Cambridge AS Chemistry

(Code: 9701)

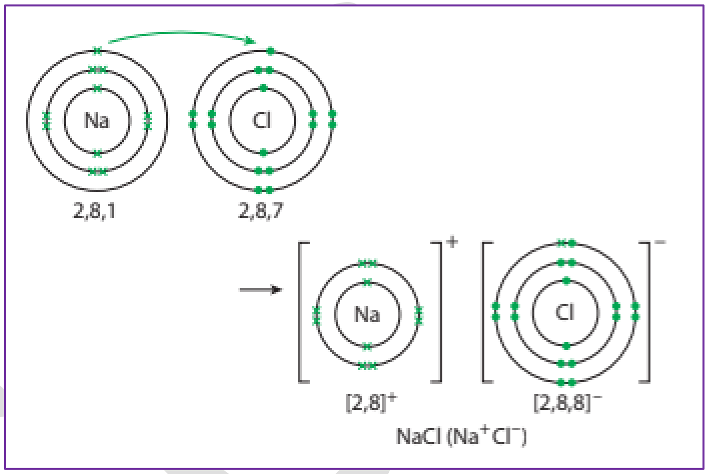
Chapter 4
Chemical bonding

Ionic bonding

How are ions formed?

One way of forming ions is for atoms to gain or lose one or more electrons.

- Positive ions are formed when an atom loses one or more electrons. Metal atoms usually lose electrons and form positive ions.
- Negative ions are formed when an atom gains one or more electrons. Non-metal atoms usually gain electrons and form negative ions.



They have an electronic configuration of a noble gas. The strong force of attraction between the positive and negative ions in the ionic crystal lattice results in an ionic bond. An ionic bond is sometimes called an electrovalent bond.

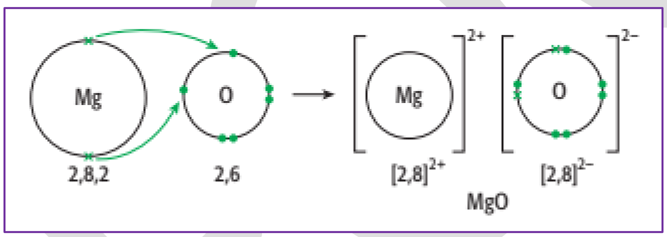
Dot-and-cross diagrams

A dot-and-cross diagram shows:

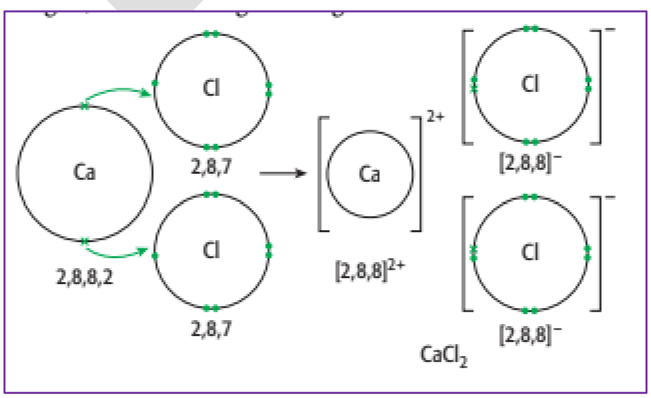
- the outer electron shells only
- that the charge of the ion is spread evenly, by using square brackets
- The charge on each ion, written at the top right-hand corner of the square brackets.

Some examples of dot-and-cross diagrams

Magnesium oxide



Calcium chloride



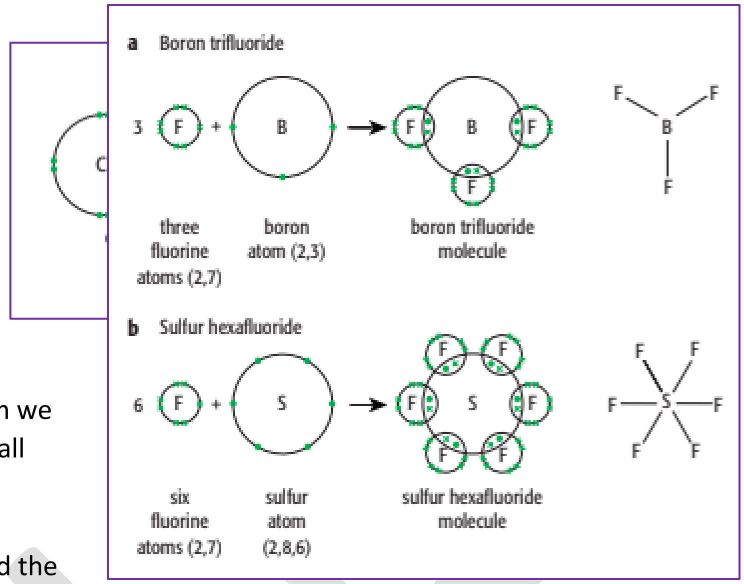
Covalent bonding

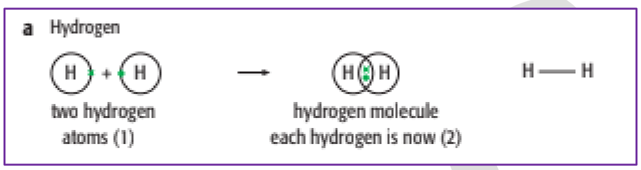
Single covalent bonds

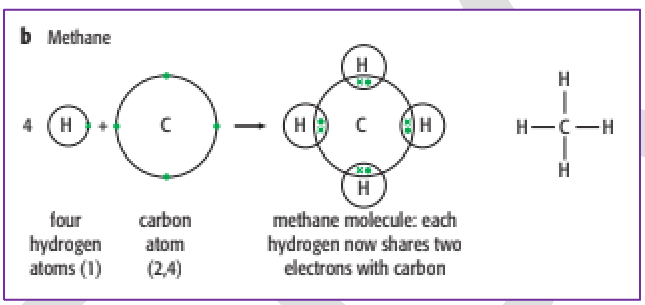
The pairs of outer-shell electrons not used in bonding are called lone pairs.

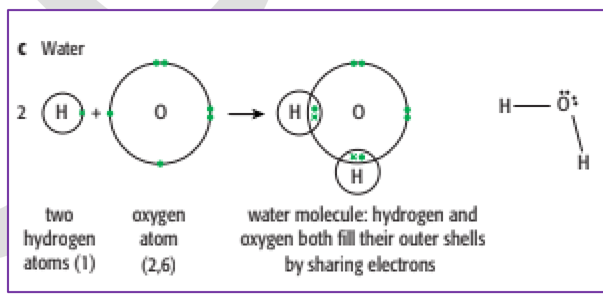
When drawing the arrangement of electrons in a molecule we:

- use a ‘dot’ for electrons from one of the atoms and a ‘cross’ for the electrons from the other atom
- if there are more than two types of atom we can use additional symbols such as a small circle or a small triangle
- we draw the outer electrons in pairs, to emphasise the number of bond pairs and the number of lone pairs.









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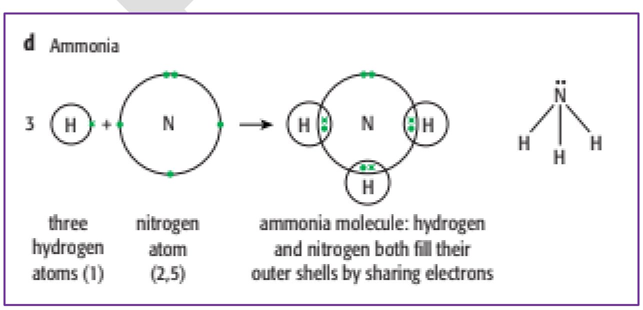
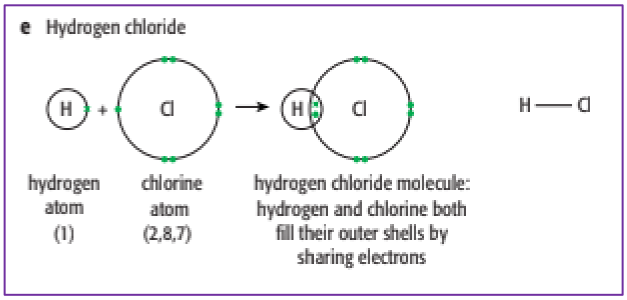
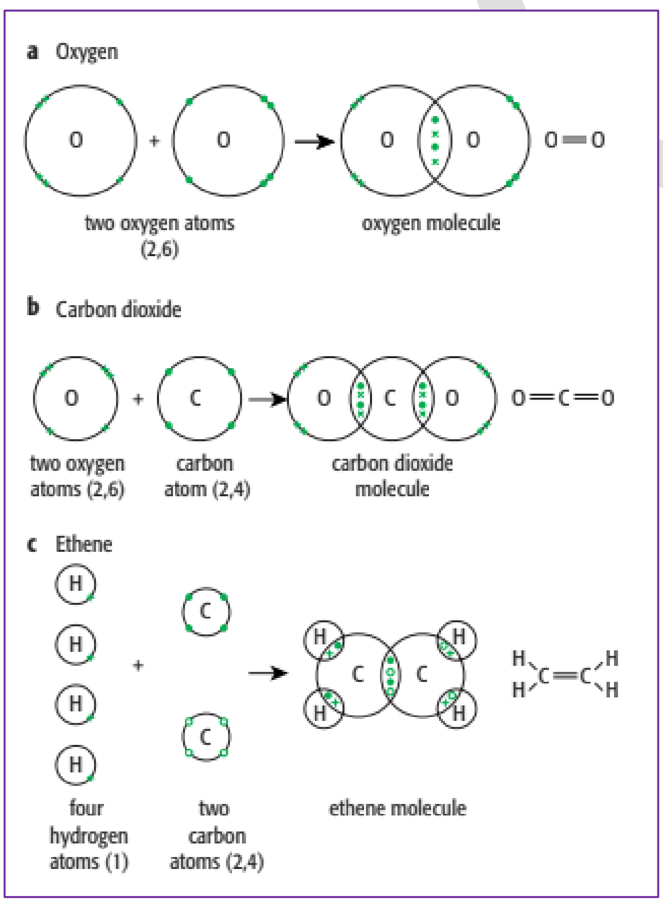


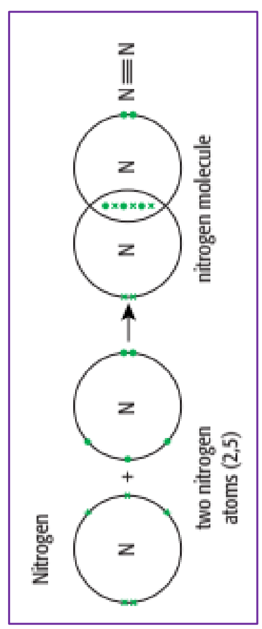


Multiple covalent bonds

Double covalent bond

Triple covalent bond



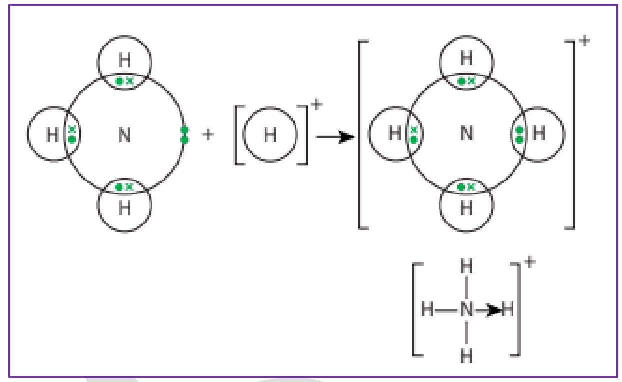


Co-ordinate bonding (dative covalent bonding)

A co-ordinate bond (or dative covalent bond) is formed when one atom provides both the electrons needed for a covalent bond.

For dative covalent bonding we need:

- one atom having a lone pair of electrons
- a second atom having an unfilled orbital to accept the lone pair; in other words, an electron-deficient compound.



Bond length and bond energy

In general, double bonds are shorter than single bonds. We measure the strength of a bond by its bond energy. Bond strength can influence the reactivity of a compound.

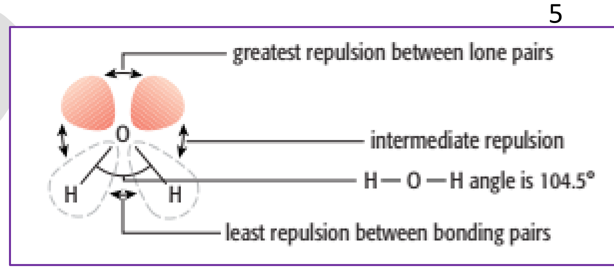
Bond	Bond energy / kJ mol^{-1}	Bond length / nm
C—C	350	0.154
C═C	610	0.134
C—O	360	0.143
C═O	740	0.116

Shapes of molecules

Electron-pair repulsion theory

The shape and bond angles of a covalently bonded molecule depend on:

- the number of pairs of electrons around each atom
- Whether these pairs are lone pairs or bonding pairs.

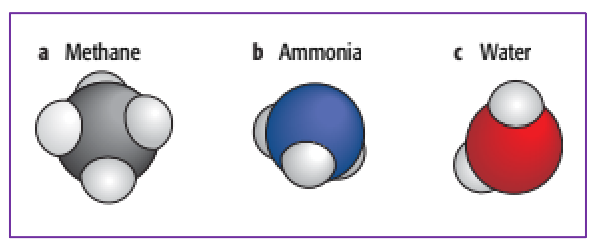


The order of repulsion is:

Lone pair–lone pair (most repulsion) > lone pair–bond pair > bond pair–bond pair (least repulsion).

Working out the shapes of molecules

In drawing three-dimensional diagrams, the triangular 'wedge' is the bond coming towards you and the dashed black line is the bond going away from you.

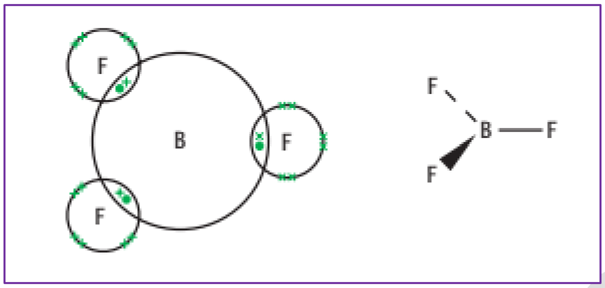


a. Methane has four bonding pairs of electrons surrounding the central carbon atom. The equal repulsive forces of each bonding pair of electrons results in a tetrahedral structure with all H—C—H bond angles being 109.5°.
b. Ammonia has three bonding pairs of electrons and one lone pair. As lone pair–bond pair repulsion is greater than bond pair–bond pair repulsion, the bonding pairs of electrons are pushed closer together. This gives the ammonia molecule a triangular pyramidal shape. The H—N—H bond angle is about 107°.

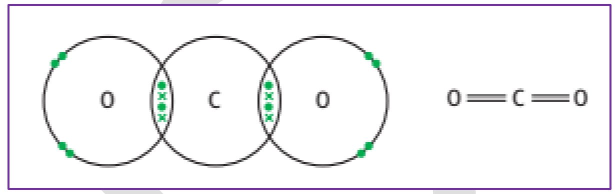
c. Water has two bonding pairs of electrons and two lone pairs. The greatest electron pair repulsion is between the two lone pairs. This results in the bonds being pushed even closer together. The shape of the water molecule is a non-linear V shape. The H—O—H bond angle is 104.5°.

More molecular shapes

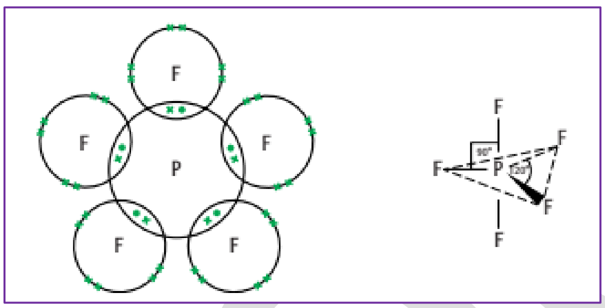
Boron trifluoride



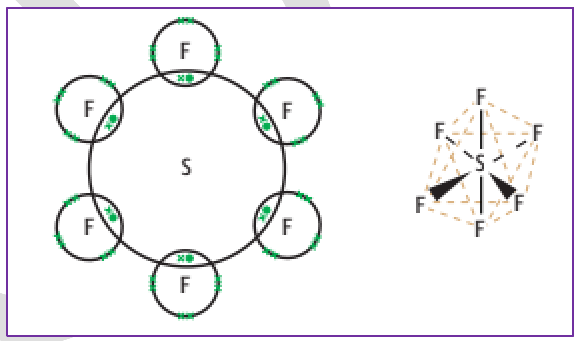
Carbon dioxide



Phosphorus pentafluoride

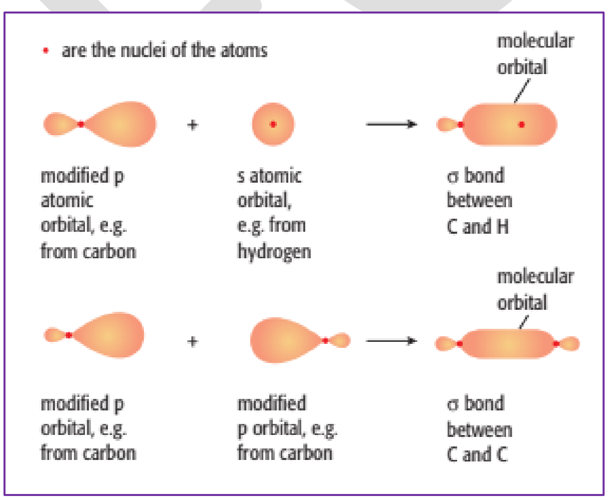


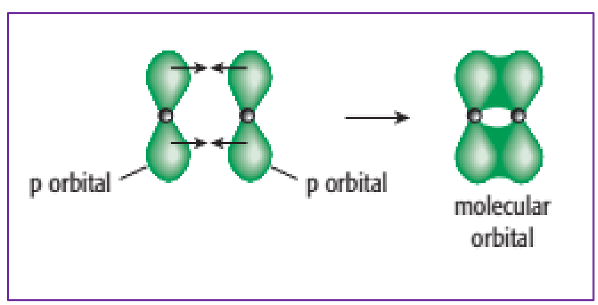
Sulfur hexafluoride



σ bonds and π bonds

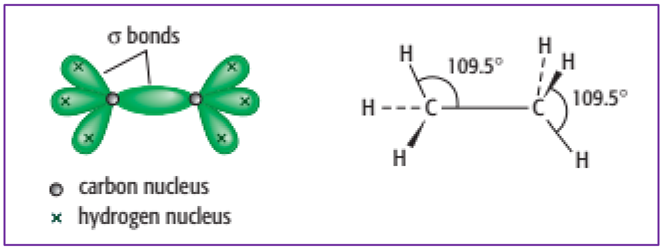
Sigma bonds (σ) are the first type of covalent bond, formed by overlap of atomic orbitals head-to-head. They are found in single, double, and triple bonds. Pi bonds (π) are the second and third types of covalent bonds, formed by overlap of p orbitals side-to-side. They only exist in double and triple bonds.



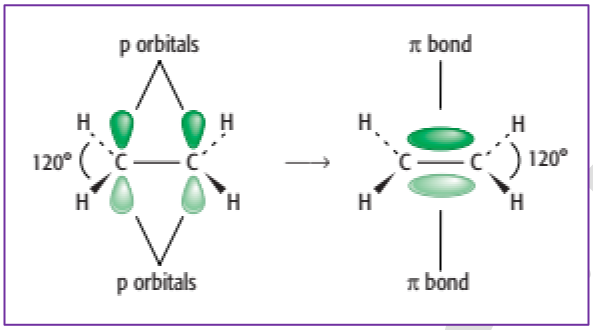


The shape of some organic molecules

Ethane



Ethene



Metallic bonding

What is a metallic bond?

The outer shell electrons occupy new energy levels and are free to move throughout the metal lattice. We call these electrons delocalised electrons (mobile electrons).

The strength of metallic bonding increases with:

- increasing positive charge on the ions in the metal lattice
- decreasing size of metal ions in the lattice
- increasing number of mobile electrons per atom.

Metallic bonding and the properties of metals

- Most metals have high melting points and high boiling points
- Metals conduct electricity
- Metals conduct heat

Intermolecular forces

There are three types of intermolecular force:

- van der Waals' forces (which are also called dispersion forces and temporary dipole–induced dipole forces)
- permanent dipole–dipole forces
- hydrogen bonding

Type of bond	Bond strength / kJ mol^{-1}
ionic bonding in sodium chloride	760
O—H covalent bond in water	464
hydrogen bonding	20–50
permanent dipole–dipole force	5–20
van der Waals' forces	1–20

Electronegativity

Electronegativity is the ability of a particular atom, which is covalently bonded to another atom, to attract the bond pair of electrons towards itself. Fluorine is the most electronegative element.

- electronegativity increases across a period from Group 1 to Group 17
- electronegativity increases up each group.

Polarity in molecules

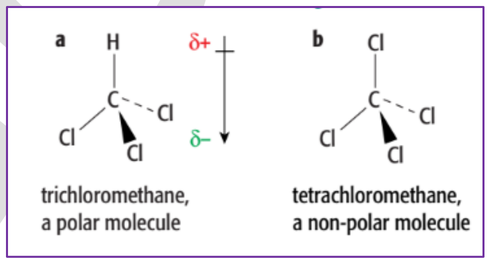
We say that the covalent bond is non-polar.

- the centre of positive charge does not coincide with the centre of negative charge
- we say that the electron distribution is asymmetric
- the two atoms are partially charged
- we show
  - – the less electronegative atom with the partial charge δ+ (‘delta positive’)
  - – the more electronegative atom with the partial charge δ– (‘delta negative’)
- we say that the bond is polar (or that it has a dipole)

In molecules containing more than two atoms, we have to take into account:

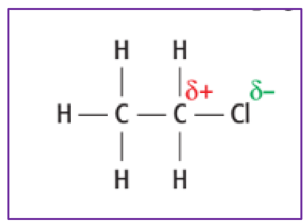
- the polarity of each bond
- the arrangement of the bonds in the molecule.

Some molecules contain polar bonds but have no overall polarity. This is because the polar bonds in these molecules are arranged in such a fashion that the dipole moments cancel each other out.



Polarity and chemical reactivity

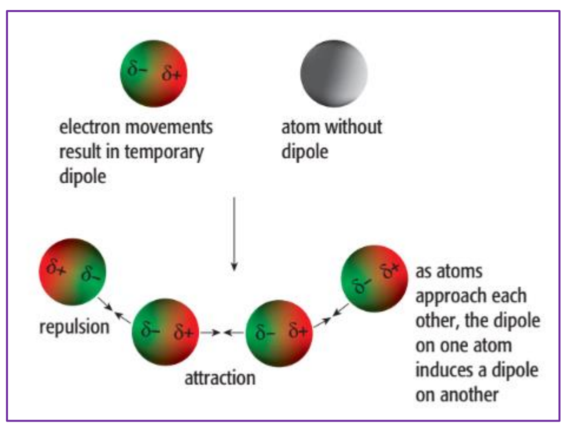
Many chemical reactions are started by a reagent attacking one of the electrically charged ends of a polar molecule; Chloroethane, C_2H_5Cl, is far more reactive than ethane, C_2H_6. This is because reagents such as OH– ions can attack the delta-positive carbon atom of the polarised C—Cl bond.

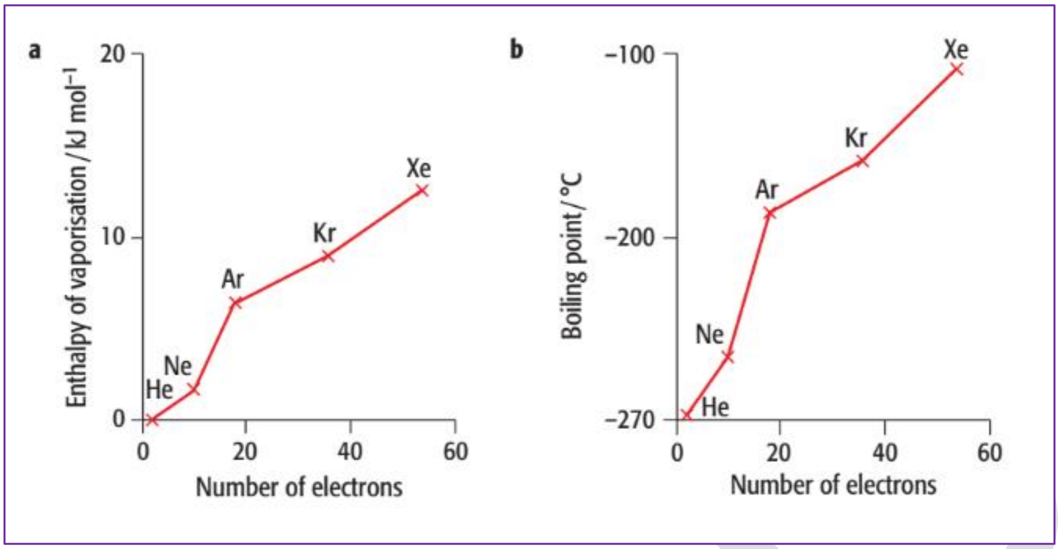


van der Waals’ forces

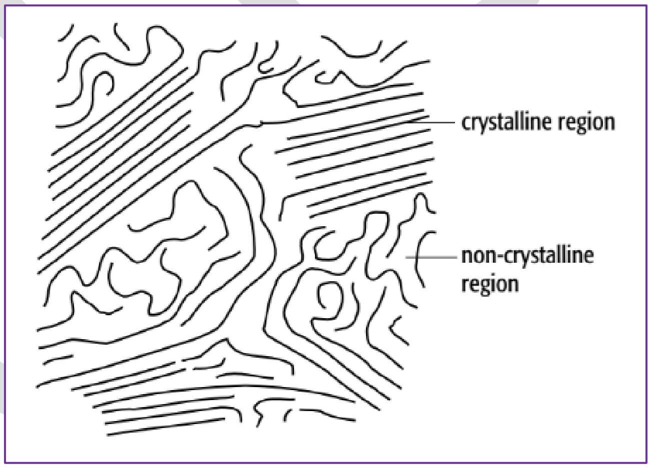
van der Waals’ forces are sometimes called temporary dipole–induced dipole forces. van der Waals’ forces increase with:

- increasing number of electrons (and protons) in the molecule
- increasing the number of contact points between the molecules – contact points are places where the molecules come close together





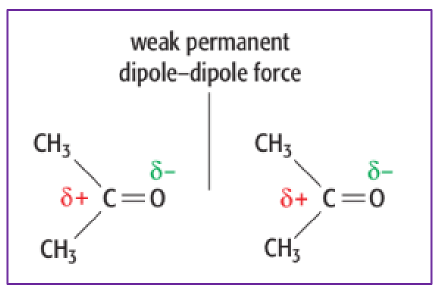
Two types of poly(ethene) are low-density poly(ethene), LDPE, and high-density poly(ethene), HDPE. Both have crystalline and non-crystalline regions in them. HDPE has more crystalline regions where the molecules are closer together than LDPE. The total van der Waals' forces are greater, so HDPE is the stronger of the two.



Permanent dipole–dipole forces

The forces between two molecules having permanent dipoles are called permanent dipole–dipole forces.

more energy is needed to break the intermolecular forces between propanone molecules than between butane molecules.



Hydrogen bonding

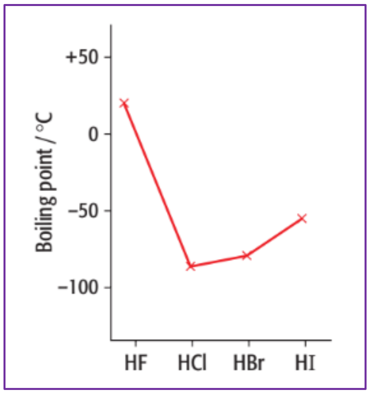
Hydrogen bonding is the strongest type of intermolecular force. For hydrogen bonding to occur between two molecules we need:

- one molecule having a hydrogen atom covalently bonded to F, O or N (the three most electronegative atoms)
- a second molecule having a F, O or N atom with an available lone pair of electrons.

The average number of hydrogen bonds formed per molecule depends on:

- the number of hydrogen atoms attached to F, O or N in the molecule
- the number of lone pairs present on the F, O or N

How does hydrogen bonding affect boiling point?



This leads to increased van der Waals' forces as the molecules get bigger. If hydrogen fluoride only had van der Waals' forces between its molecules, we would expect its boiling point to be about –90 °C.

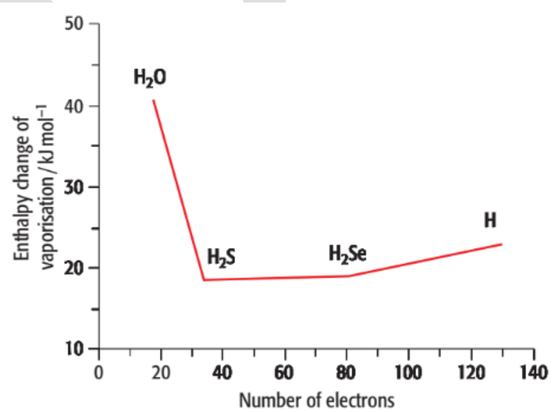
However, the boiling point of hydrogen fluoride is 20 °C, which is much higher. This is because of the stronger intermolecular forces of hydrogen bonding between the HF molecules.

The peculiar properties of water

- Enthalpy change of vaporisation and boiling point

the enthalpy change of vaporization of water is much higher. This is because water is extensively hydrogen bonded. The boiling point of water is also much higher.

- Ice is less dense than water



Bonding and physical properties

- Physical state at room temperature and pressure

  <u>Ionic compounds</u>

  Ionic compounds are solids at room temperature and pressure. This is because:

  - there are strong electrostatic forces (ionic bonds) holding the positive and negative ions together
  - the ions are regularly arranged in a lattice, with the oppositely charged ions close to each other.

  <u>Metals</u>

  Most metals have high melting points, high boiling points and high enthalpy changes of vaporisation.

  <u>Covalent compounds</u>

  It does not take much energy to overcome these intermolecular forces, so these substances have low melting points, low boiling points and low enthalpy changes of vaporisation compared with ionic compounds.

- Solubility

  Ionic compounds

  Most ionic compounds are soluble in water. This is because water molecules are polar and they are attracted to the ions on the surface of the ionic solid.

  Metals

  Metals do not dissolve in water. However, some metals, for example sodium and calcium, react with water.

  Covalent compounds

  Covalently bonded substances with a simple molecular structure fall into two groups.

  - Those that are insoluble in water. Most covalently bonded molecules are non-polar. Water molecules are not attracted to them so they are insoluble. An example is iodine.
  - Those that are soluble in water. Small molecules that can form hydrogen bonds with water are generally soluble. An example is ethanol
- Electrical conductivity

  Ionic compounds

  Ionic compounds do not conduct electricity when in the solid state. When molten, an ionic compound conducts electricity because the ions are mobile.

  Metals

  Metals conduct electricity both when solid and when molten.

  Covalent compounds

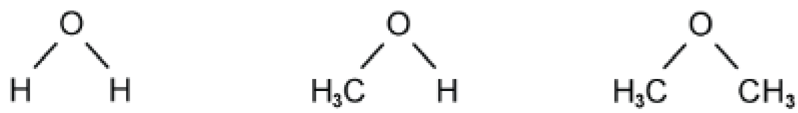
  Covalently bonded substances with a simple molecular structure do not conduct electricity.

EXERCISE

1.
   a. Ammonia, NH3, and methane, CH4, are the hydrides of elements which are next to one another in the Periodic Table. In the boxes below, draw the 'dot-and-cross' diagram of a molecule of each of these compounds. Show outer electrons only. State the shape of each molecule.
   b. Ammonia is polar whereas methane is non-polar. The physical properties of the two compounds are different.
      i. Explain, using ammonia as the example, the meaning of the term bond polarity.
      ii. Explain why the ammonia molecule is polar.
   c. State one physical property of ammonia which is caused by its polarity.
   d. When ammonia gas is mixed with hydrogen chloride, white, solid ammonium chloride is formed. State each type of bond that is present in one formula unit of ammonium chloride and how many of each type are present. You may draw diagrams.

2.

a. The structural formulae of water, methanol and methoxymethane, CH_3OCH_3, are given below.



   i. How many lone pairs of electrons are there around the oxygen atom in methoxymethane?
   ii. Suggest the size of the C-O-C bond angle in methoxymethane.

b. The physical properties of a covalent compound, such as its melting point, boiling point, vapour pressure, or solubility, are related to the strength of attractive forces between the molecules of that compound. These relatively weak attractive forces are called intermolecular forces. They differ in their strength and include the following.
   A. interactions involving permanent dipoles
   B. interactions involving instantaneous dipole-induced
   C. dipoles
   D. hydrogen bonds

   By using the letters A, B, or C, state the strongest intermolecular force present in each of the following compounds.
   For each compound, write the answer on the dotted line:

Ethanal	CH_3CHO
Ethanol	CH_3CH_2OH
methoxymethane	CH_3OCH_3
methylpropane	$(CH_3)_2CHCH_3$

c. Methanol and water are completely soluble in each other.
   i. Which intermolecular force exists between methanol molecules and water molecules that makes these two liquids soluble in each other?
   ii. Draw a diagram that clearly shows this intermolecular force. Your diagram should show any lone pairs or present on either molecule that you consider to be important.

d. When equal volumes of ethoxyethane, $C_2H_5OC_2H_5$, and water are mixed, shaken, and then allowed to stand, two layers are formed. Suggest why ethoxyethane does not fully dissolve in water. Explain your answer.

3.

a. This question is about electronegativity. The electronegativities of some elements are shown in Table 3.1 below.
   Define the term electronegativity.

b. Use Table 3.1 to explain the trend in electronegativity across the Periodic Table.

Table 3.1

Element	Electronegativity
Li	1.0
H	2.1
C	2.5
N	3.0
Cl	3.0

c. Explain how the carbon-hydrogen bond (such as in CH_4) differs from the nitrogen-hydrogen bond (such as in NH_3) in terms of the bond polarity.
d. Explain, in terms of electronegativity, why the bonding in ammonia (NH_3) is covalent but the bonding in lithium chloride (LiCl) is ionic.

4.
a. Both lithium and lithium chloride contain ions of lithium. However, the structure bonding and properties of these substances are very different. State how the ions are held together in solid lithium and in solid lithium chloride.
b. Table 4.1 below shows the melting and boiling points of lithium and lithium chloride. Explain what can be deduced from the information in Table 4.1.

Table 4.1

	Melting point (°C)	Boiling point (°C)
Lithium	180.5	1342
Lithium chloride	605.0	1382

c. Two students, A and B, are comparing the properties of lithium and lithium chloride. Student A states that both lithium and lithium chloride will conduct electricity, but Student B states that only lithium will conduct electricity. State whether Student A, Student B, or neither student is correct. Explain your answer.
d. Student A and B then went on to discuss the bonding in another substance, CaF_2. Explain, in terms of electrons, how CaF_2 is formed from its atoms.

5.

a. Alkenes contain a carbon to carbon double bond that consists of a σ bond and a π bond. Complete the diagram to show the areas of electron density for each bond. Label the σ bond and the π bond.
b. Use the information in Table 5.1 to explain why ethene contains stronger covalent bonds between carbons atoms than ethane.

Table 5.1.

Bond	Bond Length
C-C	150 pm
C=C	134 pm

c. Bond length and bond energies can be used to compare the reactivity of covalent molecules. Compare the reactivity of hydrogen halides using the information in Table 5.2.

Table 5.2

	Bond energy	Bond length (pm)
HCl	431	127
HBr	366	141
HI	299	161

d. The boiling points of the hydrogen halides are shown in Table 5.3.
e. Explain why hydrogen halides have relatively low boiling points despite having strong covalent bonds
  i. Explain why HF has a higher boiling point than HCl. You should refer to the van der Waals' forces found in each substance in your answer.
  ii. Explain why HF has a higher boiling point than HCl. You should refer to the van der Waals' forces found in each substance in your answer.

Table 5.3

Hydrogen halide	Boiling Point (K)
H-F	293
H-Cl	188
H-Br	207
H-I	238

6.

a. This question is about various polyatomic ions. The nitrate(V) ion, NO_3, is a polyatomic ion, bonded by covalent bonds. The three oxygen atoms are bonded by one single covalent bond, one double covalent bond and one coordinate bond. Draw the dot-and-cross diagram for NO_3.

b. An ionic compound has the empirical formula $H_4N_2O_3$. Suggest the formulae of the ions present in this compound.

c. Cyanide is a fast-acting chemical, which can be found in various forms and can have toxic effects on the body. Draw the dot-and-cross diagram for a CN-ion. Show the outer electrons only.

d.

i. Compare the average bond enthalpy in the cyanide ion to the average bond enthalpy of the C-N bond in methylamine, CH3NH2. Explain your answer.

ii. Explain why the C-N bond length in the cyanide ion is shorter than in methylamine.

7.

a. Amides are commonly used in industrial processes as solvents, and there are suggestions that the smallest amide, methanamide, $HCONH_2$, could function in a similar manner to water as a solvent for life on other planets. Draw the dot-and-cross diagram for methanamide, $HCONH_2$.

b. Predict and explain the H-C-N and C-N-H bond angles around the C and N atoms.

c. Predict the shape around each of the C and N atoms in $HCONH_2$.

d. State, with a reason, whether $HCONH_2$ is a polar molecule.

8.

a. The Pauling electronegativity values of different elements are shown in Fig 3.1.

H 2.1																
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.3											Al 1.5	Si 1.9	P 2.2	S 2.6	Cl 3.0
K 0.8	Ca 1.0	Sc 1.4	Ti 1.5	V 1.6	Cr 1.7	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.8	Ge 2.0	As 2.2	Se 2.6	Br 2.6

Fig. 3.1

A compound formed from magnesium and oxygen has a different structure to a compound formed from phosphorus and oxygen. Predict the type of bonds that will occur in each compound. Explain your answer.

b. Explain why the melting point of phosphorus (III) oxide, P_4O_6, is lower than that of magnesium oxide in terms of their bonding and structure.

c. Phosphorus(III) oxide, P_4O_6, contains no P-P or O-O bonds. In the P_4O_6 molecule, all oxygen atoms are bonded to two other atoms and all phosphorus atoms are bonded to three other atoms. Sketch a structure for P_4O_6.

d. Explain the difference in electronegativity shown in Fig. 3.1 between magnesium and calcium.

9.

a. Phosphorus reacts with chlorine to form PCl_5.
   i. State the shape of a molecule of PCl5 and give two different bond angles within a molecule of PCl_5.
   ii. Draw the dot-and-cross diagram of a molecule of PCl_5. Show the outer electrons only.

b. PCl_5 is an example of a compound that exists as two structures depending on the conditions.

$$2PCl_5\,(g) \rightleftharpoons [PCl_4]^+\,[PCl_6]^-(s)$$

Draw diagrams to suggest the shapes of $[PCl_4]^+$ and $[PCl_6]^-$.

c. A student suggests that the PCl_5 molecule has sp^3 hybridisation. Explain why the student is not correct.

d. Antimony(V) chloride is another Group 15 chloride. Under standard conditions, it is a liquid made from $SbCl_5$ molecules. Explain why phosphorus(V) chloride in its solid form has a higher melting point than antimony(V) chloride.

e. Under the right conditions, molecules of $SbCl_5$ join together to form Sb_2Cl_{10}. Complete Fig. 4.1 to show the bonding in Sb_2Cl_{10}.

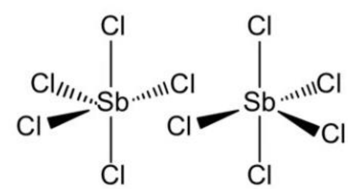


Fig. 4.1

f. The other Group 15 elements also form pentachlorides with the exception of nitrogen. Suggest a reason why nitrogen does not form NCl_5.

10.

a. Paperclips have a higher density than water. However, if a paperclip is lowered carefully onto the surface of water, the paperclip can float. When a drop of liquid soap is added to the water, the paperclip sinks. Suggest explanations for these observations.

b. Ammonia is highly soluble in water. Draw diagrams to show the two ways that intermolecular forces can form between a molecule of water and a molecule of ammonia to explain this.

c. NH_3, HCl and F_2 all exist as gases at room temperature and pressure. NH_3 has the highest boiling point of -33 °C. Predict whether HCl or F_2 has the lowest boiling point and explain why there is a difference between their boiling points.