3 Chemical bonding

Chemical reactions depend on the breaking of existing bonds and the forming of new bonds. To understand this process, you need to be aware of the different types of bonds and forces between atoms and molecules.

Ionic (electrovalent) bonding

- Ions are formed when atoms react and either gain or lose electrons. Metals usually lose electrons to form positively charged **cations** – for example, sodium forms Na^+. Hydrogen also loses its electron to form H^+; the ammonium ion, NH_4^+, is another example of a non-metallic cation.
- Non-metallic elements gain electrons to form negatively charged **anions** – for example, chlorine forms Cl^-. Groups of atoms, such as the nitrate ion, NO_3^-, may also carry negative charges.
- In forming cations or anions, the elements involved tend to either lose or gain outer electrons to attain the electronic configuration of the nearest noble gas, because these are very stable.
- You can see this when sodium reacts with chlorine to form sodium chloride:

  $Na + Cl \rightarrow Na^+ + Cl^-$

  2,8,1 2,8,7 2,8 2,8,8

  Note that 2,8 is the electronic configuration of neon, and 2,8,8 is that of argon, the two noble gases nearest in electronic configuration to sodium and chlorine respectively.

KEY TERMS

A positive ion is called a **cation**.

A negative ion is called an **anion**.

NOW TEST YOURSELF

1 Using your knowledge of the Periodic Table, predict the charges and electronic configuration of the *ions* formed by the elements in the following table.

Element	**Charge on the ion**	**Electronic configuration**
Magnesium		
Lithium		
Oxygen		
Aluminium		
Fluorine		
Sulfur		

How do we know that ions exist?

The evidence for the existence of ions comes from electrolysis. An electric current can be passed through a molten salt or an aqueous solution of the salt (Figure 3.1). This relies on the movement of ions in the solution carrying the charge, followed by the loss or gain of electrons at the appropriate electrode to form elements.

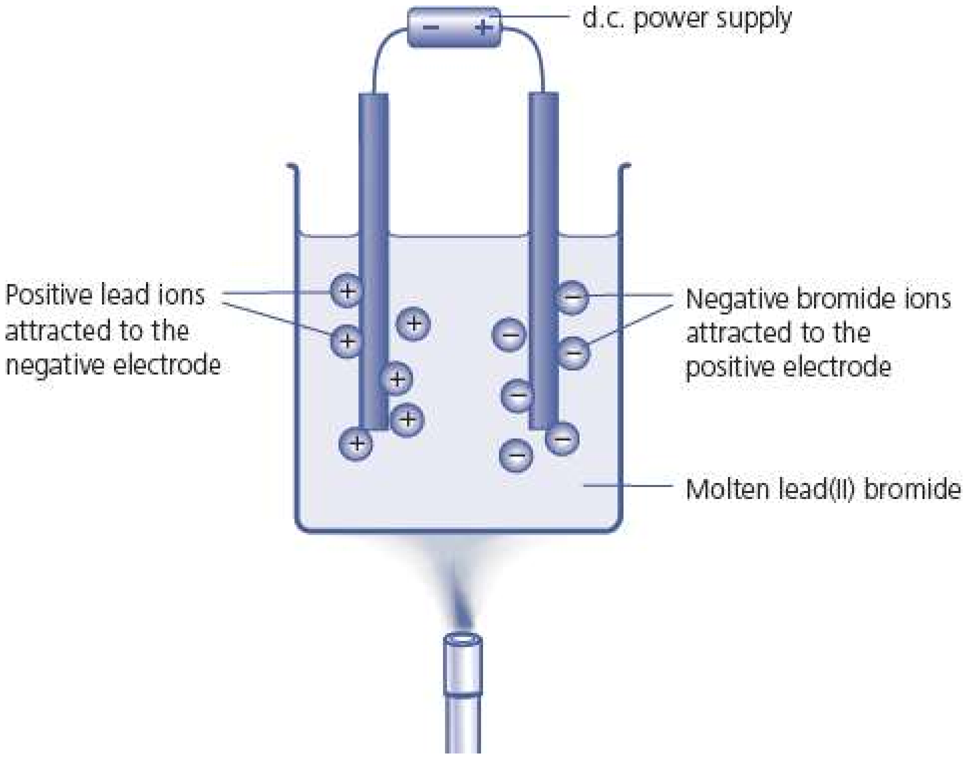


Figure 3.1 Electrolysis

Ionic crystals

In the solid state (see Chapter 4), cations and anions come together to form ionic crystals. These consist of a giant three-dimensional lattice of ions (Figure 3.2). The structure of these crystals depends on the relative sizes of the anions and cations, and on the stoichiometry of the compound concerned.

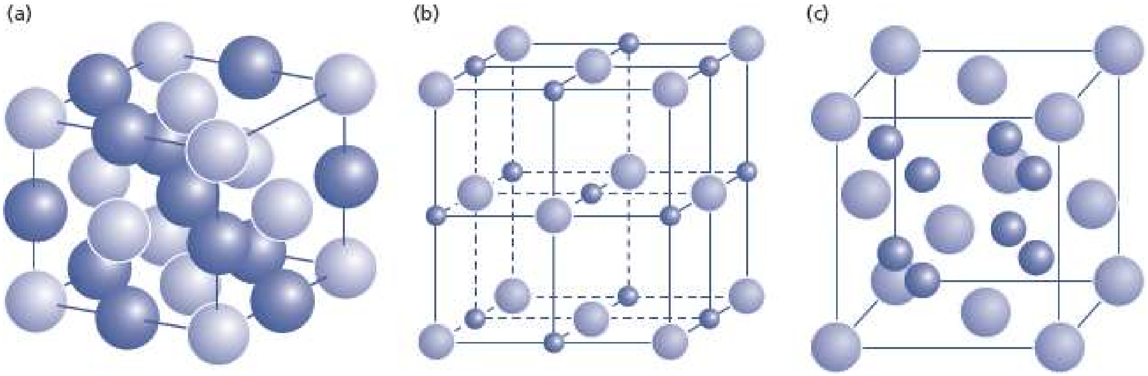


Figure 3.2 Crystal structures of (a) sodium chloride, (b) magnesium oxide, (c) calcium fluoride

The three-dimensional structure in the crystal is held together by the net attractive forces between the oppositely charged ions. There are also longer-range repulsive forces between ions of the same charge, but because these are longer range they are weaker.

Covalent and coordinate (dative) bonding

- The major difference between ionic (electrovalent) bonding and covalent bonding is that in ionic bonding, electrons are *transferred* from one atom to another to create charged ions; in covalent bonding, electrons are *shared* between atoms in pairs.
- It is important to remember that electrons do not ‘circle around the nucleus’ but exist in a volume of space surrounding the nucleus where there is a high probability of finding an electron – these are known as orbitals.
- A covalent bond is formed by the overlap of orbitals containing electrons and the attraction of these bonding electrons to the nuclei of both atoms involved.
- It is not essential to have atoms of different elements to form covalent bonds, so it is possible for an element to form molecules that have covalent bonds between the atoms, e.g. chlorine, Cl_2 (Figure 3.3).

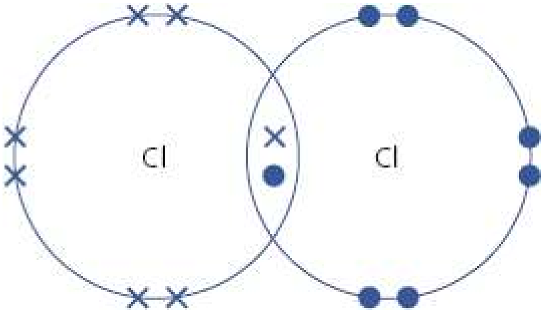


Figure 3.3 Covalent bonding in chlorine (electrons in inner shells have been omitted for clarity)

Dot-and-cross diagrams

- These are diagrams that represent the behaviour of bonding electrons in the formation of both electrovalent bonds and covalent bonds, with the electrons from one atom represented by dots and those from the other atom by crosses. The electrons are, of course, identical but this system helps to visualise what is happening as the bonds are formed.

- In an electrovalent bond, one or more electrons are transferred from one element (usually a metal) to another element (usually a non-metal). The transfer in the formation of magnesium oxide is shown in Figure 3.4.

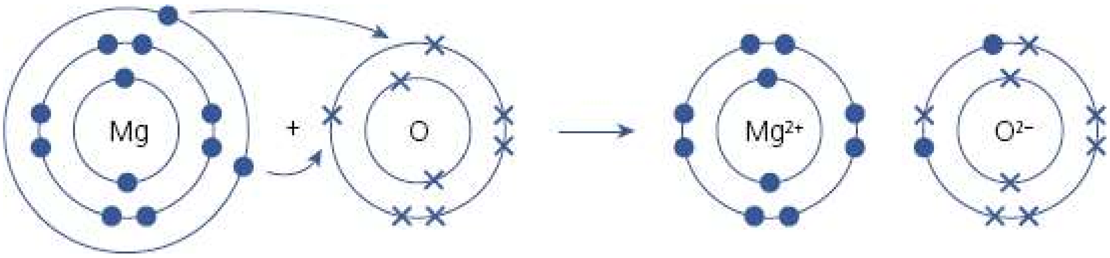


Figure 3.4 Electron transfer in the formation of magnesium oxide

NOW TEST YOURSELF

2 Use a copy of the Periodic Table to help you draw dot-and-cross diagrams for:

- a hydrogen, H_2
- b water, H_2O
- c carbon dioxide, CO_2
- d methane, CH_4
- e lithium fluoride, LiF

- The bonded atoms in a covalent compound usually have a ‘share’ of an octet of electrons associated with each atom, but this is not always the case. For example, in boron trichloride, BCl_3, there are only six outer-shell electrons associated with the boron atom (Figure 3.5).
- Coordinate (dative) covalent bonds are formed when both electrons in a pair come from the same atom, for example in NH_4^+ (Figure 3.6(a)).
- Once formed, the bond cannot be distinguished from the other covalent bonds in the compound. Figure 3.6(b) shows the same behaviour in Al_2Cl_6.

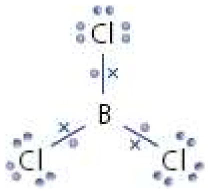


Figure 3.5 Boron trichloride

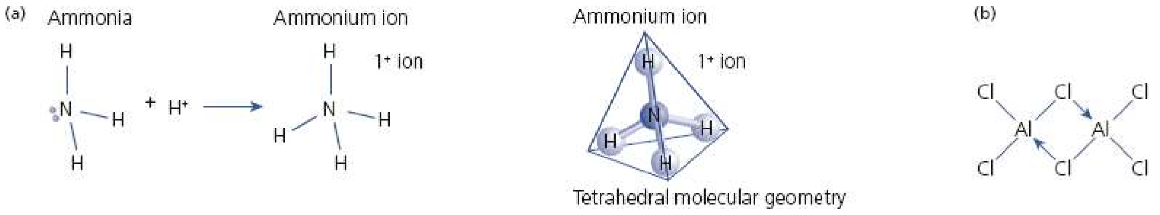


Figure 3.6 Coordinate bonding in (a) ammonium ion, (b) aluminium chloride

- There are many other examples of this type of covalent bonding – for example, in carbon monoxide, CO, and in the nitrate ion, NO_3^-, and particularly in the formation of transition metal complexes. (See Chapter 28.)
- It is possible to have multiple covalent bonds, depending on the number of pairs of bonding electrons involved. This can occur in simple molecules such as oxygen, O_2 (Figure 3.7(a)) but is particularly important in carbon compounds such as ethene, C_2H_4 (Figure 3.7(b)). (See Chapter 14.)

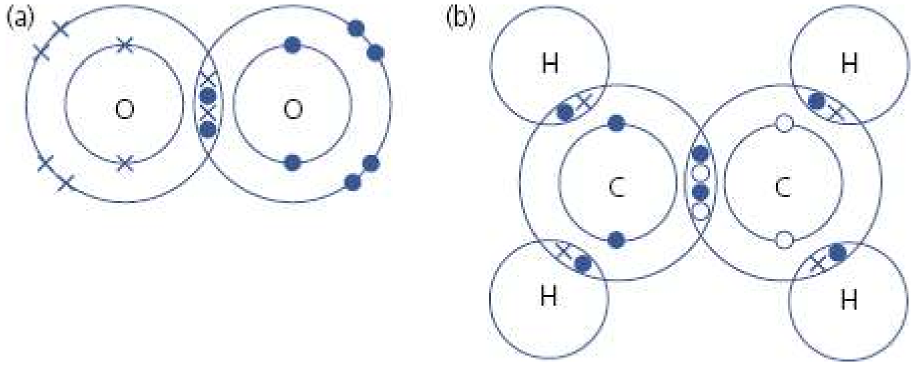


Figure 3.7 Multiple covalent bonding in (a) oxygen, (b) ethene

Simple molecular shapes

- Unlike ionic (electrovalent) bonds, which have no particular direction, covalent bonds are directional. This means that covalently bonded molecules have distinctive shapes depending on the number of bonds in a molecule – this is because the bonding pairs of electrons repel other pairs.

- Figure 3.8 shows the basic shapes that molecules containing up to four electron pairs can adopt.

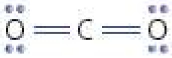
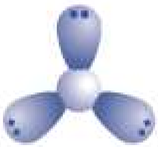
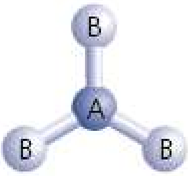
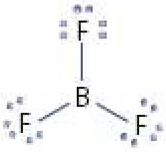
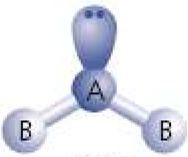
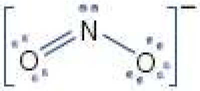
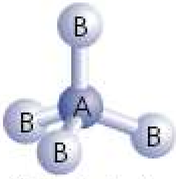
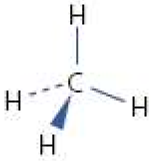
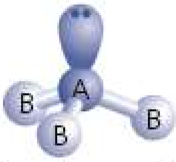
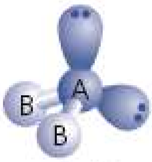
Total number of electron pairs	Electron geometry	Molecular geometry	Example
2 pairs	 Linear	 Linear	
3 pairs	 Trigonal planar	 Trigonal planar	
		 Bent	
4 pairs	 Tetrahedral	 Tetrahedral	
		 Trigonal pyramidal	
		 Bent	

Figure 3.8 Shapes of molecules

- In some circumstances more than four pairs of electrons can be involved, as in the case of sulfur hexafluoride, SF_6. The repulsion effect still applies.

In this case the molecule is octahedral.

- In addition, any non-bonding pairs (lone pairs) of electrons will repel bonded pairs but occupy rather more space. This means that the bond angles are widened.
- You can see this effect if you compare three molecules, each with four pairs of electrons – methane, CH_4, ammonia, NH_3, and water, H_2O. The normal tetrahedral angle is 109.5°, but ammonia has one lone pair of electrons, which squeezes the H–N–H bond angle to 107°. In water, the two lone pairs of electrons squeeze the H–O–H bond angle even more, reducing it to 104.5°. This is shown in Figure 3.9.

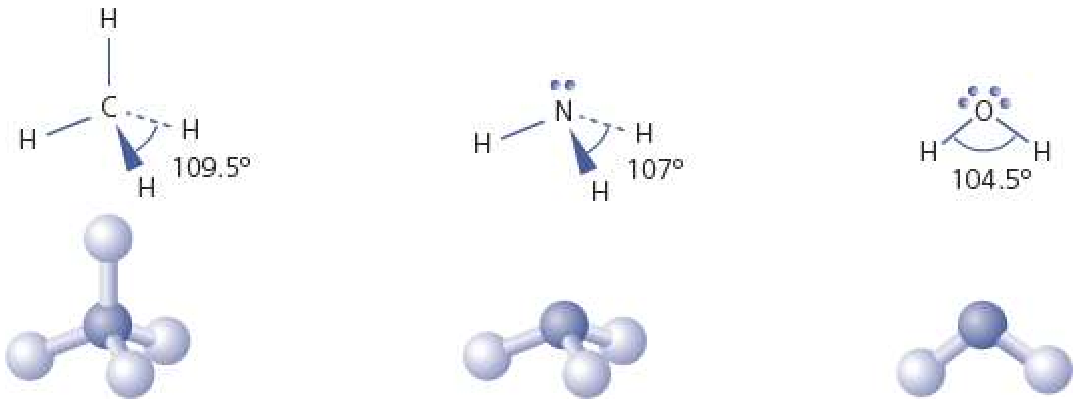


Figure 3.9 Although the three molecules shown all have four pairs of electrons arranged approximately tetrahedrally, the molecules are described as CH_4 tetrahedral, NH_3 pyramidal and H_2O bent

As electron pairs have similar (negative) charge they will repel each other. The electron pairs in the outer shell of an atom will experience the least repulsion because they are as far apart as possible. This is true for both bonded and non-bonded or lone pairs. This idea is known as the **valence-shell electron-pair repulsion theory** or **VSEPR** for short.

KEY TERM

VSEPR theory The idea that atoms in a molecule achieve an arrangement that minimises the repulsion between electron pairs.

To work out the shape of a molecule:

- Draw the dot-and-cross structure of the molecule and count the number of electron pairs around the atom.

- These pairs will be as far apart as possible around the atom, with the angles between them dependent on the number of pairs.
- Remember that orbitals containing lone pairs of electrons are larger than those containing bonded pairs and hence repel bonded pairs more strongly.
- Note that, although they influence the shape of a molecule, lone pairs are not included when describing a molecule's shape (see Figure 3.9).

NOW TEST YOURSELF

3 Use VSEPR to work out the shapes of the following molecules:

  a BeH_2

  b BF_3

  c SF_6

Giant molecular structures

As well as forming simple molecules like those shown in Figure 3.8, it is possible to form giant molecular structures. In the Cambridge syllabus, these are confined to different structural forms of carbon (diamond and graphite) and silicon dioxide, which is similar to diamond. Examples of these are shown in Figures 4.10 and 4.11 (see page **39**).

Bond properties and electronegativity

- When two atoms join by forming a covalent bond, the reaction is exothermic – energy is given out. It follows that to break that covalent bond, energy must be supplied.

KEY TERM

A **bond energy** is defined as the average standard enthalpy change for the breaking of one mole of bonds in a gaseous molecule to form gaseous atoms:

$\mathrm{Br{-}Br(g)} + \text{bond energy} \rightarrow \mathrm{2Br(g)}$

- From this you can see that **bond energies** are an indication of the strength of the forces holding the atoms together in a covalent molecule.
- Bond energies can vary from around 150 kJ $\mathrm{mol^{-1}}$ for molecules with weak bonds (such as I–I) to 350–550 kJ $\mathrm{mol^{-1}}$ for stronger bonds (such as C–C and O–H), to around 1000 kJ $\mathrm{mol^{-1}}$ for very strong bonds (such as $\mathrm{N{\equiv}N}$).
- Bond energy, E, increases with the number of electron pairs making up the bond. For example, $E(\mathrm{C{-}C}) = 350\ \mathrm{kJ\ mol^{-1}}$, $E(\mathrm{C{=}C}) = 610\ \mathrm{kJ\ mol^{-1}}$ and $E(\mathrm{C{\equiv}C}) = 840\ \mathrm{kJ\ mol^{-1}}$
- Bond length is defined as the distance between the centres of the atoms at either end of the bond. The length of a bond depends on a number of factors, particularly the number of pairs of electrons making up the bond.
- For the three carbon–carbon bonds described above, the bond lengths are C–C, 154 pm; C=C, 134 pm and $\mathrm{C{\equiv}C}$, 120 pm (1 pm is 1 picometre or 1×10^{-12} metres).
- Because most covalent bonds are formed between different atoms, and different nuclei have different attractions for electrons, it follows that the electrons in many covalent bonds are pulled closer to one atom than the other, and this leads to **bond polarity**.

KEY TERM

The effect of unequal sharing of electrons is called **bond polarity**.

Electronegativity

The degree of attraction depends on the nature of the two atoms involved – in particular, the **electronegativity** difference between the atoms involved.

KEY TERM

Electronegativity is the power of an atom to attract electrons in a covalent bond to itself.

The factors which affect the electronegativity of an atom are:

- the nuclear charge
- the atomic radius
- shielding by any inner shells or sub-shells of electrons

When we look at the Periodic Table, electronegativity can vary both across a period and down a group.

Remember that:

- Electronegativity increases from left to right across a period in the Periodic Table.
- Electronegativity decreases down a group.
- Small atoms with many protons in the nucleus have a high electronegativity.
- The bigger the difference in the electronegativities of the two atoms, the more polar the bond will be.

If the difference in electronegativity values is large enough, the bonding electron(s) will be completely transferred to the other atom. We can see this if we compare the electronegativity values for some pairs of atoms.

	F–F	**H–F**	**Li–F**
Electronegativities	4.0 4.0	2.2 4.0	1.0 4.0
Bonding	covalent	polar covalent	ionic

NOW TEST YOURSELF

4 Use the electronegativities of the elements to decide which of the following compounds is

a the most ionic

b the most covalent

Give reasons for your answers.

Compounds: MgO, MgS, Na_2O, Na_2S, SO_2

Element	**Electronegativity**

Element	**Electronegativity**
Magnesium	1.2
Sodium	0.9
Oxygen	3.5
Sulfur	2.5

Orbital overlap: σ-bonds and π-bonds

- Covalent bonds are commonly found in compounds of carbon and it is important to understand how such bonds are formed – but the same principles apply to all covalent bond formation.
- In carbon atoms, the 2s- and 2p-orbitals are quite close in energy. This means that it is possible to promote one of the 2s-electrons to the empty 2p-orbital.
- The energy required for this promotion is more than compensated for by the energy released when four bonds are formed (compared with the two bonds that could have been formed using the two 2p-orbitals that each contained a single electron). This can be seen in Figure 3.10.

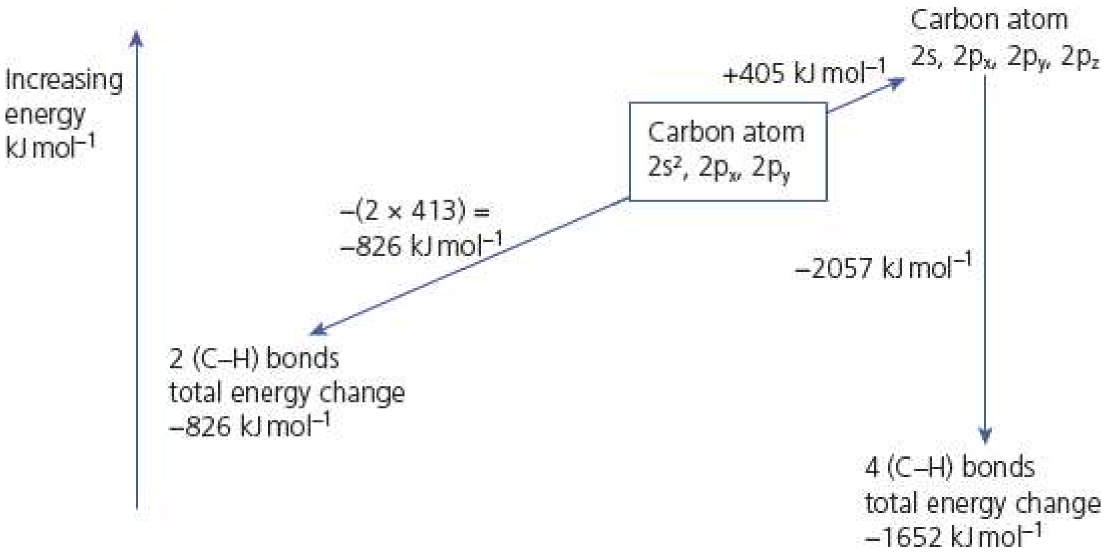


Figure 3.10 Energy benefit in forming four carbon–hydrogen bonds

- The four electrons form four identical **sigma** orbitals that each have some s characteristics and some p characteristics. These are known as sp^3 hybrid orbitals. In forming methane, CH_4, they overlap with the s-orbitals of hydrogen atoms.
- There are two other ways in which the orbitals of a carbon atom can be sigma hybridised. First the s-orbital can be hybridised with two of the p-orbitals to form three sp^2-orbitals, leaving the remaining 2p-orbital unchanged. The three sp^2-orbitals lie in a plane 120° apart, with the 2p-orbital at right angles to this. This is the type of hybrid orbital formed by the carbon atoms in ethene and benzene.
- Look at the structure of ethene. One pair of sp^2-orbitals overlap forming a σ-bond. This brings the 2p-orbitals on the two carbons close enough together for them to overlap forming a **π-bond**. The bonding in ethene is shown in Figure 3.11.

KEY TERMS

Bonds formed from the overlap of orbitals with some s character are called **sigma bonds** (σ-bonds).

Bonds formed by the overlap of p-orbitals are called **pi bonds** (π-bonds).

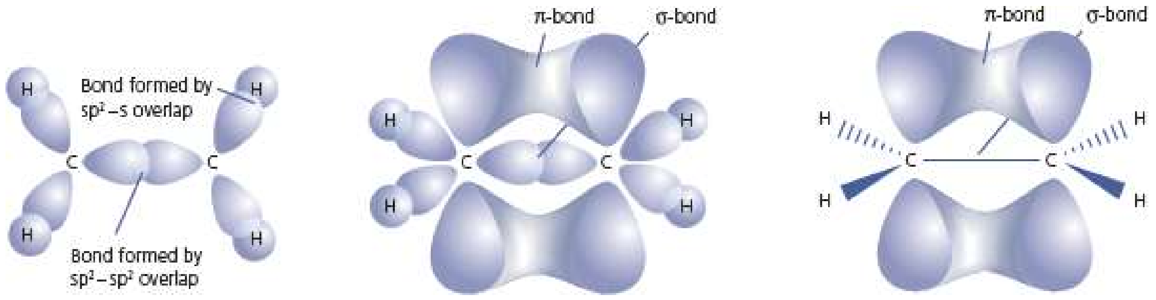


Figure 3.11 Bonding in ethene

Intermolecular forces

As well as ionic (electrovalent) bonding and covalent bonding there are a number of other forces that exist between molecules. These are:

- van der Waals’ forces
- permanent dipole–dipole interactions
- hydrogen bonds

van der Waals’ forces

- These are the weakest of the forces. They act between all particles, whether they are polar or non-polar. They exist because of the movements of electrons in atoms and molecules that in turn cause instantaneous dipoles. These induce dipoles in neighbouring particles.
- It is because of van der Waals’ forces that some substances expected to exist as gases actually form liquids. Examples of this include $CHCl_3$, Br_2 and some of the Group 18 elements.

Permanent dipole–dipole interactions

These occur between polar covalent molecules, i.e. those containing different elements. One example is hydrogen chloride, HCl, as shown in Figure 3.12. Chlorine has a higher electronegativity than hydrogen.

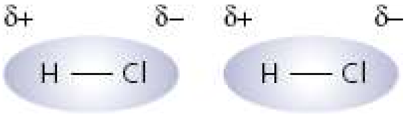


Figure 3.12 Dipole–dipole interactions in hydrogen chloride

Hydrogen bonds

- There is a particular sort of comparatively strong dipole–dipole interaction between molecules containing hydrogen bonded to nitrogen, oxygen or fluorine atoms.
- These bonds result from the lone pairs of electrons on the nitrogen, oxygen or fluorine atoms, so that the hydrogen atoms can be considered to be acting as a ‘bridge’ between two highly electronegative atoms.
- This form of bonding can have significant effects on the physical properties of the compound concerned. The most common, and important to us, is water (Figure 3.13).

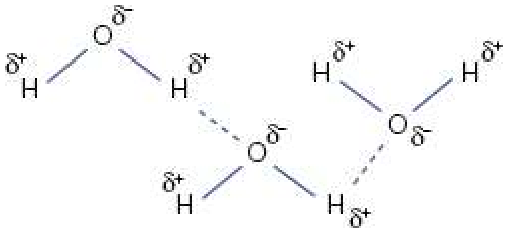


Figure 3.13 Hydrogen bonding in water

- Based on its molecular mass, water would be expected to exist as a gas at room temperature. The fact that it exists as a liquid is due to hydrogen bonding. Also, water has surface tension, which enables some insects to walk on its surface. The fact that ice is less dense than liquid water and floats on it is also a result of hydrogen bonding.
- Another of these compounds is ammonia, shown in Figure 3.14, which can be liquefied relatively easily.

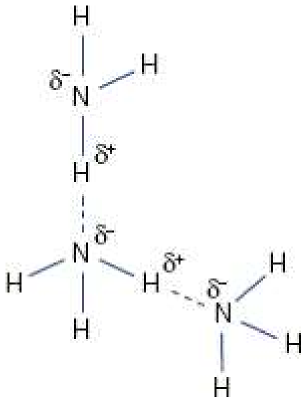


Figure 3.14 Hydrogen bonding in ammonia

Metallic bonding

- Metals have distinctive properties, many of which are based on the fact that metals have a structure involving a regular lattice of atoms, in much the same way as an ionic (electrovalent) crystal.
- The main difference is that all the atoms in a metallic lattice are the same and the outer electrons are not held by the atoms but are delocalised throughout the lattice (Figure 3.15). It is these mobile electrons that give metals their electrical conductivity.

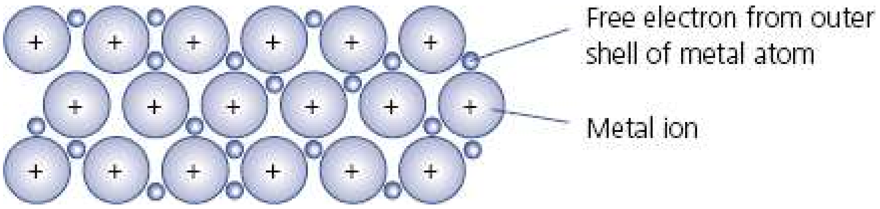


Figure 3.15 Metallic bonding

NOW TEST YOURSELF

5 For each of the materials in the table, predict the main type(s) of intermolecular forces that exist in the material.

Material	Intermolecular force
Methanol, CH_3OH	
Magnesium oxide, MgO	
Iodine chloride, ICl	
Argon, Ar	
Aluminium, Al	

Bonding and physical properties

- The type of bonding in a substance affects its physical properties.
- Ionic (electrovalent) compounds, which have giant lattices of oppositely charged ions, tend to have high melting points and boiling points. Many dissolve in water and they conduct electricity when molten.
- Covalently bonded compounds tend to be gases, liquids or low melting point solids. Many dissolve in covalent solvents and they are electrical insulators.
- Metals have a giant lattice structure with a ‘sea’ of mobile delocalised electrons. In general, metals have high melting points, can be bent and shaped, and are good electrical conductors.

REVISION ACTIVITY

a What is the difference between a covalent bond and an ionic (electrovalent) bond?

b Put the following intermolecular bonds in order of increasing bond strength, starting with the weakest:

hydrogen, permanent dipole–dipole, van der Waals'

c What is the bond angle in BF_3?

d Why is there a difference in the H–X–H bond angles in CH_4 and NH_3?

e Draw a dot-and-cross diagram to show the bonding in NH_4^+.

f The table shows the electronegativities of the elements of Period 2.

Element	Li	Be	B	C	N	O	F
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0

Use the data in the table to predict the direction of polarisation in the following bonds.

- B–F
- Li–O
- N–O

Which of these bonds is the most polar?

END OF CHAPTER CHECK

By now you should be able to:

- define electronegativity of atoms and explain its influence on bonding
- define and describe ionic bonding
- define metallic bonding
- define and describe covalent bonding and coordinate (dative covalent) bonding

- state and explain the shapes of molecules using VSEPR theory
- describe and explain hydrogen bonding, van der Waals' forces, bond polarity and bond properties
- construct and use dot-and-cross diagrams