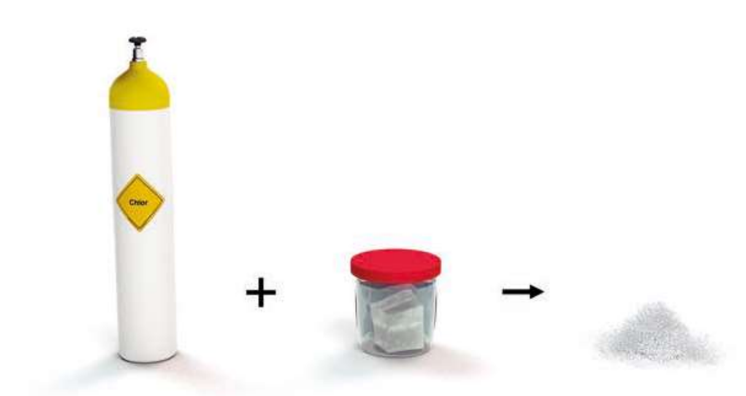
7 IONIC BONDING

We have already looked at the definition of a compound. A compound is formed when two or more elements chemically combine. In this chapter we are going to look at one way in which elements can chemically combine: by the transfer of electrons to form ionic compounds.



▲ Figure 7.1 The properties of a compound are very different from those of the elements. Sodium (an element) is a dangerously reactive metal. It is stored under oil to prevent it reacting with air or water. Chlorine (an element) is a very poisonous, reactive gas. But salt, sodium chloride (an ionic compound), is safe to eat in small quantities.

LEARNING OBJECTIVES

- Understand how ions are formed by electron loss or gain.
- Know the charges of these ions:
  - metals in Groups 1, 2 and 3
  - non-metals in Groups 5, 6 and 7
  - Ag^{+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Pb^{2+}, Zn^{2+}
  - hydrogen (H^{+}), hydroxide (OH^{-}), ammonium (NH_4^{+}), carbonate (CO_3^{2-}), nitrate (NO_3^{-}), sulfate (SO_4^{2-}).
- Write formulae for compounds formed between the ions listed above.
- Draw dot-and-cross diagrams to show the formation of ionic compounds by electron transfer, limited to combinations of elements from Groups 1, 2, 3, 5, 6 and 7 *(only outer electrons need be shown).*
- Understand ionic bonding in terms of electrostatic attractions.
- Understand why compounds with giant ionic lattices have high melting and boiling points.
- Know that ionic compounds do not conduct electricity when solid, but do conduct electricity when molten and in aqueous solution.

IONIC BONDING

Sodium chloride is probably the best-known example of an ionic compound – one that is held together by **ionic bonding**. There are lots of other ionic compounds, such as magnesium oxide, calcium fluoride and zinc bromide. What you will realise about all these compounds is that they all contain a metal combined with a non-metal.

You can recognise ionic compounds because they (usually) contain a metal.

HINT

There are one or two exceptions to this: there are ionic compounds that do not contain a metal, for example those containing the ammonium ion (such as NH_4Cl, $(NH_4)_2SO_4$. We will look at these later.

KEY POINT

This is a simplification! In reality, you don't react sodium with chlorine atoms, but with chlorine molecules, Cl_2.

KEY POINT

You can check that sodium does have a positive charge. If you look at the Periodic Table you will see that sodium has an atomic number of 11, so it has 11 protons in its nucleus. Protons have a positive charge so the charge on the nucleus is 11+. In the sodium **atom** there are 11 electrons, each with a negative charge. These cancel out the 11+ on the nucleus and there is no overall charge. However, in the sodium ion there are only 10 electrons, so with 11+ and 10– there is an overall charge of 1+.

When a non-metal such as chlorine combines with a metal such as sodium, the chlorine atom has a stronger attraction for electrons than the sodium atom and *an electron is transferred from the outer shell of the sodium atom to the outer shell of the chlorine atom*. Because an electron has a negative charge, when something gains an electron it becomes negatively charged, and when something loses an electron it becomes positively charged.

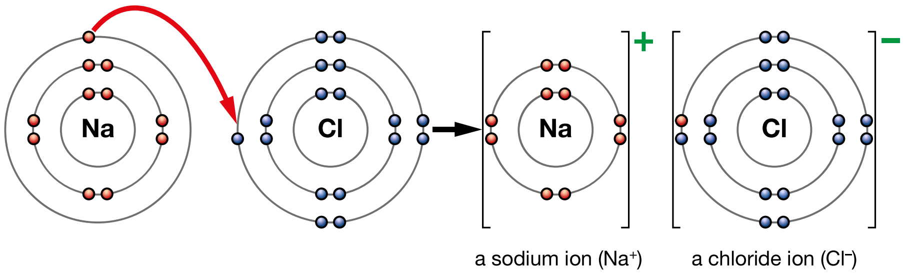


Figure 7.2 Ionic bonding in sodium chloride. Ionic bonding involves the transfer of electron(s).

The charged particles that are formed are called **ions**.

Ions are charged particles formed when atoms (or groups of atoms) lose or gain electrons. Ions can have either a positive or a negative charge.

- A positive ion is called a **cation**, for example Na^+.
- A negative ion is called an **anion**, for example Cl^-.

When an ionic compound is formed, electron(s) are transferred from a metal atom to a non-metal atom to form positive and negative ions. Ionic compounds have ionic bonding. *Ionic bonding is the strong electrostatic attraction between positive and negative ions.*

KEY POINT

Electrostatic attraction simply means that positively charged particles attract negatively charged particles.

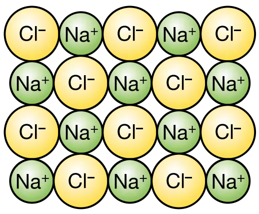


Figure 7.3 Part of the structure of a sodium chloride crystal. The structure is held together by the attraction between positive and negative ions.

Ionic bonding is often shown using **dot-and-cross diagrams**. Figure 7.4 is an example of a dot-and-cross diagram. Although the electrons are drawn as dots or as crosses, there is absolutely no difference between them in reality. The dots and the crosses simply show that the electrons have come from two different atoms. You could equally well use two different coloured dots (as in Figure 7.2), or two different coloured crosses.

IONIC BONDING IN MAGNESIUM OXIDE

A dot-and-cross diagram for MgO is shown in Figure 7.4.

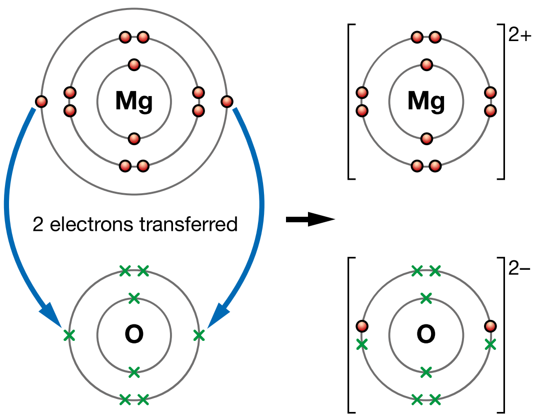
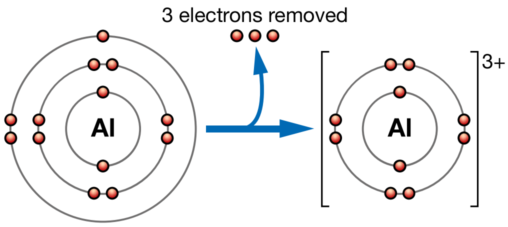


Figure 7.4 A dot-and-cross diagram for magnesium oxide. When drawing these diagrams, don't forget the charges on the ions.

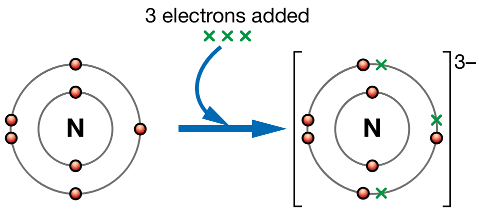
Two electrons are transferred from a magnesium atom to an oxygen atom to form Mg^{2+} and O^{2-} ions.

THE SIGNIFICANCE OF NOBLE GAS ELECTRONIC CONFIGURATIONS IN IONIC BONDING

If you look at the electronic arrangements of the ions formed in Figures 7.2, 7.4, 7.5 and 7.6, each of them has a noble gas electronic configuration: [2, 8] (the same as neon) or [2, 8, 8] (the same as argon). For the first 20 elements, atoms lose or gain electrons so that they achieve a noble gas electronic configuration. The elements in Groups 1, 2 and 3 of the Periodic Table will lose their outer shell electrons to form 1+, 2+ and 3+ ions, and the elements in Groups 5, 6 and 7 will gain electrons to form 3–, 2– and 1– ions.



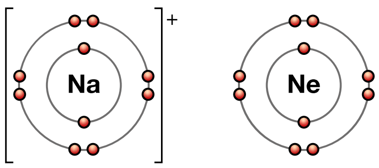
▲ Figure 7.5 An aluminium atom loses its 3 outer shell electrons to form an Al^{3+} ion.



▲ Figure 7.6 A nitrogen atom gains 3 electrons to form the nitride ion (N^{3-}).

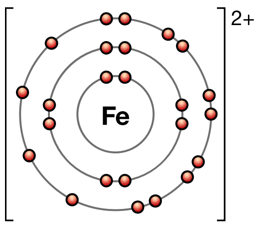
KEY POINT

We sometimes use the word **isoelectronic**, which means 'have the same number of electrons'. So, when sodium forms an ion (electronic configuration [2, 8]) it becomes isoelectronic with neon [2, 8].



▲ Figure 7.7 Na^+ and Ne are isoelectronic – they have the same number of electrons.

Elements in Groups 1, 2, 6 and 7 always form ions that are isoelectronic with the nearest noble gas atom. For example, rubidium (Rb), which is in Group 1, has 1 electron in its outer shell and will lose this outer shell electron to form a 1+ ion, which has the same number of electrons as a krypton (Kr) atom. Iodine is in Group 7, so it has 7 electrons in its outer shell; it will gain 1 electron when it forms an ion to form a 1– ion. This 1– ion has the same number of electrons as a xenon (Xe) atom.



▲ Figure 7.8 An Fe^{2+} ion – definitely not a noble gas structure!

However, there are a lot of common ions that don't have noble gas structures. Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Ag^+ and Pb^{2+} are all ions that you will come across during the International GSCE course, although you won't have to write their electronic structures. Not one of them has a noble gas structure.

OTHER EXAMPLES OF IONIC BONDING

Ionic bonds are usually formed only if small numbers of electrons need to be transferred, typically 1 or 2, but occasionally 3.

LITHIUM FLUORIDE

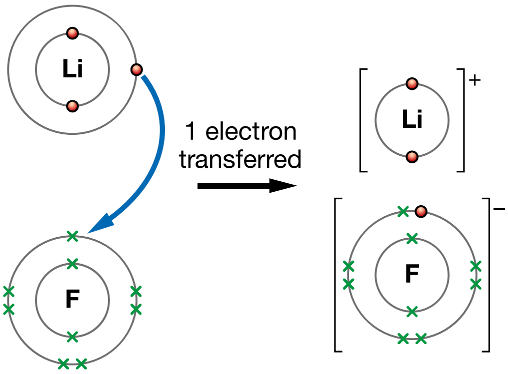


Figure 7.9 A dot-and-cross diagram for lithium fluoride

The lithium atom has 1 electron in its outer shell that is easily lost, and the fluorine has space to receive one. One electron is transferred from the lithium atom to the fluorine atom. Lithium fluoride is held together by the strong electrostatic attractions between positive lithium (Li^+) ions and the negative fluoride (F^-) ions.

CALCIUM CHLORIDE

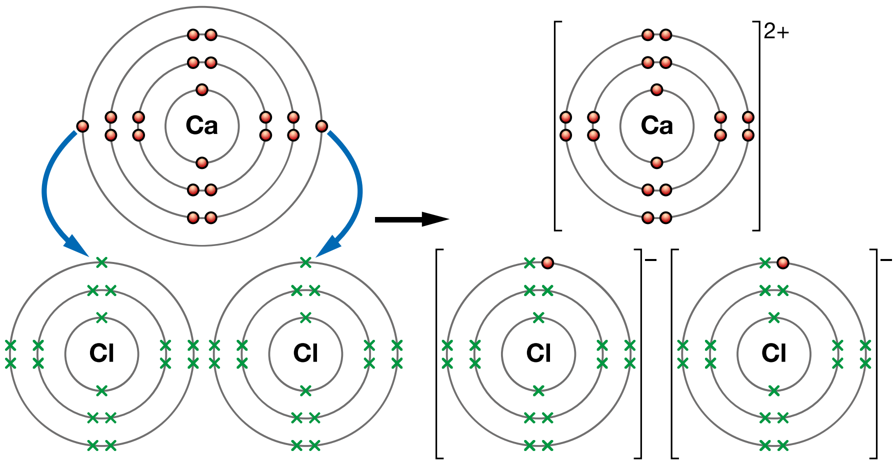


Figure 7.10 A dot-and-cross diagram to show the formation of calcium chloride.

The calcium atom [2, 8, 8, 2] has 2 electrons in its outer shell but each chlorine atom [2, 8, 7] only has room in its outer shell to take one of them. You need two chlorines for every calcium. The 2 electrons are transferred from the outer shell of a calcium atom to two chlorine atoms, one to each. The formula for calcium chloride is therefore $CaCl_2$. There will be very strong electrostatic attractions holding the ions together because of the 2+ charge on the calcium ions.

FORMULAE FOR IONIC COMPOUNDS

There are so many different ionic compounds that you might encounter at International GCSE that it would be impossible to learn all their formulae. You need a simple way to work them out. You could work out a few from first principles, using their electronic structures, but that would take ages. Others would be too difficult. You need a simple, shortcut method.

THE NEED FOR EQUAL NUMBERS OF PLUSES AND MINUSES

Ions are formed when atoms, or groups of atoms, lose or gain electrons. They carry an electrical charge, either positive or negative. Compounds are electrically neutral. Therefore in an ionic compound there must be the right number of each sort of ion, so that the total positive charge exactly cancels out the total negative charge. Obviously, then, if you are going to work out a formula, you need to know the charges on the ions.

CASES WHERE YOU CAN WORK OUT THE CHARGE ON AN ION

Any element in Group 2 has 2 outer electrons, which it will lose to form a 2+ ion. Any element in Group 6 has 6 outer electrons, and it has room to gain 2 more; this leads to a 2– ion. Similar arguments apply in the other groups shown in Table 7.1.

Table 7.1 The charges on an ion in Groups 1–7

Group in Periodic Table	Charge on ion	Example
1	1+	Na^+
2	2+	Mg^{2+}
3	3+	Al^{3+}
5	3–	N^{3-}
6	2–	O^{2-}
7	1–	Br^-

HINT

You will always have a copy of the Periodic Table, even in an exam. That means that you can always find out which group an element is in. Elements in Group 4 only form a few ionic compounds and the situation is a bit more complicated. You will need to learn that lead forms a 2+ ion (Pb^{2+}).

REMINDER

Remember that all metals form positive ions.

CASES WHERE THE NAME TELLS YOU THE CHARGE

All metals form positive ions. Names such as lead(II) oxide, iron(III) chloride or copper(II) sulfate tell you directly about the charge on the metal ion. The number after the metal tells you the number of charges, so:

- lead(II) oxide contains a Pb^{2+} ion
- iron(III) chloride contains an Fe^{3+} ion
- copper(II) sulfate contains a Cu^{2+} ion.

You cannot work out the charges for some ions, you have to learn them. Ions that need to be learnt are shown in Table 7.2.

Table 7.2 Ions that you should learn.

Charge	Substance	Ion	Charge	Substance	Ion
positive	zinc	Zn^{2+}	negative	nitrate	NO_3^-
	silver	Ag^+		hydroxide	OH^-
	hydrogen	H^+		carbonate	CO_3^{2-}
	ammonium	NH_4^+		sulfate	SO_4^{2-}

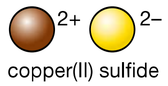
You will encounter other ions during the course, but these are the important ones for now. The ions in this list are the difficult ones – be sure to learn both the formula and the charge for each ion.

KEY POINT

Ammonium chloride (NH_4Cl) is an example of an ionic compound that does not contain a metal. There is ionic bonding between the NH_4^+ and Cl^- ions. There is, however, also covalent bonding (see Chapter 8) in this compound: the NH_4^+ ion is held together by covalent bonding.

CONFUSING ENDINGS!

Don't confuse ions such as sulf**ate** and sulf**ide**. A name like copper(II) sulf**ide** means that it contains copper and sulfur **only**. Any '**ide**' ending means that there isn't anything complicated there. Sodium chloride, for example, is just sodium and chlorine combined together. So copper(II) sulfide contains Cu^{2+} and S^{2-} ions.

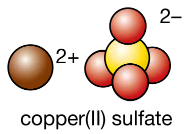


▲ Figure 7.11 Copper(II) sulfide is CuS.

HINT

Not looking carefully at word endings is one of the most common mistakes students make when they start to write formulae. Be careful!

Once you have an '**ate**' ending, it means that there is oxygen (and possibly other things) there as well. So, for example, copper(II) sulfate contains copper, sulfur and oxygen.



▲ Figure 7.12 Copper(II) sulfate is $CuSO_4$.

DEDUCING THE FORMULA FOR AN IONIC COMPOUND

EXAMPLE 1

To find the formula for sodium oxide

Sodium is in Group 1, so the ion is Na^+.

Oxygen is in Group 6, so the ion is O^{2-}.

To have equal numbers of positive and negative charges, you would need two sodium ions to provide the two positive charges to cancel the two negative charges on one oxide ion. In other words, you need:

Na^+ Na^+ O^{2-}

The formula is therefore $\mathbf{Na_2O}$.

EXAMPLE 2

To find the formula for barium nitrate

Barium is in Group 2, so the ion is Ba^{2+}.

Nitrate ions are NO_3^-. You will have to remember this.

To have equal numbers of positive and negative charges, you would need two nitrate ions for each barium ion.

The formula is $\mathbf{Ba(NO_3)_2}$.

Notice the brackets around the nitrate group. *Brackets must be written if you have more than one of these complex ions* (ions containing more than one atom). In any other situation, they are completely unnecessary.

KEY POINT

If you didn't write the brackets, the formula would look like this: $BaNO_{32}$. That would read as 1 barium, 1 nitrogen and 32 oxygens!

EXAMPLE 3

To find the formula for iron(III) sulfate

Iron(III) tells you that the metal ion is Fe^{3+}.

Sulfate ions are SO_4^{2-}.

To have equal numbers of positive and negative charges, you would need two iron(III) ions for every three sulfate ions, giving 6+ and 6– in total.

The formula is $\mathbf{Fe_2(SO_4)_3}$.

A shortcut to working out complicated formulae such as these is to just swap over the numbers in the charges. This is shown in Figure 7.13.

$$Fe^{3+}\ SO_4^{2-} \Rightarrow Fe_2(SO_4)_3$$

Figure 7.13 If you cross over the numbers in the charges you will get the formula.

CALCIUM CHLORIDE PROVIDES ANOTHER EXAMPLE

$$Ca^{2+}\ Cl^{-} \rightarrow CaCl_2$$

Figure 7.14 To work out the formula of calcium chloride we cross over the numbers in the charges. There is no extra number in front of the charge in Cl^- because we do not tend to write in a 1.

KEY POINT

Why aren't ion charges shown in formulae? Actually, they can be shown. For example, the formula for sodium chloride is NaCl. It is sometimes written Na^+Cl^- if you are trying to make a particular point, but for most purposes the charges are left out. In an ionic compound, the charges are there, whether you write them or not.

You have to be careful using this method because you can get the wrong answer when the charges on the ions are the same. For example, the formula of calcium oxide is CaO and not Ca_2O_2. When the charges on the positive and negative ions are the same you can deduce that there will be 1 of each ion in the formula, so there is no need to swap anything over.

$$Ca^{2+}\ O^{2-} \rightarrow \cancel{Ca_2O_2}$$

Figure 7.15 The formula of calcium oxide is CaO and not Ca_2O_2.

GIANT IONIC STRUCTURES

All ionic compounds form crystals that consist of lattices of positive and negative ions packed together in a regular way. A **lattice** is a regular array of particles. The lattice is held together by the strong electrostatic attractions between the positively and negatively charged ions.

Figure 7.16 A lattice fence. A lattice is a regular, repeating structure.

THE STRUCTURE OF SODIUM CHLORIDE

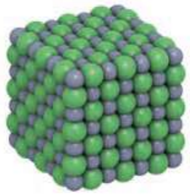


Figure 7.17 A model of a small part of a sodium chloride crystal

Figure 7.17 shows how the ions in a crystal of sodium chloride are arranged.

In diagrams, the ions are usually drawn in an 'exploded' view (Figure 7.18). Each sodium ion is surrounded by 6 chloride ions. In turn, each chloride ion is surrounded by 6 sodium ions. You have to remember that this pattern repeats itself throughout the structure over vast numbers of ions.

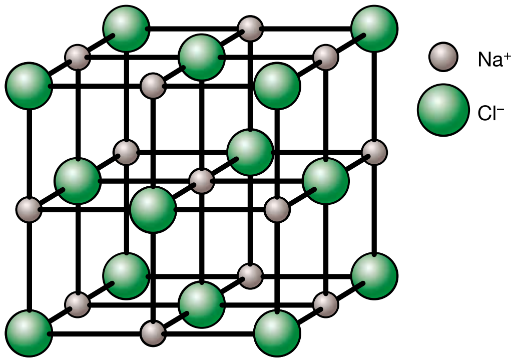


Figure 7.18 An 'exploded' view of sodium chloride. The lines in this diagram are not bonds, they are just there to help show the arrangement of the ions. Those ions joined by lines are touching each other.

HINT

This is really important: you must not talk about *molecules* of an ionic compound. This will be marked wrong in the exam and you could lose all the marks for a question!

The structure of sodium chloride is described as a **giant ionic lattice**. We are using the word '**giant**' here not in the sense of big but rather to describe a structure where there are no individual molecules. All the sodium ions in the structure attract all the chloride ions, we cannot pick out sodium chloride molecules; there are no individual molecules. The bonding in a giant ionic lattice extends throughout the structure in all directions. There is no limit to the number of particles present, all we know is that there must be the same number of sodium and chloride ions.

THE STRUCTURE OF MAGNESIUM OXIDE

Magnesium oxide, MgO, contains magnesium ions, Mg^{2+}, and oxide ions, O^{2-}. It has exactly the same structure as sodium chloride. The only difference is that the magnesium oxide lattice is held together by stronger forces of attraction. This is because in magnesium oxide, 2+ ions are attracting 2– ions. In sodium chloride, the electrostatic attractions are weaker because they are only between 1+ and 1– ions.

EXTENSION WORK

The Mg^{2+} ion is also smaller than the Na^+ ion, and the O^{2-} ion is smaller than the Cl^- ion. This causes stronger attractions but the effect of the charge on the ions is more important.

THE PHYSICAL PROPERTIES OF IONIC SUBSTANCES

Figure 7.19 Sodium chloride is crystalline

Ionic compounds have high melting points and boiling points because of the strong electrostatic forces of attraction holding the lattice together. A lot of energy has to be supplied to break the strong electrostatic forces of attraction between oppositely charged ions in the giant lattice structure.

Ionic compounds tend to be crystalline. This reflects the regular arrangement of ions in the lattice. Sometimes the crystals are too small to be seen except under powerful microscopes. Magnesium oxide, for example, is always seen as a white powder because the individual crystals are too small to be seen with the naked eye.

Ionic crystals tend to be brittle. This is because any small distortion of a crystal will bring ions with the same charge alongside each other. Like charges repel and so the crystal splits itself apart.

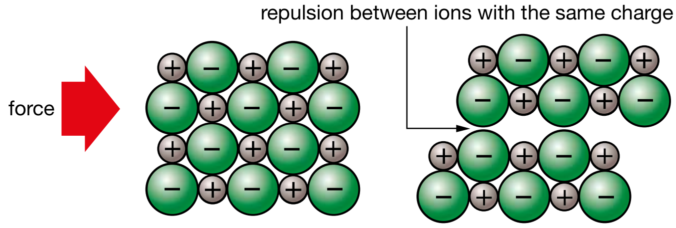


Figure 7.20 Ionic crystals tend to be brittle

KEY POINT

Organic solvents include ethanol (alcohol) and hydrocarbons, such as hexane and those found in petrol. If you are interested in these, you could explore the organic chemistry section of this book (Unit 4).

Ionic substances tend to be soluble in water.

Ionic compounds tend to be insoluble in organic solvents.

EXTENSION WORK

The reasons that ionic compounds tend to be soluble in water are quite complicated. Water is a covalent molecule (Chapter 8) but the electrons in the bonds are more attracted towards the oxygen end of the bond. This makes the oxygen slightly negative and the hydrogen slightly positive – the molecule is called **polar**. This means that reasonably strong forces can be formed between water molecules and ions, which provide the energy to break the lattice apart.

Not all ionic substances are soluble in water: magnesium oxide isn't soluble in water because the attractions between the water molecules and the ions aren't strong enough to overcome the very strong electrostatic forces of attraction between magnesium and oxide ions.

Hexane is non-polar and does not form strong enough attractions to the ions to break apart the ionic lattice.

THE ELECTRICAL CONDUCTIVITY OF IONIC SUBSTANCES

HINT

Molten just means that the salt has been melted – it is a liquid.

Ionic compounds don't conduct electricity when they are solid because the *ions* are fixed in position and are not free to move around. They do, however, conduct electricity when they are **molten** (have melted) or if they are dissolved in water (in aqueous solution). This happens because the *ions* then become free to move around. It is really important that you use the correct words when explaining this. Do not use the word 'electrons'. You must talk about the **ions** being free to move.

CHAPTER QUESTIONS

SKILLS INTERPRETATION 7

SKILLS CRITICAL THINKING 8

1 a Explain what is meant by i an ion and ii ionic bonding.

b In each of the following cases, write down the electronic configurations of the original atoms and then explain (in words or diagrams) what happens when:

i sodium bonds with chlorine to make sodium chloride

ii lithium bonds with oxygen to make lithium oxide

iii magnesium bonds with fluorine to make magnesium fluoride.

SKILLS INTERPRETATION

2 Draw dot-and-cross diagrams to show the ions formed (outer electrons only) when:

a potassium combines with fluorine

b calcium combines with bromine

c magnesium combines with iodine.

SKILLS CRITICAL THINKING

6

3 a State the formula of the ion formed by:

i magnesium
ii strontium
iii potassium
iv oxygen
v sulfur
vi caesium
vii chlorine
viii iodine
ix aluminium
x calcium
xi nitrogen

b State the name of each negative ion in a.

8

4 Work out the formulae of the following compounds:

lead(II) oxide	sodium bromide
magnesium sulfate	zinc chloride
potassium carbonate	ammonium sulfide
calcium nitrate	iron(III) hydroxide
iron(II) sulfate	copper(II) carbonate
aluminium sulfate	calcium hydroxide
cobalt(II) chloride	calcium oxide
silver nitrate	iron(III) fluoride
ammonium nitrate	rubidium iodide
sodium sulfate	chromium(III) oxide

SKILLS REASONING

6

5 Explain why sodium chloride:

a has a high melting point

b does not conduct electricity when solid

7

c conducts electricity when molten.

6 Predict, giving reasons, whether you would expect potassium chloride to have a higher or lower melting point than calcium oxide.

8 COVALENT BONDING

We met ionic compounds in Chapter 7 and in this chapter we will understand what covalent bonding is. There are a lot more covalent compounds than ionic compounds so it is important that you understand how the bonding works.

▲ Figure 8.1 Water is a covalent compound but the salt dissolved in sea water is an ionic compound.

LEARNING OBJECTIVES

- Know that a covalent bond is formed between atoms by the sharing of a pair of electrons.
- Understand covalent bonds in terms of electrostatic attractions.
- Understand how to use dot-and-cross diagrams to represent covalent bonds in:
  - diatomic molecules, including hydrogen, oxygen, nitrogen, halogens and hydrogen halides
  - inorganic molecules, including water, ammonia and carbon dioxide
  - organic molecules containing up to two carbon atoms, including methane, ethane, ethene and those containing halogen atoms.
- Explain why substances with a simple molecular structure are gases or liquids, or solids with low melting and boiling points.
- Understand that the term intermolecular forces of attraction can be used to represent all forces between molecules.
- Explain why the melting and boiling points of substances with simple molecular structures increase, in general, with increasing relative molecular mass.
- Explain why substances with giant covalent structures are solids with high melting and boiling points.
- Explain how the structures of diamond, graphite and C_{60} fullerene influence their physical properties, including electrical conductivity and hardness.
- Know that covalent compounds do not usually conduct electricity.

COVALENT BONDING

WHAT IS A COVALENT BOND?

In any bond, particles are held together by electrostatic attractions between something positively charged and something negatively charged. In a **covalent bond**, *a pair of electrons is shared between two atoms*. What holds the atoms together is *the strong electrostatic attraction between the nuclei (positively charged) of the atoms that make up the bond, and the shared pair of electrons (negatively charged).*

EXTENSION WORK

In most of the simple examples you will meet at International GCSE, each atom in a covalent bond supplies one electron to the shared pair of electrons. That doesn't have to be the case. Both electrons may come from the same atom.

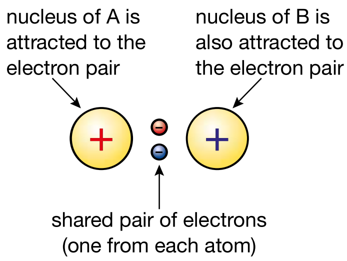


Figure 8.2 The shared pair of electrons is attracted to the nuclei of both atoms.

COVALENT BONDING IN A HYDROGEN MOLECULE

Covalent bonds are often shown using dot-and-cross diagrams.

Both hydrogen nuclei in Figure 8.3 are strongly attracted to the shared pair of electrons.

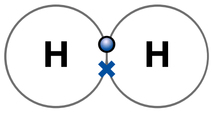


Figure 8.3 A dot-and-cross diagram for H_2

HINT

Remember that, although the electrons are drawn as dots or as crosses, there is absolutely no difference between them in reality; the dots and the crosses simply show that the electrons have come from two different atoms.

Hydrogen atoms form diatomic molecules with the formula H_2. The atoms in an H_2 molecule are joined together by a covalent bond. The covalent bond between two hydrogen atoms is very strong.

Molecules contain a certain fixed number of atoms, which are joined together by covalent bonds. Hydrogen molecules are said to be **diatomic** because they contain two atoms. Other sorts of molecule may have as many as thousands of atoms joined together, for example proteins and DNA.

THE SIGNIFICANCE OF NOBLE GAS STRUCTURES IN COVALENT BONDING

In H_2, each hydrogen atom has only one electron to share, so it can only form one covalent bond. The shared pair of electrons is in the outer shell of both, therefore each atom has the same number of electrons as a noble gas atom (helium in this case).

Does that mean that the hydrogen has turned into helium? No. The number of protons in the nucleus hasn't changed, it is the number of protons that defines what an atom is.

In virtually all of the molecules you will meet at this level, electrons will be shared so that H atoms have a total of 2 electrons in their outer shell and all other atoms will have 8 electrons in their outer shell. Some people talk about the '**octet** rule', referring to this 8. Remember, we are counting shared electrons as belonging to the outer shells of both atoms.

REMINDER

If atoms have 8 electrons in their outer shell they have the same number of electrons as a noble gas atom – they are isoelectronic with a noble gas atom.

When there is one atom in the middle and other atoms are joined to it (as in CH_4 or PCl_3) the *outer* atoms will virtually always have 8 electrons in their outer shell (or 2 if they are H). In fact, it is very difficult to think of an example where the outer atoms do not have 8 electrons. There are some molecules where the *central* atom does not have 8 electrons in the outer shell, and we will look at a couple of examples of those later on.

KEY POINT

In chemistry, we talk about things being more stable or less stable. When we do this we are usually talking about how much energy something has. Generally, the lower the energy something has, the more stable it is. Chemical reactions usually occur so that something becomes more stable. Think about holding a book: if you let go of the book, it will fall to the floor, where it has less (potential) energy, therefore it becomes more stable. When bonds form energy is given out and so the substance formed has less energy, therefore it is more stable.

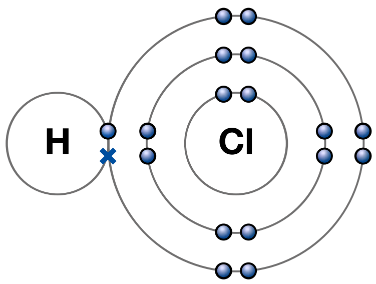


Figure 8.4 A dot-and-cross diagram for HCl.

Figure 8.5 The covalent bonding in HCl showing outer shell electrons only.

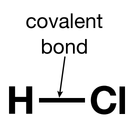


Figure 8.6 The line between the atoms represents a covalent bond.

WHY DOES HYDROGEN FORM MOLECULES?

Whenever a bond is formed (of whatever kind), energy is released, and that makes the things involved more stable than they were before. The more bonds an atom can form, the more energy is released and the more stable the system becomes. The H_2 molecule is much more stable than two separate hydrogen atoms.

COVALENT BONDING IN A HYDROGEN CHLORIDE MOLECULE

A chlorine atom has 7 electrons in its outer shell. By sharing 1 electron with a hydrogen atom, both atoms will have the same number of electrons as the nearest noble gas atom. If you look at the arrangement of electrons around the chlorine atom in the covalently bonded molecule of HCl (Figure 8.4), you will see that its electronic configuration is now [2, 8, 8]. That is the same as an argon atom. Similarly, the hydrogen now has 2 electrons in its outer shell – the same as helium.

Notice in Figure 8.4 that only the electrons in the outer shell of the chlorine are used in bonding. In the examples you will meet at International GCSE, the inner electrons never get used. In fact, the inner electrons are often left out of bonding diagrams. But be careful! In an exam, only leave out the inner electrons if the question tells you to. Another way of representing the covalent bonding in HCl is shown in Figure 8.5.

We also use lines to represent the covalent bonds between atoms, but be careful, the diagram shown in Figure 8.6 is not a dot-and-cross diagram.

COVALENT BONDING IN A CHLORINE MOLECULE (Cl_2)

A chlorine atom has 7 electrons in its outer shell. Each Cl shares 1 electron so that both Cl atoms will have 8 electrons in their outer shell.

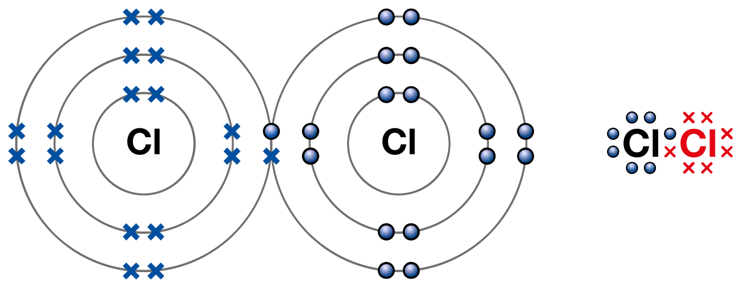


Figure 8.7 Two ways of showing the covalent bonding in Cl_2

COVALENT BONDING IN METHANE, AMMONIA AND WATER

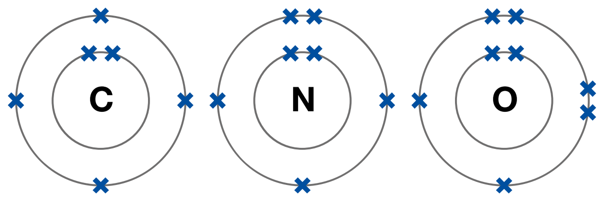
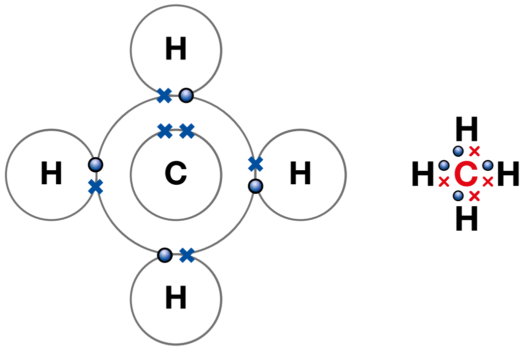


Figure 8.8 The electronic configurations of C, N and O atoms

COVALENT BONDING IN METHANE

A carbon atom has 4 electrons in its outer shell. By sharing 1 electron with each of 4 hydrogen atoms the C will have 8 electrons in its outer shell and each H will have 2 electrons in its outer shell. Therefore C forms 4 covalent bonds, 1 with each H atom. Methane has the formula CH_4.

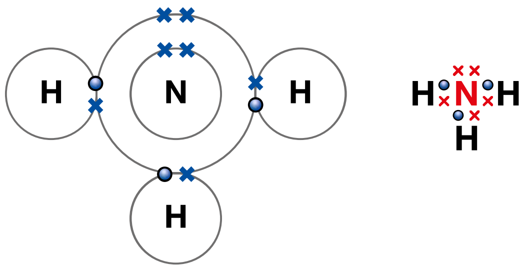


▲ Figure 8.9 Dot-and-cross diagrams for methane

COVALENT BONDING IN AMMONIA

A nitrogen atom has 5 electrons in its outer shell. It will therefore share 3 other electrons to have 8 electrons in its outer shell. In ammonia, a nitrogen atom forms 3 covalent bonds, 1 with each H atom.

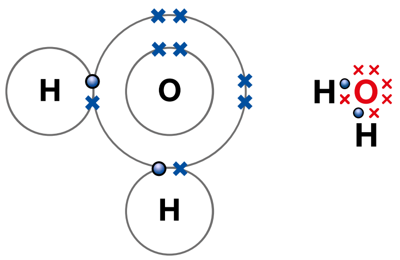
The formula of ammonia is NH_3.



▲ Figure 8.10 Dot-and-cross diagrams for ammonia

COVALENT BONDING IN WATER

An oxygen atom has 6 electrons in its outer shell. It will therefore share 2 other electrons to have 8 electrons in its outer shell. In water, an oxygen atom forms 2 covalent bonds – 1 with each H atom. The formula of water is H_2O.



▲ Figure 8.11 Dot-and-cross diagrams for water

LOOKING AHEAD

Shapes of molecules

▲ Figure 8.12 (a) A methane molecule is tetrahedral and (b) a water molecule is bent.

By understanding the bonding in a covalent molecule it is possible to work out the shape of the molecule. Pairs of electrons in the outer shell of the central atom repel each other and will therefore tend to get as far apart as possible. For example, in a methane molecule there are four pairs of electrons around the central C atom and for these to be as far away from each other as possible, they must be arranged in a tetrahedral shape. A tetrahedron (adjective: tetrahedral) is a triangular pyramid.

There are also four pairs of electrons around the central atom in water: two of these are pairs of electrons involved in covalent bonds and two are pairs of electrons in the outer shell of the oxygen which are not involved in bonding (these are often called *lone pairs of electrons* or just *lone pairs*). These four pairs of electrons are also arranged in a tetrahedral arrangement so the actual shape of a water molecule (how the atoms are arranged) is described as 'bent' or 'V-shaped'. The fact that a water molecule is bent and the electrons are attracted to a different extent by the oxygen and hydrogen atoms means that a water molecule is polar (has a slightly negative and a slightly positive end) and that a stream of water can be bent by an electrically charged object.

Figure 8.13 Water being bent by an electrically charged comb.

COVALENT BONDING IN A SLIGHTLY MORE COMPLICATED MOLECULE: ETHANE

Ethane has the formula C_2H_6. The bonding is similar to methane (Figure 8.9), except that there is a carbon–carbon covalent bond as well as the carbon–hydrogen bonds.

This is called an organic compound. You will learn more about molecules such as this in Unit 4.

HINT

When drawing molecules containing carbon and hydrogen it is useful to remember that carbon always forms 4 bonds by sharing 4 electrons, and hydrogen always forms 1 bond by sharing 1 electron. The hydrogen atoms always go on the outside, never in the middle.

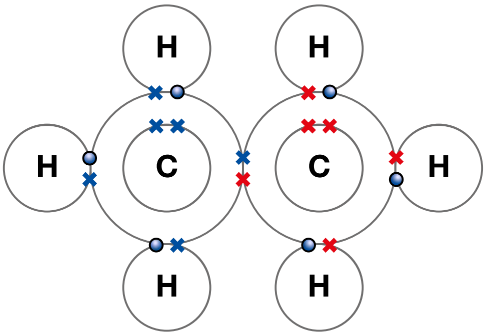


Figure 8.14 A dot-and-cross diagram for ethane

MULTIPLE COVALENT BONDING

COVALENT BONDING IN AN OXYGEN MOLECULE: DOUBLE BONDING

An oxygen atom has 6 electrons in its outer shell and so if two oxygen atoms combine, they will both share 2 electrons each; this means that each atom will have 8 electrons in its outer shell. There are therefore two shared pairs of electrons between the oxygen atoms; this is called a double covalent bond or, usually, just a **double bond**.

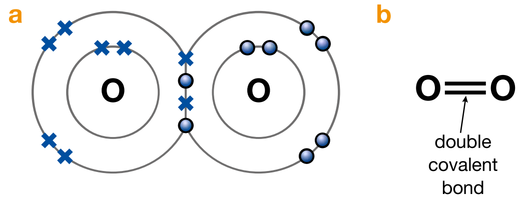
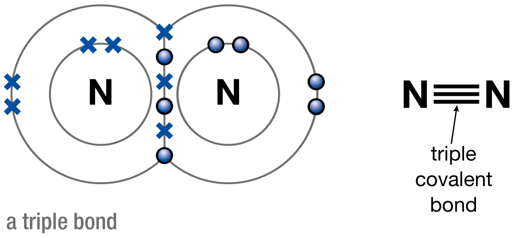


Figure 8.15 (a) A dot-and-cross diagram for O_2 and (b) the double covalent bond.

THE TRIPLE BOND IN A NITROGEN MOLECULE

A nitrogen atom has 5 electrons in its outer shell and so if two nitrogen atoms combine they will both share 3 electrons each; this means that each atom will have 8 electrons in its outer shell. There are, therefore, three shared pairs of electrons between the nitrogen atoms; this is called a triple covalent bond or, usually, just a **triple bond**.

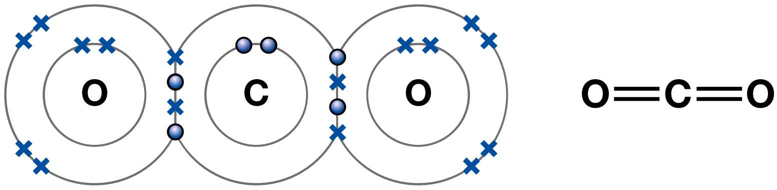


▲ Figure 8.16 N_2 has a triple bond

Nitrogen gas consists of nitrogen molecules bonded like this. The triple bond from the sharing of three pairs of electrons between the two nitrogen atoms is very strong and needs a lot of energy to break. That is why nitrogen is relatively unreactive.

COVALENT DOUBLE BONDING IN CARBON DIOXIDE, CO_2

An oxygen atom has 6 electrons in its outer shell and a carbon atom has 4. Each oxygen atom will share 2 electrons with the carbon atom. Two double bonds are formed between the carbon and the two oxygens (Figure 8.17). All atoms have 8 electrons in their outer shells.



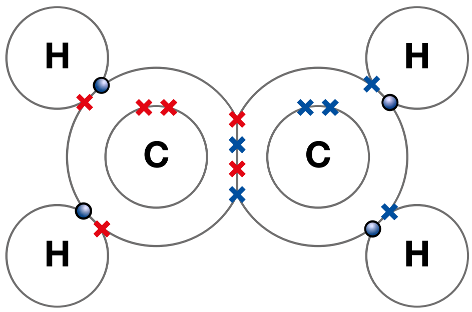
▲ Figure 8.17 CO_2 has two double bonds between atoms.

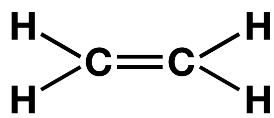
THE DOUBLE BOND IN ETHENE, C_2H_4

HINT

With organic compounds such as ethane and ethene you have to look at their names very carefully, even one different letter in the name can matter. Here, for example, ethane and ethene are completely different compounds. You will find out more about this in Unit 4.

Ethene is rather like ethane in Figure 8.14, except that it only has two hydrogen atoms attached to each carbon atom and a double bond between the carbon atoms.





▲ Figure 8.18 Ethene has a double bond between the C atoms.

ORGANIC MOLECULES CONTAINING HALOGEN ATOMS

Bromomethane has the formula CH_3Br: the 3 H atoms and the Br atom are joined to the central C atom. Br has 35 electrons and we have not learnt how to work out the electronic configuration of an atom with 35 electrons, but if

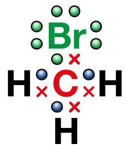


Figure 8.19 A dot-and-cross diagram for CH_3Br showing outer shells only. Although we have used different colours here for clarity, you do not need to use different colours in the exam.

you look at the Periodic Table you will see that Br is in Group 7. Because it is in Group 7 we know that it has 7 electrons in its outer shell, and will share 1 electron so that it has 8 in its outer shell. Therefore, we know that Br will form just 1 covalent bond. When you draw a dot-and-cross diagram for CH_3Br you will only be asked to show the outer electrons (Figure 8.19).

Probably the most complicated molecule for which you could be asked to draw a dot-and-cross diagram would be something like chloroethene (CH_2CHCl). When drawing chloroethene, remember that C will form 4 covalent bonds, H will form 1 and Cl will form 1. The dot-and-cross diagram (outer shells only) is shown in Figure 8.20.

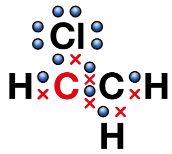


Figure 8.20 There is a double bond between the 2 C atoms. It does not matter where you put the H and Cl atoms relative to the C, and you do not have to use different colours.

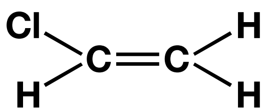


Figure 8.21 The structure of chloroethene showing the covalent bonds. This is not, however, a dot-and-cross diagram and you must not draw this if you are asked to draw a dot-and-cross diagram.

The structure of chloroethene can also be shown as illustrated in Figure 8.21.

SOME MORE DIFFICULT MOLECULES WHERE THE CENTRAL ATOM DOES NOT HAVE 8 ELECTRONS IN ITS OUTER SHELL

Although the *outer* atoms in a molecule will always have 8 (or 2 in the case of hydrogen) electrons in their outer shell, there are a few examples you may encounter where the *central* atom has more or fewer than 8 electrons in the outer shell.

BF_3

Boron is the central atom and the Fs are the outer atoms. Each F will share 1 other electron to have 8 electrons in its outer shell. This means that B only has a total of 6 electrons in its outer shell. Another way of thinking about this is that a B atom only has 3 electrons in its outer shell, and so this is the maximum number that it can share.

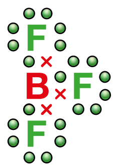


Figure 8.22 A dot-and-cross diagram for BF_3

SO_2

This is called sulfur dioxide or sulfur(IV) oxide. The central atom is S and the outer atoms are O. Each O atom has 6 electrons in its outer shell and so will need to share 2 other electrons to have 8 electrons in the outer shell. So the S atom shares 2 electrons with each of the O atoms to form two double bonds. A sulfur atom originally had 6 electrons in its outer shell and so now, if it shares 4 electrons, it has 10 electrons in its outer shell.

Figure 8.23 There are two double bonds in SO_2.

EXTENSION WORK

Atoms in Periods 3 and below (4, 5, 6, 7) can have more than 8 electrons in their outer shells. The maximum number of electrons that the central atom in a molecule can share is equal to the number of electrons in its outer shell. So, sulfur can form up to 6 bonds (in SF_6) and chlorine 7 (in $HClO_4$).

SIMPLE MOLECULAR STRUCTURES

Molecules contain fixed numbers of atoms joined by strong covalent bonds. If we look closely at liquid water, there are individual water molecules, where the H and O atoms are joined together with strong covalent bonds. But there must also be some forces between water molecules which keep them in the liquid state. These forces are **intermolecular forces**.

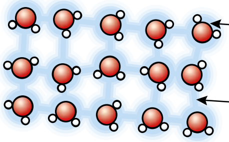


Figure 8.24 Water is a simple molecular compound.

DID YOU KNOW?
Intermolecular literally means between molecules.

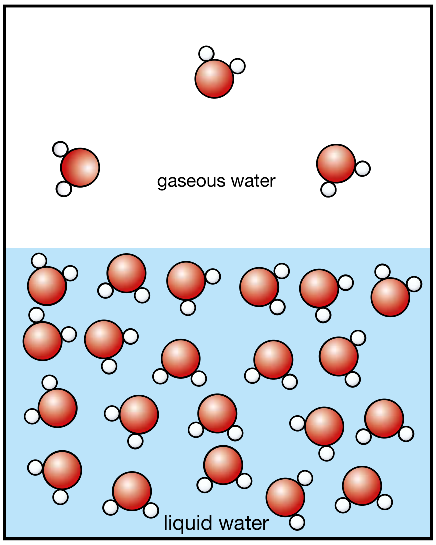


Figure 8.25 Only intermolecular forces are broken when water evaporates/boils.

These intermolecular forces between molecules are much weaker than covalent bonds. When we boil water it is only these weak intermolecular forces of attraction that are broken; covalent bonds are not broken. Looking at Figure 8.25 you can see that there are H_2O molecules in liquid water and in gaseous water. The covalent bonds between the H and O atoms in the molecules have not changed in any way. All that has changed in gaseous water is that there are no intermolecular forces, they have been broken.

When a substance consists of molecules with intermolecular forces of attraction between them, we say that it has a *simple molecular structure*. Examples of things that have simple molecular structures are H_2O, CO_2, CH_4, NH_3 and C_2H_4. These are all the things that we have drawn dot-and-cross diagrams for above. Virtually all the compounds you will encounter that have covalent bonding will have simple molecular structures.

Substances with simple molecular structures tend to be gases or liquids or solids with low melting points and boiling points. The reason for this is that not much energy is required to break the weak intermolecular forces of attractions between molecules. Remember, no covalent bonds are broken, covalent bonds are strong.

EXTENSION WORK

If you continue with chemistry you will learn that there are different types of intermolecular forces. You will come across terms like van der Waals' forces, London dispersion forces and hydrogen bonds. There is a special type of intermolecular force between water molecules called **hydrogen bonds**. Hydrogen bonding gives water some of its very special properties, for example the solid form (ice) is less dense than the liquid form.

MELTING AND BOILING POINTS INCREASE AS RELATIVE MOLECULAR MASS INCREASES

The halogens (Group 7 in the Periodic Table) all have a simple molecular structure consisting of diatomic molecules with intermolecular forces between them.

You can see from Table 8.1 that the melting points and boiling points increase as the relative molecular mass increases.

Table 8.1 The melting points and boiling points of the halogens.

Halogen	Formula	Relative molecular mass/M_r	Melting point/°C	Boiling point/°C
fluorine	F_2	38	–220	–188
chlorine	Cl_2	71	–101	–34
bromine	Br_2	160	–7	59
iodine	I_2	254	114	184

EXTENSION WORK

It is not always the case that melting and boiling points increase as the M_r increases and really the rule only applies to sets of very similar substances, such as the halogens or the alkanes (see Chapter 23). Some examples where the rule does not work are water ($M_r = 18$, boiling point = 100 °C), ethane ($M_r = 30$, boiling point = –89 °C), NH_3 ($M_r = 17$, boiling point = –33 °C) and PH_3 ($M_r = 34$, boiling point = –88 °C).

KEY POINT

We are using the term covalent molecular compounds to mean covalent compounds with a simple molecular structure.

Remember, as we melt or boil these substances we are only breaking the intermolecular forces of attraction between molecules. The boiling points increase down this group, which means we have to put in more energy to break the intermolecular forces as the relative molecular mass increases. This means that the *intermolecular forces of attraction must become stronger as relative molecular mass increases*.

This is something that we see quite often in chemistry, for example boiling points increase along the series CH_4, C_2H_6, C_3H_8 as relative molecular mass increases. This is discussed further in Chapter 23.

SOME OTHER PHYSICAL PROPERTIES OF COVALENT COMPOUNDS

Covalent molecular compounds do not conduct electricity. This is because the molecules don't have any overall electrical charge (there are no ions) and all the electrons are held tightly in the atoms or in covalent bonds and so are not able to move from molecule to molecule.

Covalent molecular substances tend to be insoluble in water. There are some exceptions to this, for example ethanol (C_2H_5OH) and substances such as NH_3 and HCl that react with water as they dissolve.

Covalent molecular substances are often soluble in organic solvents.

GIANT COVALENT STRUCTURES

DIAMOND

KEY POINT

A tetrahedron is a triangular-based pyramid. In a tetrahedral arrangement, one atom is at the centre of the tetrahedron, and the atoms it is attached to are at the four corners. Look carefully at the top five atoms in Figure 8.26 to see what this looks like. You will find other similar arrangements in this diagram.
In Figure 8.26 some carbon atoms seem to be forming only two bonds (or even one bond), but that's not really the case. We are only showing a small part of the whole structure. The structure continues in three dimensions, and each of the atoms drawn here is attached to four others. Each of the lines in this diagram represents a covalent bond.

Diamond is a form of pure carbon.

Each carbon atom has four electrons in its outer shell and it therefore forms four covalent bonds. In diamond, each carbon bonds strongly to four other carbon atoms in a *tetrahedral* arrangement. Figure 8.26 shows enough of the structure to see what is happening.

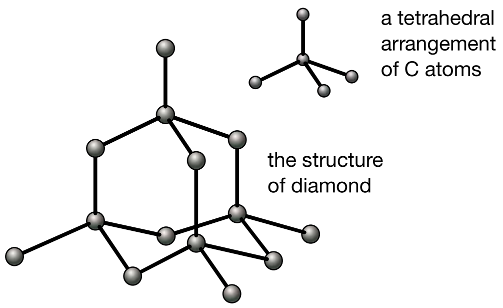


Figure 8.26 Part of the structure of diamond

This is a giant covalent structure; it continues on and on in three dimensions. It is *not* a molecule because the number of atoms joined up in a real diamond is completely variable and depends on the size of the crystal. Molecules always contain *fixed numbers* of atoms joined by covalent bonds.

Diamond has a very high melting and boiling point. This is because of the very strong carbon–carbon covalent bonds, which extend throughout the whole crystal in three dimensions. A lot of energy has to be supplied to break these strong covalent bonds, therefore diamond has very high melting and boiling points. It is important to realise how this is different from the simple molecular structures that we saw above. In order to melt or boil a substance with a simple molecular structure, such as CH_4, we only had to supply enough

Figure 8.27 Diamond (a form of carbon) is crystalline, and is the hardest naturally occurring substance.

energy to break the relatively weak intermolecular forces of attraction. In diamond there are no intermolecular forces (it has a giant structure, there are no molecules). Covalent bonds, which are very strong, must be broken in order to melt or boil it.

In general, *all substances with giant covalent structures are solids with high melting and boiling points* because a lot of energy has to be supplied to break all the strong covalent bonds throughout the giant structure. Other substances with giant covalent structures include graphite (discussed below) and silicon dioxide (SiO_2).

Diamond is very hard. Again, a lot of energy has to be supplied to break the strong covalent bonds in the giant structure. Drill bits can be tipped with diamonds for drills used on stone and rock.

Diamond doesn't conduct electricity. All the electrons in the outer shells of the carbon atoms are tightly held in covalent bonds between the atoms. None are free to move around.

EXTENSION WORK

Diamond doesn't dissolve in water or in any other solvent. This is again because of the strong covalent bonds between the carbon atoms. If the diamond dissolved, these bonds would have to be broken.
Diamond conducts heat very well (better than any other element). As one end of the crystal is heated the atoms vibrate more. The strong bonds throughout the giant structure mean that these vibrations are quickly transmitted from one end of the crystal to the other.

GRAPHITE

Graphite is also a form of carbon, but the atoms are arranged differently, although it still has a giant structure. Graphite has a *layer structure*, rather like a pack of playing cards. In a pack of cards, each card is strong but the individual cards are easily separated. The same is true in graphite.

Figure 8.28 Graphite has a structure rather like a pack of playing cards.

Figure 8.29 Graphite is soft with a layer structure.

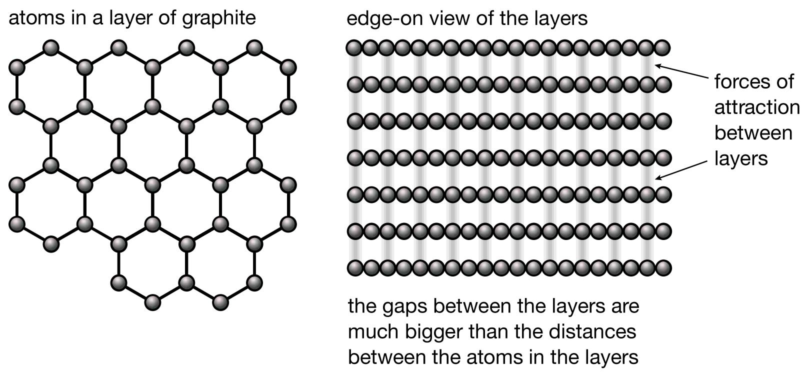


Figure 8.30 The structure of graphite. Some forces of attraction between layers have been shown. These are not bonds and could have been drawn anywhere between the layers.

EXTENSION WORK

Actually, the reason that the layers slide over each other fairly easily is more complicated than this and graphite is not a lubricant in a vacuum. Graphite being a lubricant relies on water molecules sticking to the surface; this does not happen in a vacuum.

Graphite is a soft material. Although the forces holding the atoms together in each layer are very strong, the attractions between the layers are much weaker and not much energy is needed to overcome them. Layers slide over each other and can easily be flaked off.

Graphite (mixed with clay to make it harder) is used in pencils. When you write with a pencil, you are leaving a trail of graphite layers behind on the paper. Pure graphite is so slippery that it is used as a dry lubricant, for example powdered graphite is used to lubricate locks.

Graphite has high melting and boiling points. To melt/boil graphite, you don't just have to separate the layers, you have to break up the whole structure, including the covalent bonds. That needs very large amounts of energy because the covalent bonds are so strong.

▲ Figure 8.31 Three graphite electrodes glow red hot after their removal from an electric arc furnace used to produce steel.

Graphite conducts electricity. If you look back at Figure 8.30, you will see that each carbon atom is joined to only three others. Each carbon atom uses three of its outer shell electrons to form three single covalent bonds. The fourth electron in the outer shell of each atom is free to move around throughout the whole of the layer. The electrons that are free to move throughout the layers are called **delocalised electrons**. The movement of these delocalised electrons allows graphite to conduct electricity.

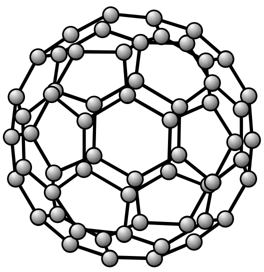
EXTENSION WORK

Some other properties of graphite are:

- *Graphite is insoluble in all solvents* because it would take too much energy to break all the strong covalent bonds.
- *Graphite is less dense than diamond* because the layers in graphite are relatively far apart. The distance between the graphite layers is more than twice the distance between atoms in each layer. In a sense, a graphite crystal contains a lot of wasted space, which isn't there in a diamond crystal.

C_{60} FULLERENE

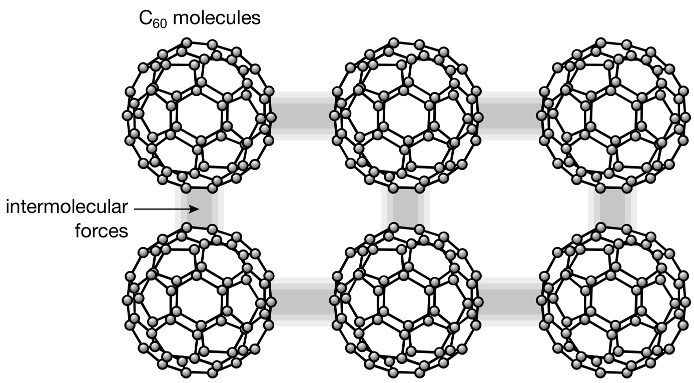
Diamond and graphite are two **allotropes** of carbon. Allotropes are different forms of the same element. Another allotrope of carbon is C_{60} fullerene. Diamond and graphite both have giant structures but C_{60} fullerene has a simple molecular structure.



▲ Figure 8.32 A C_{60} fullerene molecule. Remember that molecules consist of fixed number of atoms; each C_{60} fullerene molecule contains 60 carbon atoms joined by covalent bonds.

In solid or liquid C_{60} fullerene there are C_{60} molecules with weak intermolecular forces between them. The fact that C_{60} has a simple molecular structure has a big influence on its physical properties.

C_{60} fullerene has lower melting and boiling points than diamond and graphite. When fullerene is melted, only the relatively weak intermolecular forces of attraction must be broken. This does not require as much energy as breaking all the strong covalent bonds when diamond and graphite are melted.



▲ Figure 8.33 C_{60} fullerene has a simple molecular structure.

KEY POINT

There are different fullerenes, where the molecules contain different numbers of carbon atoms. This is why we include the C_{60} in the name.

EXTENSION WORK

Unlike diamond and graphite C_{60} fullerene does dissolve in some solvents; only relatively weak intermolecular forces of attraction have to be broken for it to dissolve.

C_{60} fullerene is not as hard as diamond. It does not take as much energy to break the intermolecular forces of attraction in C_{60} fullerene compared to breaking the strong covalent bonds in diamond.

C_{60} fullerene does not conduct electricity. Although all the carbon atoms in C_{60} only form three bonds, the fourth electron on each atom can only move around *within* each C_{60} molecule; the electrons cannot jump from molecule to molecule.

CHAPTER QUESTIONS

You will need to use the Periodic Table in Appendix A on page 320.

SKILLS CRITICAL THINKING 6

1 State whether each of the following compounds is ionic or covalent:

a MgO
b CH_3Br
c H_2O_2
d $FeCl_2$
e NaF
f HCN

SKILLS INTERPRETATION 8

2 a What is meant by a covalent bond? How does this bond hold two atoms together?

b Draw dot-and-cross diagrams (showing outer shell electrons only) to show the covalent bonding in

i methane (CH_4)
ii hydrogen sulfide (H_2S)
iii phosphine (PH_3)
iv silicon tetrachloride ($SiCl_4$)

c Draw dot-and-cross diagrams (showing outer shell electrons only) to show the covalent bonding in

i O_2
ii N_2

3 Draw dot-and-cross diagrams (showing outer shell electrons only) to show the covalent bonding in

a ethane (C_2H_6)
b ethene (C_2H_4)
c chloroethane (CH_3CH_2Cl)

SKILLS REASONING

4 Explain why carbon dioxide sublimes at –78.5 °C but diamond sublimes at around 4000 °C.

5 Hexane has the formula C_6H_{14}. It is a liquid at room temperature.

a Explain whether hexane has a simple molecular or giant structure.

b Explain whether you would expect pentane (C_5H_{12}) to have a higher or lower boiling point than hexane.

c Explain whether or not you would expect hexane to conduct electricity.

9

6 Explain the following in terms of structure and bonding:

a diamond is harder than graphite
b C_{60} fullerene has a lower melting point than graphite
c graphite conducts electricity
d diamond does not conduct electricity.

SKILLS ANALYSIS

8

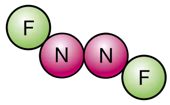
7 The table below gives details of the boiling temperatures of some substances made of covalent molecules. Arrange these substances in increasing order of the strength of their intermolecular forces and explain your order.

Substance	Boiling point/°C
ammonia	–33
ethanamide	221
ethanol	78.5
hydrogen	–253
phosphorus trifluoride	–101
water	100

(Don't panic if you don't recognise some of the names. The substances could also have been labelled A, B, C, D, E and F.)

SKILLS REASONING

8 The compound N_2F_2 has the structure:



a Explain whether you would expect the bond between the nitrogen atoms to be a single, double or triple bond.

SKILLS INTERPRETATION

b Draw a dot-and-cross diagram for N_2F_2 showing outer electrons only.

SKILLS REASONING

9 a Draw a dot-and-cross diagram (showing outer electrons only) to show the covalent bonding in BCl_3.

9

b BCl_3 is sometimes described as an *electron-deficient* compound. Explain what you think that means.

CHEMISTRY ONLY

9 METALLIC BONDING

In this chapter we will discuss the bonding in metals and explain some of the physical properties of metals in terms of structure and bonding.

▲ Figure 9.1 Metals have properties that make them useful as construction materials.

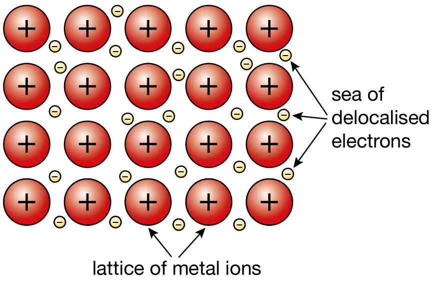
▲ Figure 9.2 Most metals are strong and all metals conduct electricity.

LEARNING OBJECTIVES

- Know how to represent a metallic lattice by a 2D diagram.
- Understand metallic bonding in terms of electrostatic attractions.
- Explain typical physical properties of metals, including electrical conductivity and malleability.

METALLIC BONDING

Sodium is a metal. When sodium atoms bond together to form the solid metal, the outer electron on each sodium atom becomes free to move throughout the whole structure. The electrons are said to be *delocalised*. These electrons are no longer attached to particular atoms or pairs of atoms, instead you can think of them as flowing around through the whole metal. When a sodium atom loses its outer electron a sodium ion (Na^+) is left behind. A metallic structure consists of *a lattice (regular arrangement) of positive ions in a sea of delocalised electrons* (Figure 9.3).



▲ Figure 9.3 The metallic structure of a metal such as sodium

HINT

Different metals have different arrangements of ions in the lattice. Do not worry too much about this when drawing a diagram of a metal. As long as you draw the ions in a regular arrangement that will be fine.

HINT

When they come to write the symbol for a metal such as sodium in equations, students who know about metallic bonding sometimes worry whether they should write it as Na or Na^+. You write it as atoms, as Na. Thinking about the structure as a whole, the number of electrons exactly balances the number of positive charges. The metal as a whole carries no charge.

Metallic bonding is the electrostatic forces of attraction between each positive ion and the delocalised electrons. This holds the structure together.

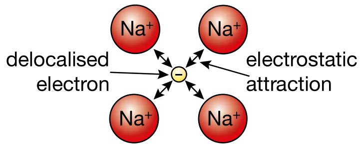


Figure 9.4 The electrostatic attraction between positively charged ions and negatively charged electrons holds the metallic structure together.

Metals have giant structures. There are no individual molecules and all the positive ions in the lattice attract all the delocalised electrons.

The ion formed by the metal depends on the number of electrons the original atom has in its outer shell. Thus all the elements in Group 1 form 1+ ions and all the elements in Group 2 form 2+ ions.

PHYSICAL PROPERTIES OF METALS

Most metals are hard and have high melting points. This suggests that the electrostatic forces of attraction between the positive ions and the delocalised electrons are strong.

In the case of sodium, only one electron per atom is delocalised, leaving ions with only one positive charge on them. The bonding in sodium is quite weak, as metals go, which is why sodium is fairly soft, with a low melting point for a metal. Magnesium has two outer electrons, both of which are delocalised into the 'sea', leaving behind ions that carry a charge of 2+. There is a much stronger electrostatic attraction between the 2+ ions and the delocalised electrons. This means that the bonding is stronger in magnesium and the melting point is higher.

METALS CONDUCT ELECTRICITY

KEY POINT

In Chapter 7 we discussed ionic compounds and how they conduct electricity when molten or in aqueous solution because the **ions** are free to move. Ionic substances do not conduct electricity when solid because the ions are not free to move. Metals conduct electricity when solid or molten because the delocalised **electrons** are free to move. It is important not to confuse this:

- ionic substances: ions move
- metals: electrons move

Metals conduct electricity because the *delocalised electrons are free to move throughout the structure*. Imagine what happens if a piece of metal is attached to an electrical power source.

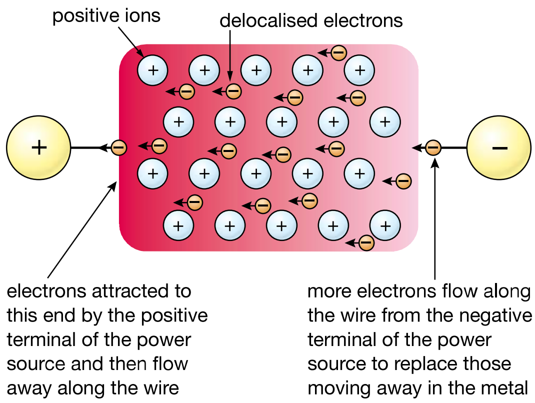
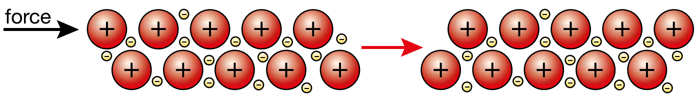


Figure 9.5 How metals conduct electricity.

METALS ARE MALLEABLE

Metals can be hammered into different shapes; this is what the word **malleable** means. When we apply a force to a piece of metal *the layers of positive ions slide over each other*. This does not affect the bonding in the structure; the positive ions are still attracted to the delocalised electrons.



▲ Figure 9.6 Metals are malleable because the layers of positive ions can slide over each other without changing the bonding.

Metals can also be described as **ductile**. This means that they can be drawn out into wires. The explanation is the same as why they are malleable.

CHAPTER QUESTIONS

SKILLS INTERPRETATION

1 Draw simple 2D diagrams to show the structure of:

a potassium metal

b calcium metal

SKILLS CRITICAL THINKING

SKILLS REASONING

2 a A solid metal is often described as having 'a lattice of positive ions in a sea of delocalised electrons'. State the electronic configuration of a magnesium atom and use it to explain what this phrase means.

b Metallic bonds are not fully broken until the metal has first melted and then boiled. Sodium, magnesium and aluminium are three consecutive elements in the Periodic Table. The boiling points of sodium, magnesium and aluminium are 890 °C, 1110 °C and 2470 °C, respectively. Explain these values in terms of the electronic configurations of the elements and metallic bonding.

c Explain why all these elements are good conductors of electricity.

d Explain why all these metals are malleable.

3 This question uses ideas from Chapters 7, 8 and 9. In these chapters you have met the following types of structure and bonding:

giant metallic structure

giant covalent structure

giant ionic structure

covalent molecular structure

Some information about some substances is given below. In each case state what type of structure and bonding it has.

a Substance A melts at 2300 °C. It doesn't conduct electricity even when it is molten. It is insoluble in water.

b Substance B is a colourless gas.

c Substance C is a yellow solid with a low melting point of 113 °C. It doesn't conduct electricity and it is insoluble in water.

d Substance D forms brittle orange crystals which melt at 398 °C. It dissolves freely in water to give an orange solution.

e Substance E is a pink-brown flexible solid. It conducts electricity.

f Substance F is a liquid with a boiling point of 80 °C. It is insoluble in water.

g Substance G is a silvery solid which melts at 660 °C. It is used in overhead power cables.

END OF CHEMISTRY ONLY

CHEMISTRY ONLY

10 ELECTROLYSIS

In this chapter we will look at what happens when we pass electricity through various substances.

Some things don't change when we pass electricity through them. For example, if you attach a piece of copper to a battery and make a complete circuit you may notice that the copper gets hot, but apart from that there is no other change. However, when you pass electricity through a solution of potassium iodide, a chemical change occurs, and hydrogen gas and iodine are formed. We will learn about why this happens in this chapter.

▶ Figure 10.1 This photograph shows what happens if you connect a solution of potassium iodide into a simple electrical circuit. If you look at what is happening in the solution, you can see obvious signs of chemical change. Some coloured substance is being produced at the positive electrode and a gas is being given off at the negative electrode.

LEARNING OBJECTIVES

- Understand why covalent compounds do not conduct electricity.
- Understand why ionic compounds conduct electricity only when molten or in aqueous solution.
- Know that anion and cation are terms used to refer to negative and positive ions, respectively.
- Describe experiments to investigate electrolysis, using inert electrodes, of molten compounds (including lead(II) bromide) and aqueous solutions (including sodium chloride, dilute sulfuric acid and copper(II) sulfate) and to predict the products.
- Write ionic half-equations representing the reactions at the electrodes during electrolysis and understand why these reactions are classified as oxidation or reduction.
- Practical: Investigate the electrolysis of aqueous solutions.

WHY THINGS CONDUCT ELECTRICITY

Before we continue, we need to remind ourselves about why things do or don't conduct electricity. In order for things to conduct electricity, there must be charged particles present and these charged particles must be free to move. The charged particles will be either electrons or ions; it is important that you are clear which one you are talking about.

METALS

If you remember, the structure of a metal is made up of a lattice of positive ions surrounded by a sea of delocalised electrons. Metals conduct electricity because the delocalised electrons are free to move.

IONIC COMPOUNDS

These are compounds such as sodium chloride and potassium iodide. Ionic compounds don't conduct electricity when they are solid because the ions are held tightly in position in the lattice – they are not free to move around (they can only vibrate). They do, however, conduct electricity when they are molten (have melted) or if they are dissolved in water (in aqueous solution). This happens because the ions then become free to move around.

Remember that ionic compounds are made up of positive ions and negative ions:

- anions are negative ions
- cations are positive ions.

We will look at where these names come from later in the chapter.

COVALENT COMPOUNDS

Covalent molecular compounds are substances such as hexane (C_6H_{14}), methane (CH_4) and carbon dioxide (CO_2). These do not conduct electricity in any state or in solution. Covalent molecular compounds consist of individual molecules. These molecules don't have any overall electrical charge, so there are no charged particles to move around. Also, all the electrons are held tightly in the atoms or in covalent bonds and so they are not able to move from molecule to molecule.

REMINDER

The arrow here shows that this is a reversible reaction. Reversible reactions are discussed in Chapter 21.

There are some exceptions to this, such as covalent compounds that form ions as they react with water, for example ammonia:

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Ammonia solution conducts electricity because there are ions which are free to move.

Hydrogen chloride gas dissolves in water to form hydrochloric acid (HCl(aq)). Hydrogen chloride ionises in water:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

PASSING ELECTRICITY THROUGH COMPOUNDS: ELECTROLYSIS

When metals conduct electricity you will not notice anything happening, except perhaps that the metal gets hotter. When you pass electricity through an ionic compound, either molten or in solution, a chemical reaction occurs.

Electrolysis is a chemical change caused by passing an electric current through a compound which is either molten or in solution.

SOME OTHER IMPORTANT WORDS

An **electrolyte** is a liquid or solution that undergoes electrolysis. Electrolytes all contain ions. The movement of the ions is responsible for both the conduction of electricity and the chemical changes that take place.

The electricity is passed into and out of the electrolyte through two **electrodes**. Carbon is frequently used for electrodes because it conducts electricity and is chemically fairly **inert** (this means that it does not react with things). Platinum is also fairly inert and can be used instead of carbon. Various other metals are sometimes used as well.

HINT

Remember **PANiC**: positive anode, negative (is) cathode.

The positive electrode is called the **anode**. The negative electrode is called the **cathode**.

THE ELECTROLYSIS OF MOLTEN COMPOUNDS

ELECTROLYSING MOLTEN LEAD(II) BROMIDE, $PbBr_2$

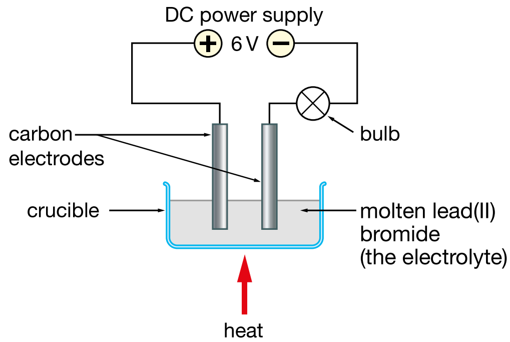


Figure 10.2 Electrolysing molten lead(II) bromide

KEY POINT

The power supply can be a 6 volt battery or a power pack. It doesn't matter which. The voltage isn't critical either.

Nothing at all happens until the lead(II) bromide melts. Then:

- the bulb lights up, showing that electrons are flowing through it
- there is bubbling around the electrode (the anode) connected to the positive terminal of the power source as brown bromine gas is given off
- nothing seems to be happening at the electrode (the cathode) connected to the negative terminal of the power source, but afterwards metallic lead is found underneath it
- when you stop heating and the lead(II) bromide solidifies again, everything stops, there is no more bubbling and the bulb goes out.

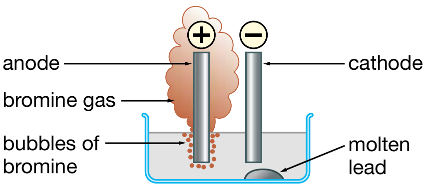


Figure 10.3 What happens when the lead(II) bromide melts and electricity passes through it (the bulb also lights up).

EXPLAINING WHAT IS HAPPENING

Lead(II) bromide is an ionic compound. The solid consists of a giant structure of lead(II) ions (Pb^{2+}) and bromide ions (Br^-) packed regularly in a crystal lattice. The ions are locked tightly in the lattice and aren't free to move. The solid lead(II) bromide doesn't conduct electricity. As soon as the solid melts, the ions become free to move around.

As soon as you connect the power source in Figure 10.2, it pumps any mobile electrons away from the left-hand electrode towards the right-hand one. This means that there are extra electrons at the right-hand electrode, so it is negative. The left-hand electrode is positive because some of the electrons have been removed from it. The positive lead(II) ions in the molten lead(II) bromide are attracted to the negative electrode, the cathode. When they get there, each lead(II) ion picks up two electrons from the electrode and forms neutral lead atoms (Figure 10.4). These fall to the bottom of the container as molten lead. This can be represented by a **half-equation**.

$$Pb^{2+} + 2e^- \rightarrow Pb$$

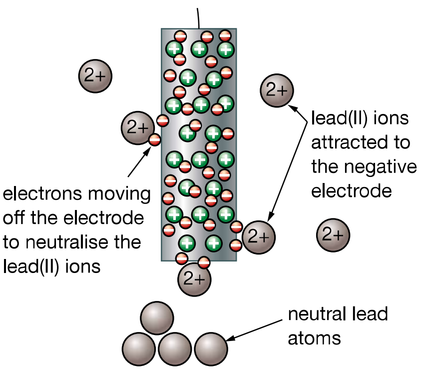


Figure 10.4 The reaction at the cathode

The power source pumps new electrons along the wire to replace the electrons that have been removed from the cathode.

Bromide ions are attracted to the positive electrode, the anode (Figure 10.5). When they get to the positive electrode, the extra electron which makes the bromide ion negatively charged moves onto the electrode. This is because this electrode is short of electrons.

KEY POINT

Half-equations show either oxidation or reduction reactions (see below). Electrons are shown as e^- in half-equations.

The loss of the extra electron converts each bromide ion into a bromine atom:

$$Br^- \rightarrow Br + e^-$$

KEY POINT

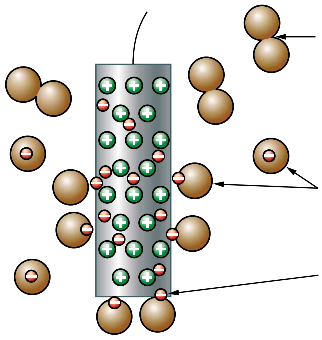
A bromine atom has only 7 electrons in its outer shell so it joins to another Br atom to form a covalent bond. Both atoms then have 8 electrons in their outer shell.

These join in pairs to make bromine molecules:

$$2Br \rightarrow Br_2$$

Overall:

$$2Br^- \rightarrow Br_2 + 2e^-$$



▲ Figure 10.5 The reaction at the anode

KEY POINT

It is really important to use the correct terms when talking about the reactions at the electrodes. Brom*ide* ions are attracted to the anode, where they lose electrons to form brom*ine* molecules. Do not confuse bromide and bromine.

The new electrons on the electrode flow back into the power source. Because electrons are flowing in the external circuit, the bulb lights up.

KEY POINT

The external circuit is the wire, power pack, the bulb and the electrodes. **Electrons** flow in the external circuit but **ions** flow in the electrolyte.

We sometimes talk about ions being **discharged** at the electrodes. Discharging an ion means that it loses its charge. This happens either by giving up electron(s) to the electrode or receiving electron(s) from it. We can therefore say that bromide ions and lead(II) ions were discharged at the electrodes.

ELECTROLYSIS AND REDOX

You will learn more about **oxidation** and **reduction** reactions in Chapter 14. Oxidation and reduction are words used to describe what is happening to things in certain chemical reactions. We can define oxidation and reduction as follows:

- *Oxidation occurs when something loses electrons.*
- *Reduction occurs when something gains electrons.*

We usually simply shorten this to oxidation is loss of electrons and reduction is gain of electrons. A way of remembering this is the mnemonic OILRIG.

HINT

OILRIG:
Oxidation
Is
Loss of electrons
Reduction
Is
Gain of electrons

If we look again at the electrode equations in the electrolysis of lead(II) bromide, we see that the lead(II) ions gain electrons at the cathode:

$$Pb^{2+} + 2e^- \rightarrow Pb$$

Gain of electrons is reduction. The lead(II) ions are reduced to lead atoms.

The bromide ions lose electrons at the anode:

$$2Br^- \rightarrow Br_2 + 2e^-$$

Loss of electrons is oxidation. Bromide ions are oxidised to bromine molecules.

If something loses electrons something else must gain electrons and so oxidation and reduction always occur at the same time: we talk about **redox** reactions, **red**(uction)**ox**(idation). In the reactions going on at the electrodes each equation only shows one of the processes occurring, either oxidation or reduction, and so we call these *half-equations*. Both these reactions involve ions and so, in the exam, you may be asked to write *ionic half-equations* representing the reactions at the electrodes.

THE ELECTROLYSIS OF OTHER MOLTEN SUBSTANCES

If we carry out electrolysis of molten sodium chloride, we get sodium at the cathode (negative electrode) and chlorine at the anode (positive electrode). The ionic half-equations are:

cathode: $Na^+ + e^- \rightarrow Na$ reduction

Sodium ions are reduced to sodium atoms.

anode: $2Cl^- \rightarrow Cl_2 + 2e^-$ oxidation

Chloride ions are oxidised to chlorine molecules.

These half-equations must always balance in terms of the number of atoms on each side, but also in terms of the charges; the total charge must be the same on both sides. This is why we need 2 electrons in the second half-equation but only 1 in the first.

Let us look at another example, the electrolysis of molten aluminium oxide (Al_2O_3). We get aluminium at the cathode and oxygen at the anode. Aluminium is in Group 3 in the Periodic Table and so an aluminium atom has 3 electrons in its outer shell. You may remember from Chapter 7 that this means that Al forms a 3+ ion. This 3+ ion will be attracted to the negative electrode in electrolysis and we will get the reaction:

$Al^{3+} + 3e^- \rightarrow Al$

In order to cancel out the 3+ charge on the Al^{3+} ion we need to add 3 electrons. The total charge on the left-hand side is zero (**3+** + **3–**), which is the same as on the right-hand side. Another way to think about this is that if an aluminium atom loses 3 electrons to form an Al^{3+} ion, we must put those electrons back in order to form the atom again. This is a reduction reaction because the Al^{3+} ion gains electrons.

When we electrolyse molten aluminium oxide, the half-equation for the reaction at the anode is:

$2O^{2-} \rightarrow O_2 + 4e^-$

Each O^{2-} ion has 2 'extra' electrons and oxygen atoms go around in pairs, so we must remove 4 electrons to form O_2. These are shown on the right-hand side of the half-equation. There are two Os on each side and the total charge on each side is 4–. This is an oxidation reaction.

HINT

A common mistake is to put the electrons on the wrong side of the half-equation. Check the charges to make sure you have the same total charge on both sides.

When molten zinc(II) chloride is electrolysed, zinc is obtained at the cathode and chlorine at the anode:

cathode: $Zn^{2+} + 2e^- \rightarrow Zn$ reduction

anode: $2Cl^- \rightarrow Cl_2 + 2e^-$ oxidation

We can make the following generalisations from the reactions above:

- If you electrolyse a molten ionic compound only containing two elements, you will get the metal at the cathode (because metals form positive ions) and the non-metal at the anode (because non-metals form negative ions).
- Reduction always occurs at the cathode and oxidation always occurs at the anode.

HINT

A way of remembering this is AN OX RED CAT or AN OILRIG CAT.

You can probably see now that positive ions are known as cations because they are attracted to the cathode (negative electrode). Negative ions are known as anions because they are attracted to the anode (positive electrode).

Not all ionic compounds can be electrolysed when they are molten. Some break up into simpler substances before their melting point. For example, copper(II) carbonate breaks into copper(II) oxide and carbon dioxide, even on gentle heating. It is impossible to melt it.

THE ELECTROLYSIS OF AQUEOUS SOLUTIONS

When aqueous solutions are electrolysed the products are not always the same as when molten salts are electrolysed.

Safety Note: Wear eye protection. Do not smell the chlorine, especially if you have asthma. Once chlorine is detected the current must be switched off.

ACTIVITY 5

PRACTICAL: INVESTIGATING THE ELECTROLYSIS OF AQUEOUS SOLUTIONS

We can investigate the electrolysis of an aqueous solution such as sodium chloride solution using the apparatus shown in Figure 10.6.

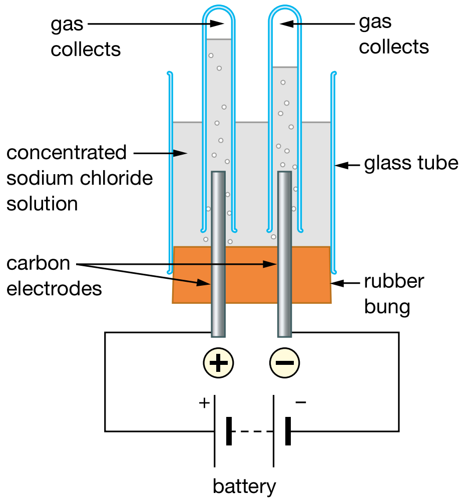


Figure 10.6 Electrolysis of sodium chloride solution

The following procedure is used:

- Set up the apparatus as shown in Figure 10.6. The glass tube, rubber bung and electrodes together are sometimes called an **electrolytic cell**.
- Pour concentrated sodium chloride solution into the glass tube.
- Place a test-tube containing sodium chloride solution over each electrode. The test-tubes must not completely cover the electrodes or ions will be unable to flow and there will be no current.
- Connect the battery/powerpack to the electrodes.
- The experiment should be done in a fume cupboard (fume hood) or well-ventilated room because chlorine gas is poisonous.

We can see if something is happening by looking for bubbles of gas or a metal forming at the electrodes. Any gases can be tested.

The tests for gases are covered in Chapter 18.

In this experiment we see bubbles of gas at both electrodes. When the gases are tested we find that hydrogen forms at the negative electrode (cathode) and chlorine forms at the positive electrode (anode).

KEY POINT

We would expect to get the same volume of hydrogen as chlorine. However, in reality we appear to obtain less chlorine than expected because it is more soluble in water.

THE ELECTROLYSIS OF SODIUM CHLORIDE SOLUTION

When molten sodium chloride is electrolysed, the products at the electrodes are:

anode: chlorine

cathode: sodium

When you electrolyse sodium chloride solution you do not get the same products as when you electrolyse molten sodium chloride. Although chlorine is still formed at the anode, hydrogen is produced at the cathode rather than sodium. The hydrogen at the cathode comes from the water.

Water is called a *weak electrolyte*. It ionises very slightly to give hydrogen ions and hydroxide ions:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Whenever you have water present, you have to consider these ions *as well as* the ions in the compound you are electrolysing.

KEY POINT

The reversible sign shows that as water molecules break up to form hydrogen ions and hydroxide ions, these ions are recombining to make water again.

AT THE CATHODE

The solution contains $Na^+(aq)$ and $H^+(aq)$, and these are both attracted to the negative electrode (cathode). However, sodium is a very reactive metal. This means that it is very difficult to add an electron to a sodium ion to convert it back to a sodium atom. Hydrogen is less reactive than sodium so it is easier to add an electron to a hydrogen ion to form a hydrogen atom. Each hydrogen atom formed combines with another one to make a hydrogen molecule:

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

Remember that the hydrogen ions come from water molecules splitting up. Each time a water molecule ionises, it also produces a hydroxide ion. There is a build-up of these in the solution around the cathode. These hydroxide ions make the solution alkaline in the region around the cathode.

KEY POINT

The more reactive something is, the greater tendency it has to form an ion. This means that the more reactive something is, the more difficult it is to turn it back into an atom. For positive ions, the lower the position of an element in the reactivity series, the more easily it will accept an electron. The reactivity series is discussed in Chapter 14.

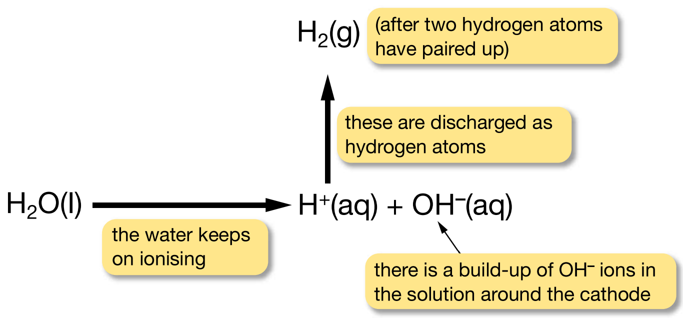


Figure 10.7 The process of electrolysing solutions

KEY POINT

Because the hydrogen ions are discharged (removed from the solution as hydrogen gas), they can no longer react with the hydroxide ions and reform water. The ionisation of the water becomes a one-way process.

There is an alternative way of looking at this cathode reaction, starting from neutral water molecules, which can be thought of as taking electrons directly from the cathode:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

You can see more easily why the solution becomes alkaline using this half-equation as $OH^-(aq)$ ions are produced.

HINT

You might come across either half-equation in the exam. Either should be accepted in answers.

AT THE ANODE

EXTENSION WORK

If the sodium chloride solution is dilute, you get noticeable amounts of oxygen produced as well as chlorine. This comes from the hydroxide ions:

$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$

It is unlikely that you will be asked about this at International GCSE.

$Cl^-(aq)$ and $OH^-(aq)$ are both attracted by the positive anode. It is slightly easier to remove electrons from (oxidise) the hydroxide ion than from the chloride ion, but there isn't much difference. There are, however, many, many more chloride ions present in the solution, and so it is mainly these that are oxidised at the anode:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

THE REMAINING SOLUTION

If the electrolysis is carried on for a long time, we can work out what the final solution remaining at the end will be. The ions in the solution were:

from NaCl: Na^+ $\cancel{Cl^-}$

from H_2O: $\cancel{H^+}$ OH^-

Cl^- and H^+ ions were removed from the solution by being discharged at the electrodes, so we are left with Na^+ and OH^-, sodium hydroxide solution.

THE ELECTROLYSIS OF COPPER(II) SULFATE SOLUTION USING INERT ELECTRODES

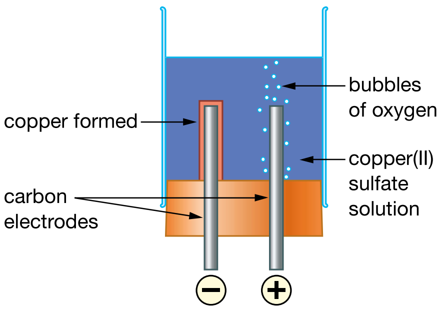


Figure 10.8 Electrolysis of copper(II) sulfate solution using inert electrodes produces copper at the cathode and oxygen gas at the anode.

The copper(II) ions and hydrogen ions (from the water) will be attracted to the cathode. Copper is below hydrogen in the reactivity series, which means that it is easier to add electrons to copper ions to form an atom. The cathode will get coated with pink-brown copper:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad \text{reduction}$$

Sulfate ions and hydroxide ions (from the water) will be attracted to the anode. Sulfate ions aren't easy to oxidise. Instead, you get oxygen from the oxidation of hydroxide ions from the water:

$$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^- \qquad \text{oxidation}$$

There is an alternative way of looking at this anode reaction. The equation this time is:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

You can see more easily why the solution becomes acidic using this half-equation: $H^+(aq)$ ions are produced. You may come across either half-equation in the exam.

If the electrolysis is continued for a long time the copper(II) ions will eventually all be used up, and so the colour of the solution will fade from blue to colourless. What is left in the solution? The ions originally present were:

from $CuSO_4$: $\cancel{Cu^{2+}}$ SO_4^{2-}

from water: H^+ $\cancel{OH^-}$

Copper ions and hydroxide ions are discharged at the electrodes. Hydrogen ions from the water aren't being discharged and neither are the sulfate ions. The solution turns into dilute sulfuric acid (H_2SO_4). The electrolysis will then continue as for dilute sulfuric acid (see below).

EXTENSION WORK

The reason that we keep stressing the use of inert electrodes is that what the electrode is made of can sometimes affect the products you get. If you use copper electrodes oxygen gas is not produced at the anode but rather the anode gets smaller.

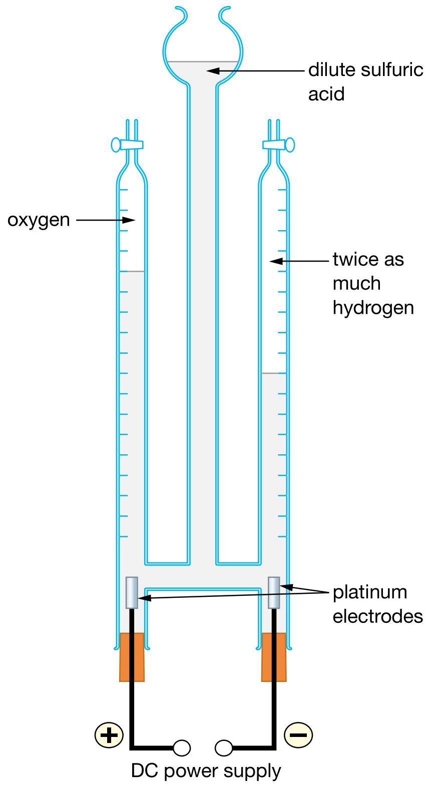


Figure 10.9 Apparatus for electrolysing dilute sulfuric acid and measuring the volume of gases produced.

DID YOU KNOW?

This experiment could be used to show that the formula of water is H_2O.

THE ELECTROLYSIS OF DILUTE SULFURIC ACID USING INERT ELECTRODES

In this case, the only positive ions arriving at the cathode are hydrogen ions (from the acid and the water). These are discharged to give hydrogen gas:

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

At the anode – as with copper(II) sulfate solution – sulfate ions and hydroxide ions (from the water) arrive. The sulfate ions are too difficult to oxidise, and so you obtain oxygen from the oxidation of hydroxide ions from the water:

$$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$$

Twice as much hydrogen is produced as oxygen. Look at the half-equations above. For every 4 electrons that flow around the circuit, you would get 1 molecule of oxygen. But 4 electrons would produce 2 molecules of hydrogen. You get twice the number of molecules of hydrogen as of oxygen. Twice the number of molecules occupy twice the volume.

Actually, when we do this experiment the amount of hydrogen we obtain is more than twice as much as the oxygen. This is because oxygen is more soluble in water than hydrogen. What we sometimes do to stop this happening is to carry out the electrolysis experiment for a few minutes first in order to saturate the water with oxygen and then start to collect the gases; this gives much better results.

THE ELECTROLYSIS OF SOME OTHER SOLUTIONS USING INERT ELECTRODES

HOW TO WORK OUT WHAT WILL HAPPEN

- If the metal is high in the reactivity series, you get hydrogen produced at the cathode instead of the metal.
- If the metal is below hydrogen in the reactivity series, you obtain the metal at the cathode.
- If you have solutions of halides (chlorides, bromides or iodides), you obtain the halogen (chlorine, bromine or iodine) at the anode. With other common negative ions (sulfate, nitrate, hydroxide), you obtain oxygen at the anode.

potassium
sodium
lithium
calcium
magnesium
aluminium
(carbon)
zinc
iron
(hydrogen)
copper
silver
gold

decreasing reactivity

Figure 10.10 The reactivity series shows metals in order of how reactive they are from most reactive to least reactive. This is discussed more in Chapter 14.

EXTENSION WORK

This leaves the problem of what you obtain if you have a moderately reactive metal such as zinc, for example. Reasonably concentrated solutions will give you the metal. Very dilute solutions will give you mainly hydrogen. In between, you will get both. At International GCSE you probably won't have to worry about this. The examples you will see in exams are always clear.

The table shows some simple examples of these rules.

Table 10.1 The electrolysis of solutions using inert (carbon or platinum) electrodes

Cathode (–)			Anode (+)	
Solution	**Product**	**Half-equation**	**Product**	**Half-equation**
$KI(aq)$	hydrogen	$2H^+(aq) + 2e^- \rightarrow H_2(g)$	iodine	$2I^-(aq) \rightarrow I_2(aq) + 2e^-$
$MgBr_2(aq)$	hydrogen	$2H^+(aq) + 2e^- \rightarrow H_2(g)$	bromine	$2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$
$H_2SO_4(aq)$	hydrogen	$2H^+(aq) + 2e^- \rightarrow H_2(g)$	oxygen	$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$
$CuSO_4(aq)$	copper	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	oxygen	$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$

WHAT WOULD HAPPEN WITH NON-ELECTROLYTES?

For electrolysis to work, there have to be ions present. The current in the external circuit (with the bulb and power source) can flow only if there are ions which can move and be discharged.

If you tried to electrolyse a covalent compound (either molten or in solution), there wouldn't be a current flow because there aren't any ions. Nothing else would happen either. Sugar, for example, is a non-electrolyte; it doesn't undergo electrolysis. It won't conduct electricity, and won't be decomposed by it, either in solution or when molten.

Simple experiments like those described in this chapter give you an easy way of finding out whether a substance is ionic or not. If it undergoes electrolysis, either molten or in solution, it must contain ions. If it doesn't undergo electrolysis, it doesn't contain ions.

KEY POINT

There are exceptions to this: covalent compounds that are electrolytes in solution. These include acids and ammonia solution.

!

Safety Note: Wear eye protection. Do not smell the chlorine, especially if you have asthma. Once chlorine is detected the current must be switched off.

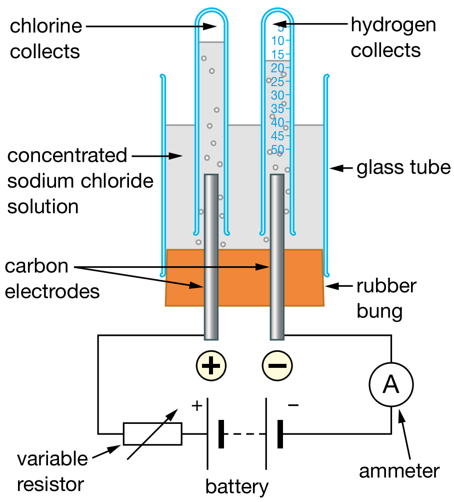


Figure 10.11 We can use this apparatus for a quantitative electrolysis experiment.

ACTIVITY 6

▼ PRACTICAL: QUANTITATIVE ELECTROLYSIS

Quantitative means related to numbers. We can investigate how *much* product we get in an electrolysis experiment. We could, for example, investigate the effect of changing the current on the amount of hydrogen produced at the cathode in the electrolysis of sodium chloride solution. To do this we would use similar apparatus to that in Figure 10.6, but we would also have to put a variable resistor and an ammeter into the circuit to allow us to vary and measure the current. We would also have to use a gas burette or measuring cylinder to measure the volume of gas produced. We would use the following procedure:

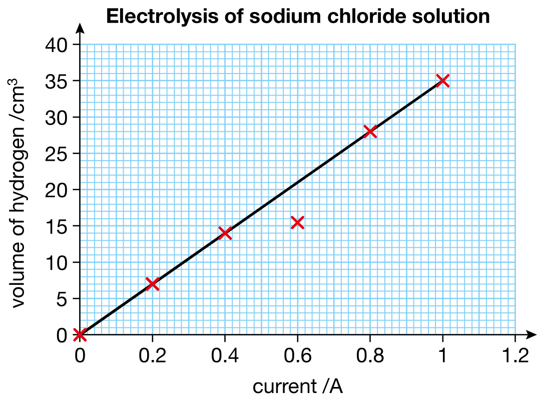
- Set up the apparatus as shown in Figure 10.11.
- Pour 50 cm^3 of concentrated sodium chloride solution into the glass tube.
- Place a gas burette (or measuring cylinder) filled with sodium chloride solution over the cathode.
- Turn on the powerpack/connect the battery and set the current to 0.2 A using the variable resistor.

- Take an initial reading on the gas burette. (We have to start the current flowing so that we can see what the current is, therefore we only take a reading on the gas burette after we have turned on the power.)
- Start the timer.
- Stop the timer after 5 minutes and note the final reading on the gas burette.
- Repeat for currents of 0.4 A, 0.6 A, 0.8 A and 1.0 A.
- Repeat each experiment to get more reliable results.

A set of results for this experiment could be:

Current/A	Volume of hydrogen gas produced/cm^3
0.20	7.0
0.40	13.9
0.60	15.1
0.80	28.0
1.0	34.9

We can plot this data on a graph (Figure 10.12).



▲ Figure 10.12 How changing the current affects the volume of hydrogen produced at the cathode.

Because the current is continuous data, we draw a line of best fit through the points. The reading at 0.6 A is an anomalous point and we do not include this when drawing our line of best fit. The reading at 0.6 A is too low and could have occurred because the current that we used was too low or some gas escaped.

The line of best fit is a straight line that goes through the origin and so we can say that we have a proportional relationship: the volume of gas produced is directly proportional to the current passed through the solution.

CHAPTER QUESTIONS

SKILLS REASONING

7

1 State what is formed at the cathode and at the anode during the electrolysis of the following substances. Assume that carbon electrodes were used each time.

a Molten lead(II) bromide

b Molten zinc chloride

c Sodium iodide solution

d Molten sodium iodide

e Copper(II) chloride solution

f Dilute hydrochloric acid

g Magnesium sulfate solution

h Sodium hydroxide solution

SKILLS PROBLEM SOLVING

2 Copy and complete the following half-equations for reaction at the anode or cathode, and state whether each involves oxidation or reduction. Electrons have been put in for the first four but not for the ones after that.

a $Mg^{2+} + e^- \rightarrow Mg$

b $Al^{3+} + e^- \rightarrow Al$

c $2Br^- \rightarrow Br_2 + e^-$

d $O^{2-} \rightarrow O_2 + e^-$

e $Cl^- \rightarrow Cl_2$

f $Ni^{2+} \rightarrow Ni$

g $OH^- \rightarrow O_2 + H_2O$

h $H_2O \rightarrow O_2 + H^+$

i $H_2O \rightarrow H_2 + OH^-$

SKILLS REASONING

3 Some solid potassium iodide was placed in an evaporating basin. Two carbon electrodes were inserted and connected to a 12 volt DC power source and a light bulb. The potassium iodide was heated. As soon as the potassium iodide was molten, the bulb came on. Purple fumes were seen coming from the positive electrode, and lilac flashes were seen around the negative one.

a Explain why the bulb didn't come on until the potassium iodide melted.

SKILLS CRITICAL THINKING

6

b State the name of the positive electrode.

8

c Name the purple fumes seen at the positive electrode, and write the ionic half-equation for their formation.

d The lilac flashes seen around the negative electrode are caused by the potassium which is formed. The potassium burns with a lilac flame. Write the ionic half-equation for the formation of the potassium.

6

e State the products formed at the electrodes if molten sodium bromide is electrolysed instead of molten potassium iodide.

8

f Write the ionic half-equations for the reactions occurring during the electrolysis of molten sodium bromide.

SKILLS CRITICAL THINKING

9

4 For electrolysis of each of the following
   i write the ionic half-equation for the reaction occurring at the cathode
   ii write the ionic half-equation for the reaction occurring at the anode
   iii state what has been oxidised and what has been reduced.

a Molten lead(II) bromide using carbon electrodes

b Sodium chloride solution using carbon electrodes

c Calcium bromide solution using carbon electrodes

d Copper(II) sulfate solution using platinum electrodes

e Aluminium nitrate solution using carbon electrodes

f Molten magnesium iodide using carbon electrodes

g Dilute hydrochloric acid using platinum electrodes

SKILLS INTERPRETATION, REASONING

8

5 You are asked to find out whether two compounds, S and T, are electrolytes or non-electrolytes. S melts at 1261 °C and is soluble in water. T melts at 265 °C and is insoluble in water. Describe, with the aid of diagrams, how you would find out if each of these substances was an electrolyte or a non-electrolyte. In each case say what you would look for to help you to decide.

6 When copper(II) sulfate solution is electrolysed using copper electrodes the reaction at the cathode is the same as with inert electrodes but no oxygen is given off at the cathode. Instead the anode gets smaller as copper ions go into solution. The half-equation for the reaction at the anode is:

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

a Write the half-equation for the reaction at the cathode.

SKILLS REASONING

b When copper(II) sulfate solution is electrolysed using inert electrodes the blue colour of the solution fades and the solution becomes more acidic.
   i Explain these observations.

9

   ii Predict and explain what happens to the colour and acidity of the solution when copper(II) sulfate solution is electrolysed with copper electrodes.

END OF CHEMISTRY ONLY

UNIT QUESTIONS

You may need to refer to the Periodic Table on page 320.

SKILLS CRITICAL THINKING 4

1 Hydrogen is the most common element in the universe.
The melting point and boiling point of hydrogen are shown in the table:

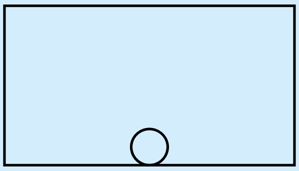
Melting point/°C	–259
Boiling point/°C	–253

a Put a cross in the box to show a temperature at which hydrogen is a liquid. **(1)**

–265 °C ☐ –260 °C ☐ –255 °C ☐ –250 °C ☐

SKILLS INTERPRETATION 6

b The circle in the diagram represents 1 molecule of hydrogen. Complete the diagram to show the arrangement of particles in liquid hydrogen. You should add at least 10 more circles to the diagram. **(2)**



SKILLS PROBLEM SOLVING 8

c Hydrogen has three isotopes, the least common of which is tritium, ^{3}H. Use the Periodic Table to work out the number of protons, neutrons and electrons in an atom of tritium. **(3)**

Number of protons:

Number of neutrons:

Number of electrons:

d Hydrogen reacts with nitrogen to form ammonia (NH_3).

7

i The electronic configuration of a nitrogen atom is (put a cross in one box): **(1)**

2, 2, 3 ☐ 2, 5 ☐ 2, 8, 4 ☐ 2, 2, 8, 2 ☐

SKILLS CRITICAL THINKING 8

ii Draw a dot-and-cross diagram, showing outer electrons only, to show the bonding in an ammonia molecule. **(2)**

6

e Ammonia forms salts that contain the ammonium ion. Put a cross in the box to show which of the following formulae for ammonium compounds is incorrect.

NH_4SO_4 ☐ NH_4NO_3 ☐ NH_4Cl ☐ $(NH_4)_2CO_3$ ☐

5

f Two more compounds that contain hydrogen are water and ethanol. Put a cross in the box to show a method that can be used to separate a mixture of ethanol and water. **(1)**

crystallisation	☐	simple distillation	☐
filtration	☐	fractional distillation	☐

(Total 10 marks)

SKILLS CRITICAL THINKING 6

2

a Complete the following passage by using the words below. You may use the words once, more than once, or not at all. **(4)**

mass number	atomic number	groups	periods
protons	electrons	outer shell	nucleus

The elements in the Periodic Table are arranged in order of ______________.

The vertical columns are called ______________ and contain elements

which have the same number of ______________ in their ______________.

5

b Put a cross next to the symbol(s) of elements that are non-metals. **(2)**

H ☐ V ☐ Pb ☐ Ar ☐ W ☐

SKILLS REASONING 6

c Silicon is an element that shows some of the properties of metals and non-metals. It is sometimes called a *metalloid*.

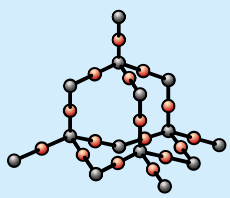
i Two properties of silicon are:

- silicon conducts electricity
- silicon forms an oxide (SiO_2) that reacts with hot concentrated sodium hydroxide.

Explain which of these is not a property of metals. **(2)**

SKILLS ANALYSIS, REASONING 8

ii The structure of silicon dioxide (SiO_2) is shown in the diagram. This structure continues in all directions.



Explain in terms of electronic configurations and bonding whether the grey or red circles in this diagram represent silicon atoms. **(3)**

iii By referring to the diagram in part **ii** explain whether you would expect SiO_2 to be a solid, liquid or gas at room temperature. **(2)**

(Total 13 marks)

SKILLS INTERPRETATION, REASONING 7

3 Strontium is an element in Group 2 of the Periodic Table and bromine is an element in Group 7.

a Explain what happens in terms of electrons when an atom of strontium combines with an atom of bromine to form strontium bromide. You may draw a diagram to illustrate your answer. **(3)**

b Explain in terms of structure and bonding whether you would expect strontium bromide to have a high or a low melting point. **(3)**

c Explain what you understand by the term ‘relative atomic mass’ of an element. **(2)**

SKILLS PROBLEM SOLVING 10

d The natural abundances of the two isotopes of bromine are:

^{79}Br 50.69%

^{81}Br 49.31%

Calculate the relative atomic mass of bromine. Give your answer to 2 decimal places. **(2)**

SKILLS CRITICAL THINKING 6

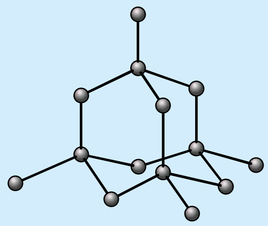
e The formula of strontium nitrate is (put a cross in one box): **(1)**

$SrNO_3$ ☐ $Sr(NO_3)_2$ ☐ $SrNO_{32}$ ☐ Sr_3N_2 ☐

(Total 11 marks)

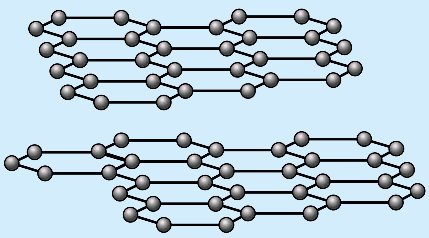
SKILLS REASONING 9

4 The diagram represents the structure of diamond, a form of carbon.

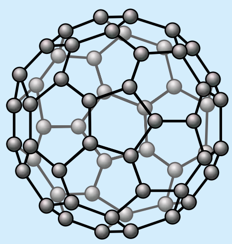


a Explain in terms of structure and bonding why diamond is very hard. **(2)**

b Two more forms of carbon are graphite and C_{60} fullerene. Part of the structure of graphite and a molecule of C_{60} fullerene are shown in the diagram.



graphite



C_{60} fullerene

i Explain whether graphite or C_{60} fullerene has the higher boiling point. **(4)**

ii Explain why graphite conducts electricity. **(2)**

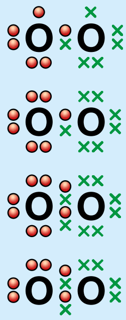
iii Explain why C_{60} fullerene does not conduct electricity. **(2)**

(Total 10 marks)

SKILLS ANALYSIS 7

5

a Oxygen gas has the formula O_2. Which of the following is a correct dot-and-cross diagram showing the bonding in O_2 (outer shells of electrons only are shown). Circle one of the diagrams. **(1)**



SKILLS CRITICAL THINKING 6

b Oxygen reacts with potassium to form potassium oxide. Put a cross in one box to indicate what the formula of potassium oxide is. **(1)**

PO ☐ KO ☐ K_2O ☐ KO_2 ☐

SKILLS ANALYSIS

c Oxygen reacts with carbon to form carbon dioxide. Which diagram shows the covalent bonds in carbon dioxide? Circle one diagram. **(1)**

$$O{=}C{-}O$$

$$O{=}C{=}O$$

$$O{=}C{\equiv}O$$

$$O{-}C{-}O$$

(Total 3 marks)

SKILLS PROBLEM SOLVING 7

6

In an experiment to find the empirical formula of lead oxide, a small porcelain dish was weighed, filled with lead oxide and weighed again. The dish was placed in a tube and heated in a stream of hydrogen. The hydrogen reduced the lead oxide to a bead of metallic lead. When the apparatus was cool, the dish and its bead of lead were weighed together.

Mass of porcelain dish = 17.95 g

Mass of porcelain dish + lead oxide = 24.80 g

Mass of porcelain dish + lead = 24.16 g

(A_r: O = 16, Pb = 207)

a Calculate the mass of lead in the lead oxide. **(1)**

b Calculate the mass of oxygen in the lead oxide. **(1)**

9

c There are three different oxides of lead: PbO, PbO_2 and Pb_3O_4. Use your results from **a** and **b** to find the empirical formula of the oxide used in the experiment. **(3)**

(Total 5 marks)

SKILLS PROBLEM SOLVING 7

7 Copper reacts with concentrated nitric acid to produce copper(II) nitrate solution and nitrogen dioxide gas.

$$Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

A student carried out an experiment to make some copper(II) nitrate crystals.

a The student started with 2.00 g of copper and added excess nitric acid. Calculate the maximum mass of copper(II) nitrate, $Cu(NO_3)_2$, which could be obtained. (A_r: N = 14, O = 16, Cu = 63.5) **(3)**

SKILLS EXECUTIVE FUNCTION 5

b Explain the method the student could use to obtain crystals of copper(II) nitrate from the copper nitrate solution. **(3)**

SKILLS PROBLEM SOLVING 7

c The copper nitrate crystallises out of the solution as $Cu(NO_3)_2{\cdot}3H_2O$. The student did some calculations and worked out that he should make 7.61 g of crystals. He actually only made 5.23 g. Calculate the percentage yield of the student's experiment. **(2)**

(Total 8 marks)

CHEMISTRY ONLY

SKILLS PROBLEM SOLVING 9

8 If pyrite (FeS_2) is heated strongly in air it reacts according to the equation:

$$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

Iron can be extracted from the iron(III) oxide produced, and the sulfur dioxide can be converted into sulfuric acid. In this question you can assume that the molar volume of any gas at rtp is 24 dm^3.

a Calculate the mass of iron(III) oxide that can be obtained from 480 kg of pure pyrite. (A_r: O = 16, S = 32, Fe = 56) **(3)**

b Calculate the volume of sulfur dioxide (measured at rtp) produced from 480 kg of pyrite. **(2)**

c The next stage of the manufacture of sulfuric acid is to convert the sulfur dioxide into sulfur trioxide (SO_3) by reacting it with oxygen.

i Write a balanced equation for this reaction. **(2)**

ii Calculate the volume of oxygen (measured at rtp) needed for the complete conversion of the sulfur dioxide produced in **b** into sulfur trioxide. **(2)**

(Total 9 marks)

SKILLS CRITICAL THINKING 7

9 Strontium hydroxide, $Sr(OH)_2$, is only sparingly soluble in water at room temperature. In an experiment to measure its solubility, a student made a saturated solution of strontium hydroxide. She pipetted 25.0 cm^3 of this solution into a conical flask, added a few drops of methyl orange indicator and then titrated it with 0.100 mol/dm^3 hydrochloric acid from a burette. She needed to add 32.8 cm^3 of the acid to neutralise the strontium hydroxide.

$$Sr(OH)_2(aq) + 2HCl(aq) \rightarrow SrCl_2(aq) + 2H_2O(l)$$

5

a Explain what is meant by a *saturated solution*. **(1)**

SKILLS PROBLEM SOLVING 8

b Calculate the number of moles of HCl in 32.8 cm^3 of 0.100 mol/dm^3 hydrochloric acid. **(1)**

c Calculate the concentration of the strontium hydroxide in mol/dm^3. **(3)**

d The solubility of a substance is usually measured in units of g per 100 g of water. The mass of 1 dm^3 of water is 1000 g. Use the value that you obtained in **c** to calculate the solubility of strontium hydroxide as g of strontium hydroxide per 100 g of water. (A_r: H = 1, O = 16, Sr = 88) **(2)**

SKILLS EXECUTIVE FUNCTION 7

e The calculation used in **d** gives only an approximate value for the solubility because the volume changes when a substance is dissolved in water. Describe an experiment that the student could carry out to determine a more accurate value for how much strontium hydroxide dissolves in 100 g of water at this temperature. You can assume that you are given 50 cm^3 of saturated strontium hydroxide solution. You should include a description of the apparatus you would use and the measurements you would make. **(5)**

(Total 12 marks)

SKILLS PROBLEM SOLVING 8

10 A student carried out some experiments using dilute sulfuric acid.

a He found that 25.0 cm^3 of 0.100 mol/dm^3 sodium hydroxide solution was neutralised by 20.0 cm^3 of the dilute sulfuric acid.

The equation for the reaction is

$$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

Calculate the concentration of the sulfuric acid in mol/dm^3. **(4)**

9

b 100 cm^3 of this same sulfuric acid was reacted with magnesium.

$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$$

i Magnesium is a metal. Describe the structure and bonding in a piece of magnesium. **(3)**

ii Magnesium is malleable. Explain in terms of structure and bonding why magnesium is malleable. **(2)**

iii Calculate the amount in moles of sulfuric acid that was used. **(1)**

iv The student used 0.100 g of magnesium in the experiment. Work out whether the sulfuric acid or the magnesium was in excess. **(2)**

v Calculate the volume of hydrogen gas that would be produced at rtp in this experiment. (Assume that the molar volume at rtp of hydrogen is 24 000 cm^3.) **(2)**

vi When the student did the experiment they collected 94 cm^3 of gas. Calculate the percentage yield of the experiment. **(1)**

c The student electrolysed the solution of magnesium sulfate.

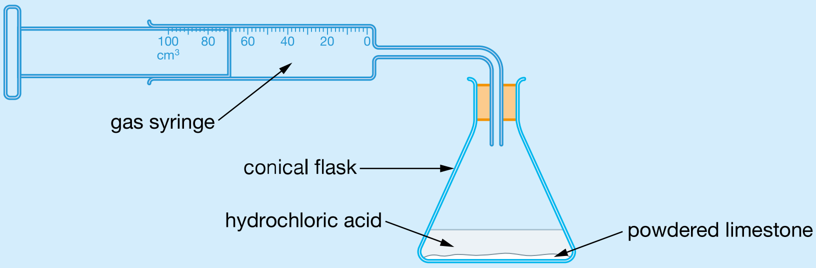
i State the name of the product formed at the cathode. **(1)**

ii Oxygen gas is formed at the anode. Write an ionic half-equation for the formation of oxygen at the anode. **(2)**

(Total 18 marks)

SKILLS CRITICAL THINKING 3

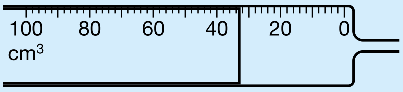
11 A class of 11 students carried out an experiment to determine how much calcium carbonate ($CaCO_3$) was in a sample of limestone. Each student was given a different mass of limestone, which they added to 50 cm³ of dilute hydrochloric acid and then measured the volume of carbon dioxide produced using the apparatus shown below.



a Name a piece of apparatus that could be used to measure out 50 cm³ of dilute hydrochloric acid. **(1)**

4

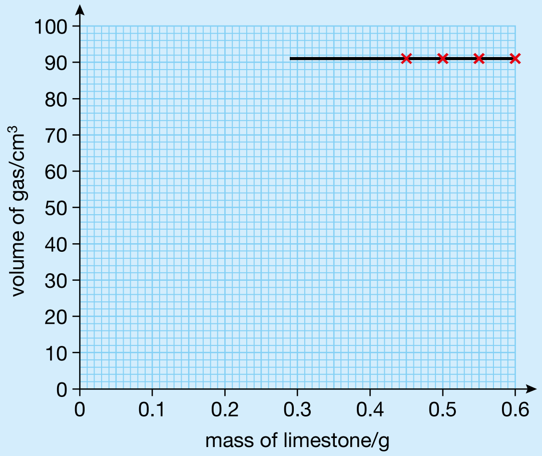
b The diagram shows the reading from the experiment carried out by Student 2.



Complete the table with the volume of gas collected by Student 2. **(1)**

Student	Mass of limestone/g	Volume of gas produced/cm³
1	0.10	22
2	0.15	
3	0.20	37
4	0.25	56
5	0.30	66
6	0.35	78
7	0.40	88
8	0.45	91
9	0.50	91
10	0.55	91
11	0.60	91

c Some of the data have been plotted on the graph below. Plot the rest of the data on the graph and draw another straight line of best fit. **(3)**



d The teacher realised that one of the student's results was incorrect.

SKILLS ANALYSIS

i Explain which student's result is incorrect. **(2)**

SKILLS DECISION MAKING

ii Suggest one thing that could have gone wrong with the student's experiment to produce this result. **(1)**

SKILLS REASONING

e Explain why the volume of gas produced in the experiments carried out by Students 8–11 is the same. **(2)**

SKILLS ANALYSIS

f Use the graph to determine the mass of limestone that reacts exactly with the hydrochloric acid. **(1)**

SKILLS PROBLEM SOLVING

g The equation for the reaction between calcium carbonate and hydrochloric acid is

$$CaCO_3(s) + 2HCl(\ldots) \rightarrow CaCl_2(aq) + H_2O(\ldots) + CO_2(g)$$

i Complete the equation by adding the missing state symbols. **(2)**

ii Calculate the mass of calcium carbonate that would produce 91 cm^3 of carbon dioxide at rtp. **(3)**

(Assume that the molar volume of a gas at rtp is 24 000 cm^3.)

iii Calculate the percentage of calcium carbonate in the sample of limestone. **(2)**

(Total 18 marks)

END OF CHEMISTRY ONLY