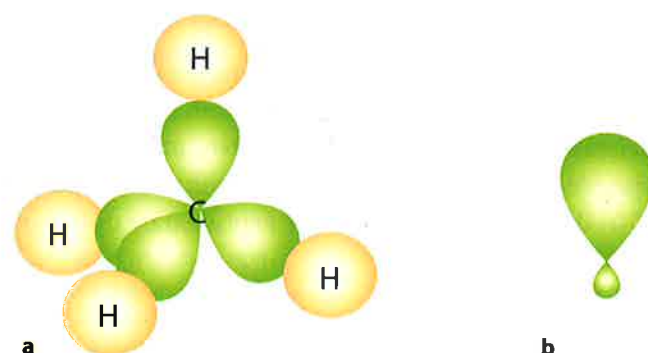


Figure 4.128 a Four sp^3 hybrid orbitals point towards the vertices of a tetrahedron and are better set up for bonding to the H atoms. b One sp^3 orbital.

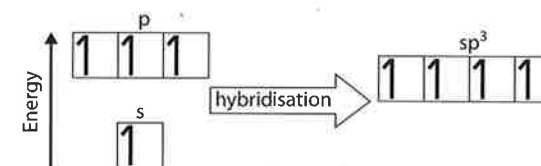


Figure 4.129 The new sp^3 orbitals are identical except for direction.

The four sp^3 hybrid orbitals have the same energy (Figure 4.129) – they are degenerate. The overall energy of the s and p orbitals does not change when they undergo hybridisation, so the energy of one sp^3 hybrid orbital is the average of the energies of the s and three p orbitals they were formed from. The sp^3 orbitals are therefore much closer in energy to the p orbitals than to the s orbitals.

Bonding in methane, CH_4

Methane contains only single bonds between carbon atoms (Figure 4.130). These are σ bonds formed when sp^3 hybrid orbitals on the carbon atom overlap head-on with the s orbitals of each H atom.

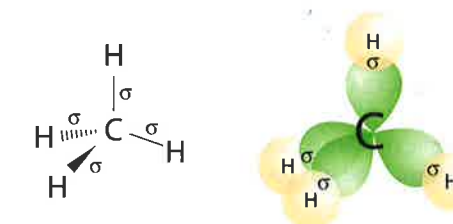


Figure 4.130 Bonding in methane.

Bonding in ethene, C_2H_4

The Lewis structure for ethene is:



The arrangement of atoms around each carbon atom is trigonal planar, and the molecule is planar overall (Figure 4.131a). Of the three p orbitals on each carbon atom, one is not in the same plane as the hydrogen atoms or the other carbon atom – this p orbital is not involved in hybridisation. Mixing the other two p orbitals and one s orbital produces three sp^2 orbitals pointing towards the corners of an equilateral triangle (Figure 4.131b). This leaves one p orbital, containing one electron, perpendicular to the single bond (σ) framework on each C atom (Figure 4.132). These p orbitals are involved in the formation of the π component of the double bond. The double bond has two different components – a sigma bond, which results from the head-on overlap of two sp^2 orbitals, and a pi bond which arises from the side-on overlap of two parallel p orbitals.

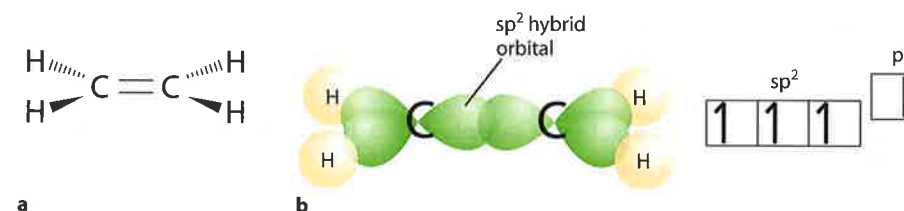


Figure 4.131 The a structure of and b hybridisation in ethene.

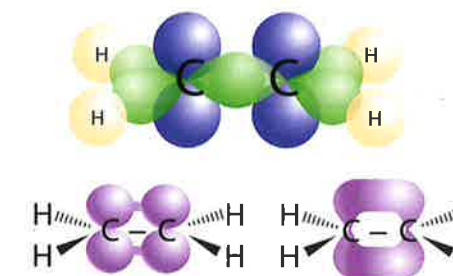


Figure 4.132 The unused p orbitals in ethene overlap side-on to form the π component of the double bond.



Figure 4.133 Only the p orbitals that point towards the hydrogen atoms are involved in hybridisation.

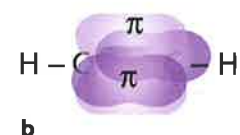


Figure 4.134 **a** The formation of σ bonds in ethyne. **b** The formation of π bonds in ethyne; the two π bonds are shown in different shadings for clarity.

The bonding in ethyne, C_2H_2

The Lewis structure for ethyne is:



The linear shape means that one s and one p orbital on each carbon atom are hybridised to produce two sp hybrid orbitals at 180° to each other. The two p orbitals at 90° to the C–H bonds are not involved in the hybridisation – only the p orbitals shown in Figure 4.133 are involved.

Hybridisation of one s and one p orbital produces two sp hybrid orbitals pointing away from each other at 180° on both carbon atoms. These are used to form σ bonds between the carbon atoms and also to the hydrogen atoms (Figure 4.134a). This leaves two p orbitals on each carbon atom that are not involved in hybridisation. These p orbitals overlap side-on to produce two π bonds (Figure 4.134).

Table 4.25 shows that the number of hybrid orbitals is always the same as the number of atomic orbitals from which they were produced.

Hybridisation	Orbitals used	Hybrid orbitals produced	Shape
sp	$1 \times s, 1 \times p$	2	linear
sp ²	$1 \times s, 2 \times p$	3	trigonal planar
sp ³	$1 \times s, 3 \times p$	4	tetrahedral

Table 4.25 Hybrid orbitals.

Determining the hybridisation of an atom in a molecule or ion

In order to determine the hybridisation of a particular atom in a molecule or ion, the basic shape – the arrangement of electron domains (electron pairs) on the central atom – must be determined. Table 4.26 shows how the basic shape relates to the hybridisation of the central atom.

Electron domains	Basic shape	Hybridisation
2	linear	sp
3	trigonal planar	sp ²
4	tetrahedral	sp ³

Table 4.26 Relationship between hybridisation and basic shape.

The hybridisation scheme adopted in a molecule depends on the shape of the molecule.

Several examples follow.

With organic molecules this can be simplified:

- when a carbon atom forms just single bonds, the shape is tetrahedral and the hybridisation is sp³
- when a carbon atom forms a double bond, the shape is trigonal planar and the hybridisation is sp²
- when a carbon atom forms a triple bond, the shape is linear and the hybridisation is sp.

BF₃

The Lewis structure for boron(III) fluoride is shown in Figure 4.135. There are three electron domains, which give rise to a trigonal planar shape, and therefore the boron atom is sp² hybridised.

NH₃

The Lewis structure for ammonia is shown in Figure 4.136. There are four electron domains – three bonding pairs of electrons and one lone pair. So the basic shape is tetrahedral and the hybridisation of the nitrogen atom is sp³.

CO₂

The Lewis structure for carbon dioxide is shown in Figure 4.137. There are two electron domains around the carbon atom – two double bonds. So the basic shape is linear and the hybridisation of the carbon atom is sp.

O₃

The Lewis structure for ozone is shown in Figure 4.138. There are three electron domains around the central oxygen atom, and so the basic shape is trigonal planar and the hybridisation of the central atom is sp².

Table 4.27 shows the hybridisation of the central atom in several molecules and ions.

Electron domains	Basic shape	Hybridisation	Examples
2	linear	sp	CO ₂ , HCN, C ₂ H ₂ , NO ₂ ⁺
3	trigonal planar	sp ²	BF ₃ , SO ₃ , NO ₃ [–] , CO ₃ ^{2–} , SO ₂ , BF ₃ , NO ₂ [–]
4	tetrahedral	sp ³	CCl ₄ , XeO ₄ , NH ₄ ⁺ , BCl ₄ [–] , SO ₄ ^{2–} , PO ₄ ^{3–} , NH ₃ , PCl ₃ , XeO ₃ , H ₃ O ⁺ , ClO ₃ [–] , SOCl ₂ , H ₂ O, SCl ₂ , ClF ₂ ⁺

Table 4.27 Hybridisation of central atoms.



Is hybridisation real? There is evidence from ultraviolet photoelectron spectroscopy to suggest that it is not. Why then do we still use this theory? There is a more advanced theory of bonding called molecular orbital theory, but this is much more complicated and does not allow us to draw lines (bonds) between atoms in the same way. Is a more advanced theory always more useful? What are the implications of using something that we know to be nothing more than a mathematical device for making predictions? How can we justify this?

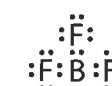


Figure 4.135 The Lewis structure for BF₃.

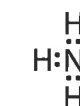


Figure 4.136 The Lewis structure for NH₃.



Figure 4.137 The Lewis structure for CO₂.



Figure 4.138 The Lewis structure for O₃.

Extension

Other hybridisation schemes, involving d orbitals, can be used to rationalise the bonding in 5- and 6-coordinate molecules – sp³d² for an octahedral shape for example.

Nature of science

A key feature in many scientific arguments and theories is a clear distinction between cause and effect. There is often some confusion at this level about whether hybridisation is something that causes the shape of a molecule to be how it is or whether hybridisation is just a simplified treatment of bonding that allows us to rationalise the shape of molecules based on a reasonably straightforward and accessible theory.

? Test yourself

- 17 Predict the hybridisation of the central atom in each of the following
- | | | | |
|--------------------|---------------------|---------------------------------|--------------------|
| a BCl ₃ | d CCl ₄ | g PCl ₄ ⁺ | i SeO ₃ |
| b NCl ₃ | e BeCl ₂ | h OCN ⁻ | j FNO |
| c OCl ₂ | f H ₂ S | | |
- 18 What is the hybridisation of the nitrogen atoms in each of the following?
- | |
|---------------------------------|
| a N ₂ H ₄ |
| b N ₂ H ₂ |
- 19 What is the hybridisation of the carbon atoms in each of the following?
- | | | | |
|---------------------------------|---------------------------------|---------------------------------|--------------------|
| a C ₂ F ₄ | b C ₂ F ₂ | c C ₂ F ₆ | d COF ₂ |
|---------------------------------|---------------------------------|---------------------------------|--------------------|

Exam-style questions

- 1 What is the formula of the compound formed between lithium and nitrogen?
- | | | | |
|--------------------|--------------------|---------------------|----------------------------------|
| A LiN ₂ | B LiN ₃ | C Li ₃ N | D Li ₃ N ₂ |
|--------------------|--------------------|---------------------|----------------------------------|
- 2 Which of the following contains both ionic and covalent bonding?
- | | | | |
|--------|----------------------|--------------------|--------------------|
| A NaCl | B NH ₄ Cl | C CCl ₄ | D PCl ₃ |
|--------|----------------------|--------------------|--------------------|
- 3 What is the shape of NO₂⁺?
- | | |
|----------|-------------------|
| A Linear | C Trigonal planar |
| B Bent | D Tetrahedral |
- 4 Which of the following is polar?
- | | | | |
|-------------------|--------------------|-------------------|--------------------|
| A CO ₂ | B CCl ₄ | C BF ₃ | D PCl ₃ |
|-------------------|--------------------|-------------------|--------------------|

- 5 Which of the following molecules exhibit(s) hydrogen bonding?

- | | | | |
|----------------------|------------------------------------|--------|----------------------|
| I NH ₃ | II CH ₃ NH ₂ | III HF | IV CH ₃ F |
| A I, II and III only | C I and III only | | |
| B IV only | D III and IV only | | |

- 6 In which of the following are the molecules arranged in order of increasing boiling point (lowest first)?

- | | | |
|----------------------------------|---------------------------------|----------------------------------|
| A NH ₃ | N ₂ | Br ₂ |
| B H ₂ O | H ₂ S | H ₂ Se |
| C CH ₃ Cl | CH ₂ Cl ₂ | CHCl ₃ |
| D C ₄ H ₁₀ | C ₃ H ₈ | C ₂ H ₅ OH |

- 7 What is the F–B–F bond angle in BF₄⁻?

- | | | | |
|----------|--------|--------|-------|
| A 109.5° | B 107° | C 120° | D 90° |
|----------|--------|--------|-------|

- 8 Which of the following will be the worst conductor of electricity?

- | | |
|-------------------------|-------------------------|
| A Mg(s) | C MgCl ₂ (l) |
| B SiCl ₄ (l) | D C(graphite,s) |

- 9 When the compounds C₂H₆, C₂H₄, C₂H₂ and C₆H₆ are arranged in order of increasing C–C bond lengths (shortest first) the correct order is:

- | | | | |
|---------------------------------|-------------------------------|-------------------------------|-------------------------------|
| A C ₂ H ₆ | C ₂ H ₄ | C ₂ H ₂ | C ₆ H ₆ |
| B C ₆ H ₆ | C ₂ H ₄ | C ₂ H ₂ | C ₂ H ₆ |
| C C ₂ H ₂ | C ₆ H ₆ | C ₂ H ₄ | C ₂ H ₆ |
| D C ₂ H ₂ | C ₂ H ₄ | C ₆ H ₆ | C ₂ H ₆ |

- HL 10 The number of π bonds and hybridisation of C in a molecule of hydrogen cyanide, HCN, are:

- | | number of π bonds | hybridisation |
|---|-------------------|-----------------|
| A | 3 | sp ² |
| B | 2 | sp |
| C | 1 | sp ² |
| D | 2 | sp ³ |

- HL 11 Which of the following contains delocalised electrons?

- | | | | |
|-------------------|------------------|--------------------|--------------------|
| A CO ₂ | B O ₃ | C SiO ₂ | D OCl ₂ |
|-------------------|------------------|--------------------|--------------------|

HL 12 In which of the following is the distribution of electron pairs around the central atom octahedral?

- A BCl_4^- B SF_4 C PCl_4^+ D XeF_4

- 13 a** Describe the principles of the valence shell electron pair repulsion theory for predicting the shapes of molecules. [4]
b Predict the shapes and bond angles of the following molecules: [4]
 i PCl_3
 ii CO_2
c Explain why carbon dioxide is a non-polar molecule but sulfur dioxide is polar. [3]
d Draw a Lewis structure for carbon monoxide and explain whether it has a shorter or longer C–O bond length than carbon dioxide. [3]

14 Explain the following in terms of structure and bonding.

- a** Sodium oxide has a high melting point and does not conduct electricity when solid but conducts electricity when molten. [4]
b Sodium has a lower melting point than magnesium. [3]
c Phosphine, PH_3 , has a lower boiling point than ammonia, NH_3 , and arsine, AsH_3 . [3]
d Silicon dioxide has a much higher melting point than carbon dioxide. [3]

HL 15 a Explain the term 'hybridisation'.

- b** Predict the hybridisation of the carbon atoms in ethene (C_2H_4) and ethyne (C_2H_2). [2]
c Explain, by reference to ethene and ethyne, what is meant by the terms 'sigma bond' and 'pi bond'. [4]

HL 16 a Use the valence shell electron pair repulsion theory to predict the shapes and bond angles of the following molecules or ions:

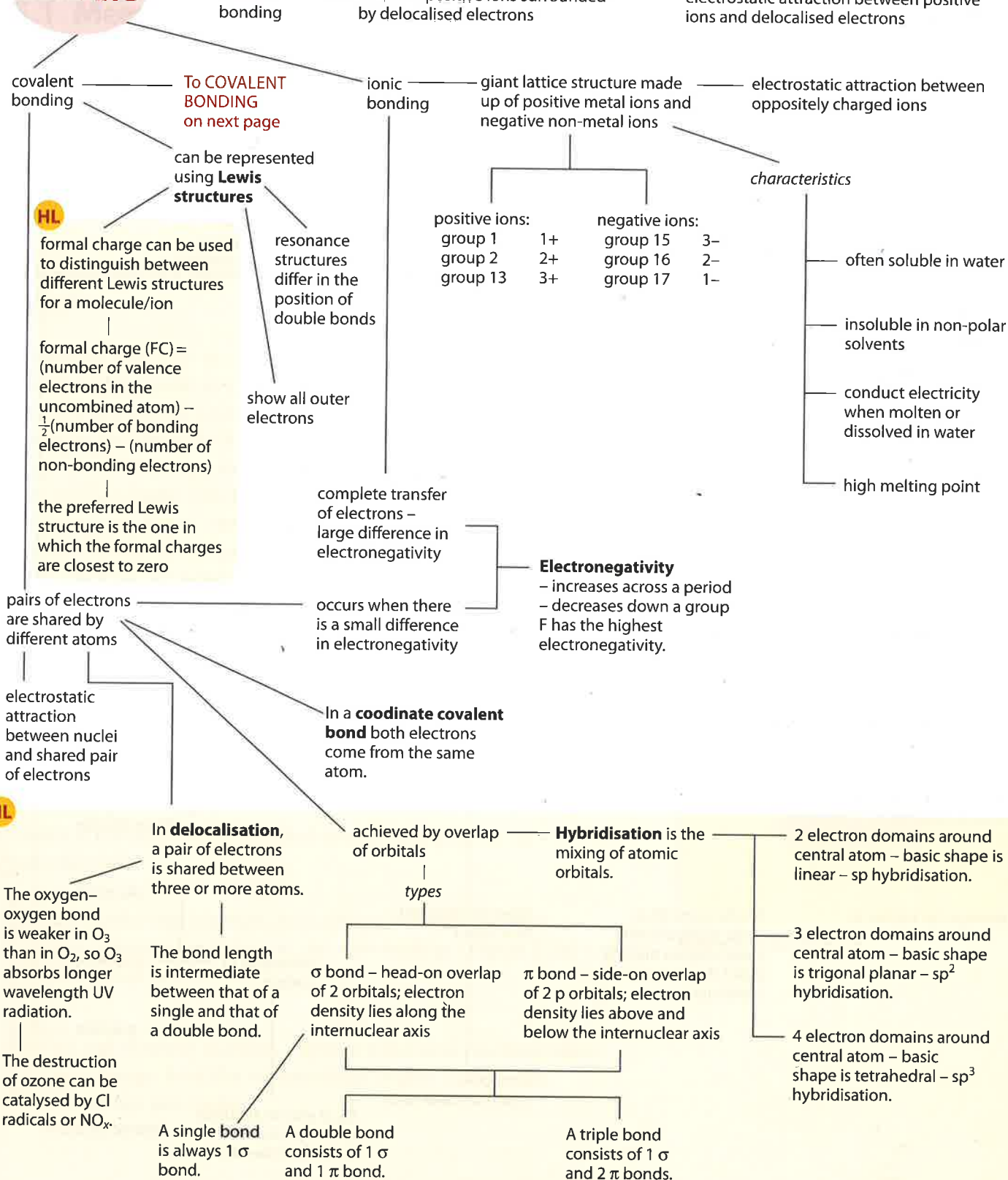
- i SO_4^{2-} ii XeF_4 iii SF_4

b Explain whether XeF_4 is polar or non-polar. [2]

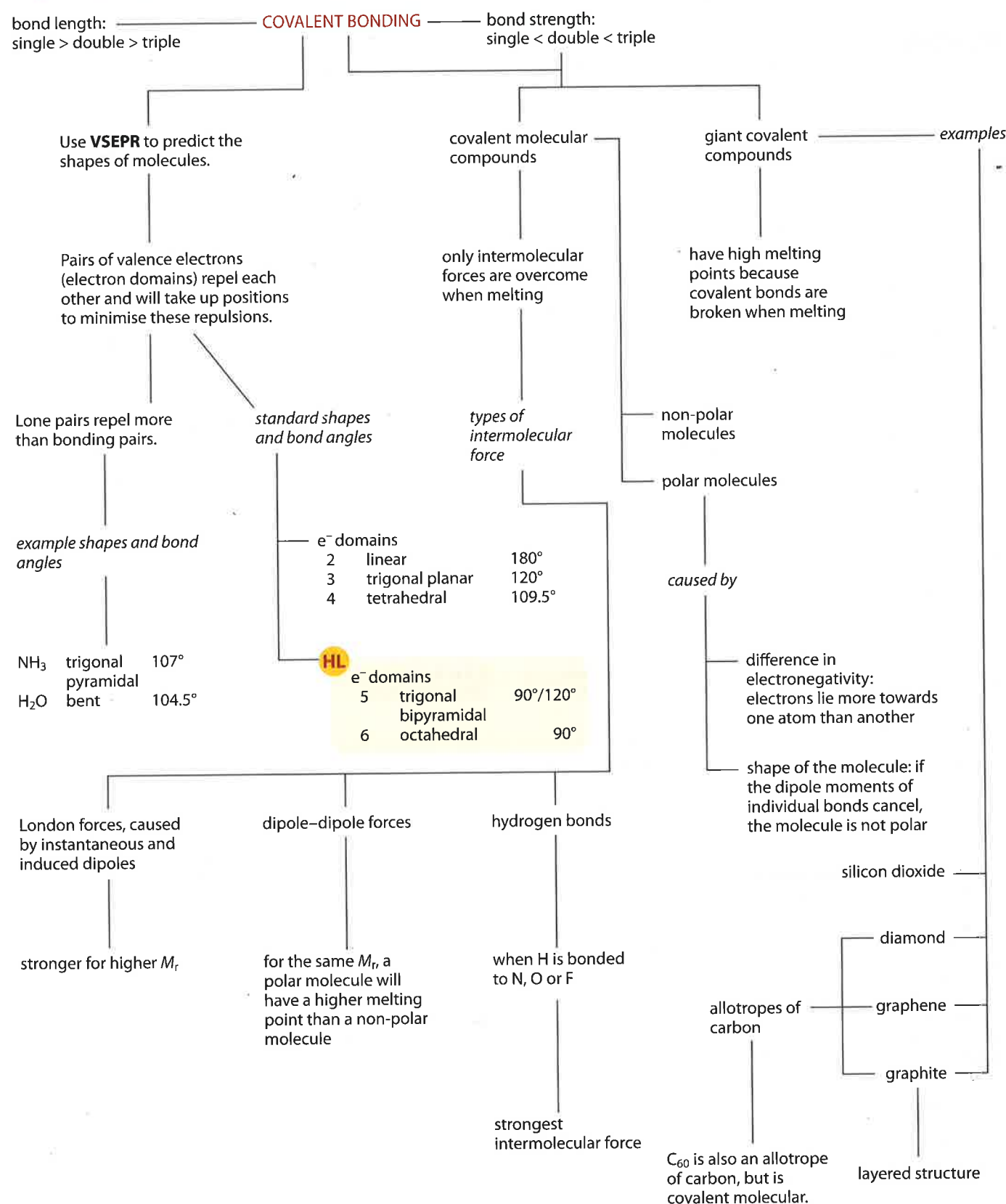
c Explain how you would expect the S–O bond length in SO_4^{2-} to compare with that in SO_2 . [2]

Summary

BONDING



Summary – continued



Energetics/thermochemistry 5

5.1 Measuring energy changes

Heat and temperature

Heat and **temperature** are very different things that often get confused.

Heat is a form of energy that flows from something at a higher temperature to something at a lower temperature.

Temperature is a measure of the average kinetic energy of particles.

Internal energy is the name given to the total amount of energy (kinetic and potential) in a sample of a substance. If a 100 g block of iron at 100 °C is placed in contact with a 50 g block of iron at 50 °C, heat will flow from the hotter block to the colder one until they are at the same temperature. When they are at the same temperature, the 100 g block of iron will have higher internal energy simply because there is more of it, but the average kinetic energy of the particles in the two blocks will be the same because they are at the same temperature.

We often use the words *system* and *surroundings* to describe what is happening in terms of energy flow in chemical reactions.

The 'system' is our chemical reaction and the 'surroundings' is everything else in the Universe (Figure 5.1)!

Exothermic and endothermic reactions and enthalpy changes

Chemical reactions may be classified as either **exothermic** or **endothermic**.

In an exothermic reaction, heat energy is transferred from a system (chemical reaction) to the surroundings (Figure 5.2a) – the surroundings get hotter.

In an endothermic reaction, a system (chemical reaction) takes in heat energy from the surroundings (Figure 5.2b) – the surroundings get cooler.

Learning objectives

- Understand the difference between heat and temperature
- Explain what is meant by exothermic and endothermic reactions
- Draw enthalpy level diagrams for exothermic and endothermic reactions
- Understand what is meant by stability
- Understand the principle of experimental methods for determining enthalpy changes
- Work out enthalpy changes from experimental data

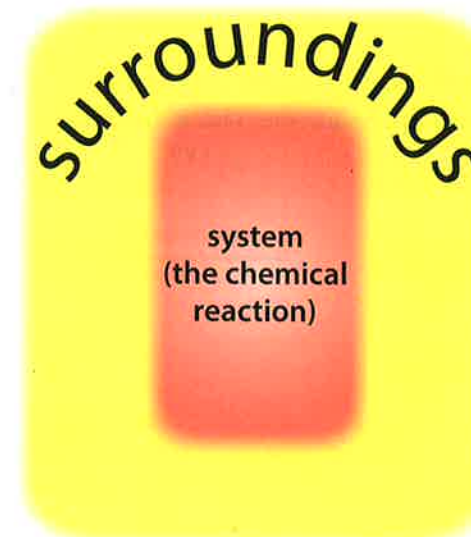


Figure 5.1 The Universe!