ESAT Guide

Chemistry

June 2025

Contents

INTRODUCTION

This is worth reading before you use this guide.

We have three aims in writing this guide:

First, we want to set out what we expect you to know for the ESAT. We do this by basing each part of the guide on the relevant part of the specification.

Second, we want to encourage you to think deeply and carefully about science and mathematics and to develop a good understanding of the topics in the specification. To help with this, we have added a lot of discussion and examples as well as some exercises throughout the guide.

Third, we want to make sure that all candidates have access to a free resource to help them prepare for the ESAT.

How to use this guide

You do not need to work through all this guide as you will find that you know many of the topics in the specification very well already. Use this guide as a resource to help you clarify and review topics that you are less familiar with. We have broken down our discussion to fit exactly with the specification to make things as simple to navigate as possible.

What this guide is not

This guide is not a comprehensive textbook: we do not cover every topic to the same level of detail, and we do not develop every topic from scratch. It is also not a substitute for sustained hard work and preparation. It is a resource to help you and to guide you in the right direction.

Should I take an ESAT course?

We do not recommend that you take a course, and we do NOT endorse any courses. No one from the ESAT development team teaches on any courses. All the resources you need to prepare are available from the UAT-UK website and are entirely free.

A final note

We have used boxes throughout the guide to help you navigate.

The relevant part of the specification is found in these sorts of boxes:

Specification

examples in these sorts of boxes:

Examples

and exercises [answers are at the end of each section] in these sorts of boxes:

Exercises

We hope to be able to update and, if necessary, correct the guide now and again. Look at the date on the front page to see when the guide was last edited.

C1. Atomic structure

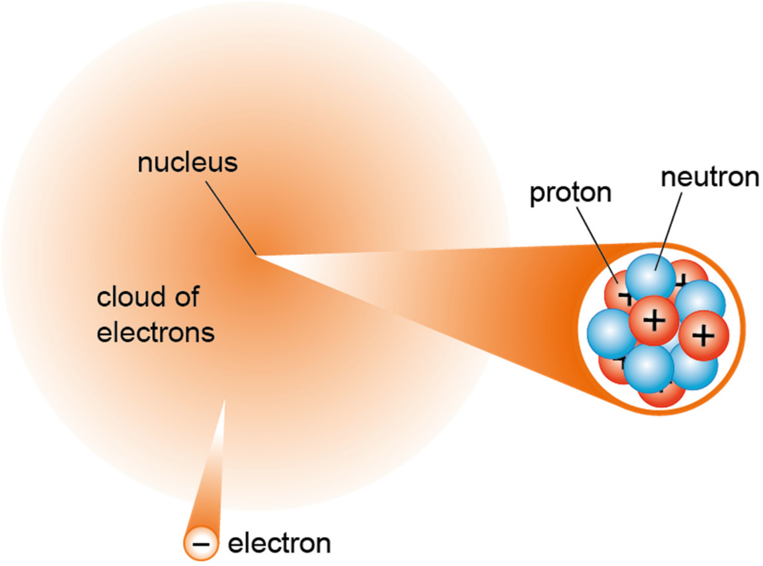
C1.1 Describe the structure of the atom as a central nucleus (containing protons and neutrons) surrounded by electrons moving in shells/energy levels.

C1.2 Know the relative masses and charges of protons, neutrons and electrons, and recognise that most of the mass of an atom is in the nucleus.

C1.3 Know and be able to use the terms *atomic number* and *mass number*, together with standard notation (e.g. ${}^{12}_{6}C$), and so be able to calculate the number of protons, neutrons and electrons in any atom or ion.

A subatomic particle is a particle that is found within an atom. The atom contains three main subatomic particles: protons, neutrons and electrons.

An atom



Particles found in the nucleus, which is at the centre of the atom, are called nucleons. Protons and neutrons are found in the nucleus.

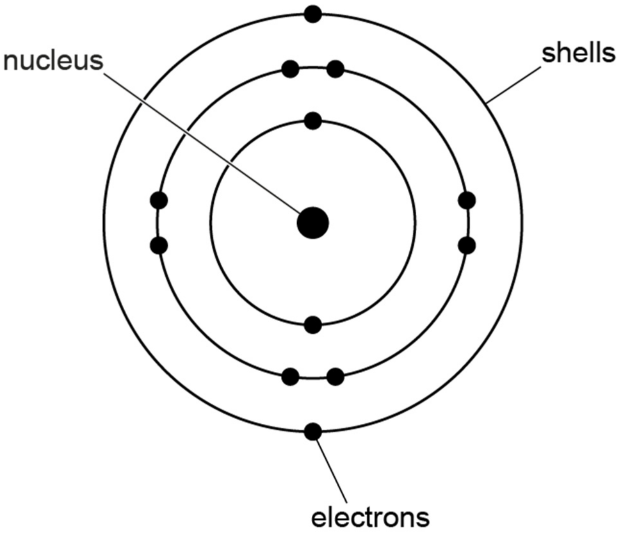
The nucleus and the electrons are very, very small compared to the overall size of the atom, an atom is mostly empty space. The diameter of a nucleus is less than $\frac{1}{20000}$ that of an atom.

Electrons move around the nucleus.

It has been found that electrons can have only certain energies and, for electron counting purposes, a diagram with concentric circles to represent the shells/energy levels and dots or crosses to represent the electrons is used.

Remember though that atoms are 3-dimensional objects and not flat as the ‘dot and cross’ diagrams suggest.

Electrons around the nucleus



Protons, neutrons and electrons have very small masses.

The mass of a proton is very nearly the same as the mass of a neutron, and is 1837 times greater than that of an electron. The mass of an electron is considered negligible in calculations.

The approximate relative masses of these particles are:

particle	relative mass
proton	1
neutron	1
electron	negligible

As protons and neutrons are the only particles with a significant mass, most of the mass of an atom is in the nucleus.

Protons and electrons have very small charges. Neutrons have no charge.

The charge on a proton is exactly the same as the charge on an electron, but it is opposite in sign. The nucleus is therefore positively charged.

The relative charges of these particles are:

particle	**relative charge**
proton	+1
neutron	0
electron	-1

Atoms have no overall charge (they are neutral) and therefore the positive charge on the nucleus must be balanced by the negative charge of the electrons. As the amount of charge on protons and electrons is equal, the numbers of these particles in an atom must be the same.

Ions are formed by (neutral) atoms gaining or losing electrons.

If an atom loses one or more electrons, there will be more protons in the nucleus than there are electrons and a positively charged ion is formed.

If an atom gains one or more electrons, there will be more electrons than there are protons in the nucleus and a negatively charged ion is formed.

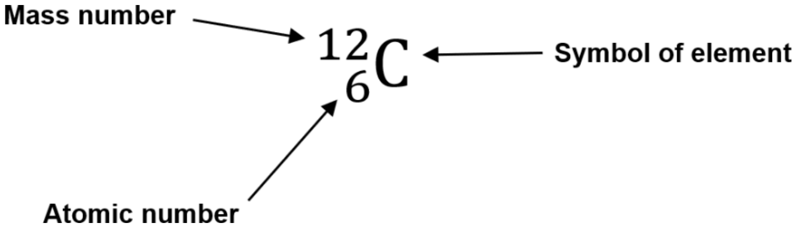
The number of protons in the nucleus of an atom is called the atomic number.

The atomic number is characteristic of an element. There cannot be fractions of protons and so atomic numbers are integers. The element hydrogen has atomic number 1, helium has atomic number 2, lithium has atomic number 3, and so on.

All atoms of an element have the same atomic number and therefore the same number of protons in their nuclei. For example, the atomic number of carbon is 12, therefore every atom of carbon has 12 protons.

The number of protons plus the number of neutrons in an atom is called the mass number.

The atomic number, mass number and symbol of the element are used as follows:



If the atomic number and mass number of an atom (or ion) is known, the number of neutrons can be calculated:

$$\text{number of neutrons} = \text{mass number} - \text{atomic number}$$

$$n = (p + n) - p$$

(n and p represent the numbers of neutrons and protons, respectively)

For the example of carbon above: $n = 12 - 6 = 6$

If the atomic number of an atom is known, the number of electrons is also known:

$$\text{atomic number} = \text{number of protons} = \text{number of electrons}$$

$$p = e$$

(e represents the number of electrons)

For the example of carbon above: atomic number = $6 = p = e$

If the atomic number and charge on an ion is known, the number of electrons can be calculated.

For positively charged ions:

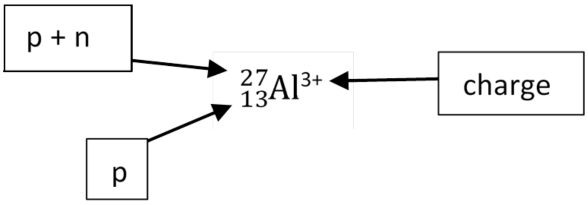
$$\text{number of electrons} = \text{atomic number} - \text{charge on ion}$$

$$e = p - \text{charge}$$

For negatively charged ions:

$$\text{number of electrons} = \text{atomic number} + \text{charge on ion}$$

$$e = p + \text{charge}$$



The atomic number shows the number of protons. In this example, it is 13, so there are 13 protons.

The mass number shows the number of protons plus the number of neutrons. In this example, it is 27.

$$p + n = 27$$

$$n = 27 - p = 27 - 13 = 14$$

The charge shows that the aluminium atom has lost 3 electrons in forming the ion.

$$e = 13 - 3 = 10$$

So, in $^{27}_{13}Al^{3+}$ there are 13 protons, 14 neutrons and 10 electrons.

Chemical reactions involve the losing/gaining or sharing of electrons. Reactions do not involve the nucleus and so the number of protons in an atom does not change during a chemical reaction.

Exercise 1

An atom of zinc has an atomic radius of 135 picometres (pm). Its nucleus has a radius that is $\frac{1}{27000}$ of that of the atom.

What is the radius of a zinc nucleus in femtometres (fm)?

[1 pm = 1×10^{-12} m; 1 fm = 1×10^{-15} m]

Exercise 2

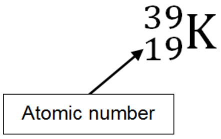
How many protons, neutrons and electrons are there in the calcium ion $^{41}_{20}Ca^{2+}$?

C1.4 Use the atomic number to write the electron configurations of the first 20 elements in the Periodic Table (H to Ca) in comma-separated format (e.g. 2,8,8,1 for a potassium atom).

Electrons move around the nucleus in shells.

(The term ‘shell’ will be used throughout this resource and is equivalent to the term ‘energy level’.)

The number of electrons in an atom of an element is given by the atomic number of the element.



As the atomic number of potassium is 19, there are 19 electrons in every potassium atom.

The electron configuration of an atom or ion is a description of how the electrons are arranged around the nucleus.

The maximum number of electrons that can fit in the first three shells, when considering the first 20 elements, is as follows:

shell	maximum number of electrons
1st	2
2nd	8
3rd	8

Using this information, the arrangement of the 19 electrons in a potassium atom can be determined:

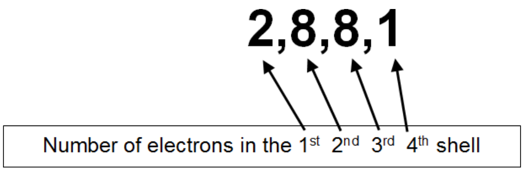
2 electrons in the 1st shell

8 electrons in the 2nd shell

8 electrons in the 3rd shell

1 electron in the 4th shell

Therefore, the electron configuration of a potassium atom is:



To determine the electron configuration of a positively charged ion, remember that electrons have been removed from the highest occupied shell of the atom. The number of electrons removed is the same as the charge.

For example, a potassium ion has the formula K^+, the ion has a single positive charge, so the electron configuration of the K^+ ion is 2,8,8.

To determine the electron configuration of a negatively charged ion, remember that electrons have been added to the atom. The number of electrons added is the same as the charge.

For example, Fluorine has atomic number 9 and fluoride ions have the formula F^-. This means that there are 9 + 1 = 10 electrons in a fluoride ion.

The electron configuration of a fluoride ion, F^-, is 2,8.

The shells are filled with electrons in energy order (low to high).

The shell with the lowest energy is the 1st shell, the 2nd shell is the next lowest in energy, and so on.

To work out the electron configuration of any atom or ion of the first 20 elements, assume that the electrons are in the lowest available shell (in energy). When one shell is full, the next highest one is used and a comma is put between the numbers.

Hydrogen has atomic number 1. Its atoms have 1 electron and the electron configuration is 1.
Helium has atomic number 2. Its atoms have 2 electrons and the electron configuration is 2.

Lithium has atomic number 3. Its atoms have 3 electrons. Two of these electrons will fill the 1st shell. The third electron goes into the 2nd shell; this is shown by a comma. The electron configuration is 2,1.

To check that you have written the correct electron configuration for an atom, remember that:

sum of the numbers in the electron configuration = number of electrons in the atom = atomic number

And for ions, the number of electrons can be calculated:

For positively charged ions: number of electrons = atomic number – charge on ion

For negatively charged ions: number of electrons = atomic number + charge on ion

Exercise 3

What is the electron configuration of an argon atom?

[atomic number of Ar is 18]

Exercise 4

What is the electron configuration of a magnesium ion, $_{12}Mg^{2+}$?

Exercise 5

What is the electron configuration of a phosphide ion, P^{3-} ?

[atomic number of P is 15]

C1.5 Know the definition of isotopes as atoms of an element with the same number of protons but different numbers of neutrons (so having different mass numbers). Use data, including that from a mass spectrometer, to identify the number and abundances of different isotopes of elements.

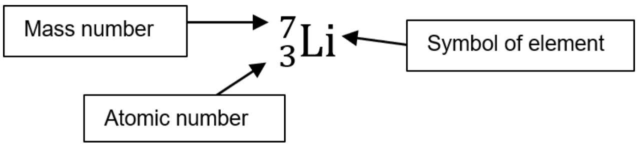
Atoms that have the same number of protons in their nuclei are atoms of the same element. These atoms have the same atomic number.

But not all atoms of an element have the same mass. It is possible for a different number of neutrons to be present in an atom of the same element. As the number of neutrons is different, the mass number will also be different.

Atoms of an element that have different masses, and so number of neutrons, are called isotopes.

The word ‘isotope’ is derived from two Greek roots, ‘isos’ meaning equal/the same, and ‘topos’ meaning place, so isotopes are in the same place in the Periodic Table – they are the same element.

A particular isotope is identified by giving both the atomic and mass numbers, using the standard notation.



For example, there are three isotopes of hydrogen:

$$^{1}_{1}\mathrm{H} \quad ^{2}_{1}\mathrm{H} \quad ^{3}_{1}\mathrm{H}$$

The numbers of protons and neutrons in each isotope are:

	$^{1}_{1}\mathrm{H}$	$^{2}_{1}\mathrm{H}$	$^{3}_{1}\mathrm{H}$
number of protons	1	1	1
number of neutrons	0	1	2

The number and abundances of isotopes of an element can be found using the mass spectrum of the element.

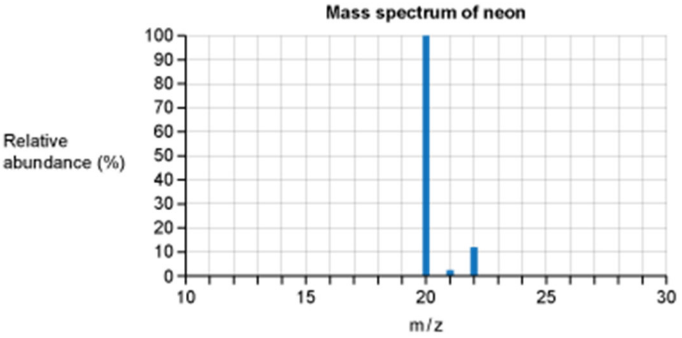
In a mass spectrometer, atoms (or molecules) are ionised, accelerated, and then ions with different masses (and charges if more than one electron is removed) separate as they drift through the machine and the ions are then detected.

The spectrum is a plot of the number of ions, of a particular mass-to-charge ratio (m/z), against m/z values.

A mass spectrum shows the mass-to-charge ratio (m/z) of the ions on the x-axis, and the y-axis gives information on the number of ions of any particular m/z value detected.

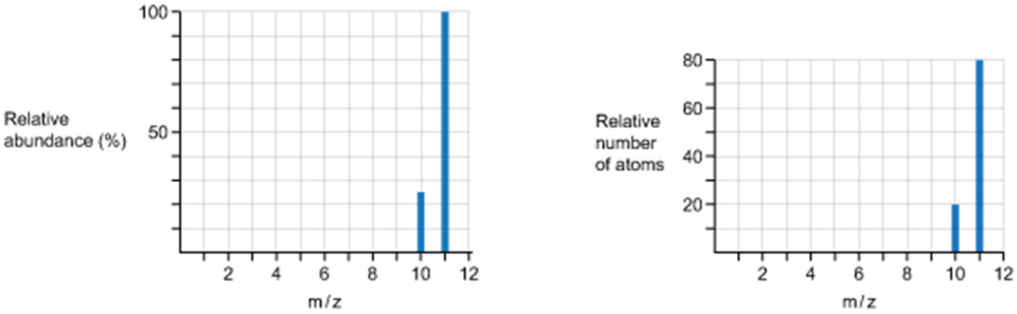
The y-axis may have ‘arbitrary units’ or might show relative abundance. If relative abundance is shown, the m/z peak caused by the most abundant ion is given a value of 100% and all other peaks are then given heights relative to this

Mass spectrum of neon



There are 3 peaks in the mass spectrum of neon, therefore neon has 3 isotopes with masses of 20, 21 and 22.

Mass spectrum of boron



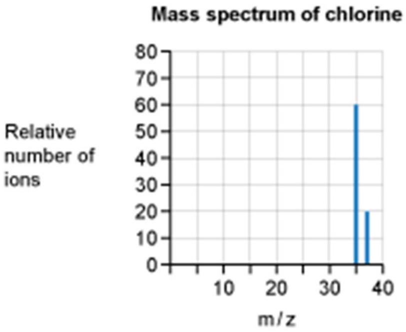
There are two peaks in the above mass spectrum of boron, so there are two isotopes of boron with m/z values of 10 and 11. The mass numbers of the two isotopes are 10 and 11.

The ratio of the peaks for m/z 10 : 11 is 1 : 4, so there are four times as many atoms of boron with a mass of 11 as there are with a mass of 10.

In this sample of boron, 80% of the atoms are boron-11 ($^{11}_{5}B$) and 20% are boron-10 ($^{10}_{5}B$)

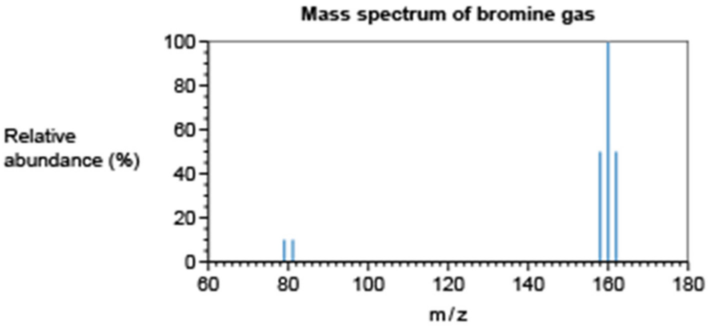
Exercise 6

Using the mass spectrum of chlorine atoms, determine the number and abundance of chlorine isotopes.



Exercise 7

Using the mass spectrum of bromine gas, determine the number and abundances of the isotopes of bromine.



C1.6 Know and use the concept of relative atomic mass, A_r, including calculating values from given data.

The relative atomic mass, A_r , of an element is the weighted mean of the mass numbers of the isotopes of an element. In doing so, the abundances of the various isotopes of the element are taken into account when calculating the average.

For example, in a sample of chlorine atoms 75% are ${}^{35}_{17}\mathrm{Cl}$ and 25% are ${}^{37}_{17}\mathrm{Cl}$

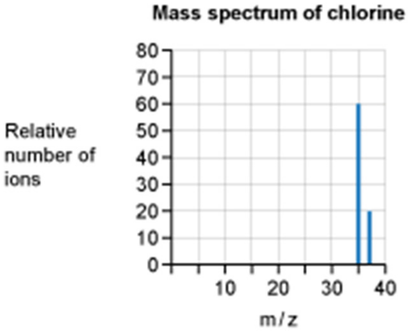
$$A_r\,(\mathrm{Cl}) = \left(\frac{75}{100}\times 35\right) + \left(\frac{25}{100}\times 37\right)$$

$$A_r\,(\mathrm{Cl}) = \frac{2625}{100} + \frac{925}{100}$$

$$A_r\,(\mathrm{Cl}) = \frac{3550}{100} = 35.5$$

Data can also be presented as a mass spectrum, such as that of atomic chlorine:

Mass spectrum of chlorine



The calculation would then have been:

$$A_r\,(\mathrm{Cl}) = \left(\frac{60}{80}\times 35\right) + \left(\frac{20}{80}\times 37\right)$$

$$A_r\,(\mathrm{Cl}) = \frac{2100}{80} + \frac{740}{80}$$

$$A_r\,(\mathrm{Cl}) = \frac{2840}{80} = 35.5$$

The mass-to-charge ratio (m/z) data obtained from mass spectra are not the absolute masses of the ions but are relative to $\frac{1}{12}$ the mass of an atom of carbon-12 (${}^{12}_{6}\mathrm{C}$)

The word ‘relative’ means ‘compared to’, as in a ratio is being calculated.

With data presented as percentages: a% of ${}^{q}X$, b% of ${}^{r}X$, c% of ${}^{s}X$, ... in a sample of 100 atoms of the element: *a* have a mass of q, *b* have a mass of r, and *c* have a mass of s, ...

The general formula for calculating the relative atomic mass is:

$$A_r\,(X) = \frac{(a\times q)+(b\times r)+(c\times s)+\ldots}{100}$$

With data presented on a mass spectrum, the relative numbers of the various isotopes are obtained from values on the y-axis: *a* the value for ${}^{q}X$, *b* the value for ${}^{r}X$, *c* the value for ${}^{s}X$, … the expression becomes:

$$A_r\,(X) = \frac{(a\times q)+(b\times r)+(c\times s)+\ldots}{(a+b+c+\ldots)}$$

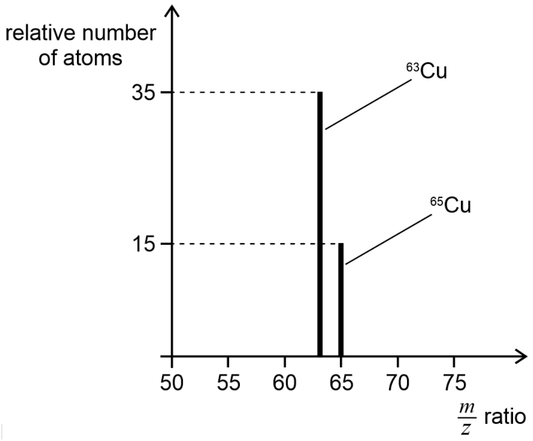
Exercise 8

Mass spectrometry of a sample of boron showed 80% ${}^{11}_{5}B$ and 20% ${}^{10}_{5}B$.

What is the relative atomic mass of boron?

Exercise 9

Calculate the relative atomic mass of copper from the mass spectrum shown below.



Solutions to Exercises 1 to 9

Exercise 1

$$\frac{\text{radius of nucleus}}{\text{radius of atom}} = \frac{1}{27000}$$

radius of nucleus = $\frac{135 \times 1000}{27000}$ (changing from pm to fm)

= 5 fm

Exercise 2

The atomic number is 20, therefore there are 20 protons. The mass number is 41.

n = mass number – atomic number = 41 – 20 = 21

The charge is 2+

e = atomic number – charge = 20 – 2 = 18

In the ion, there are: 20 protons, 21 neutrons and 18 electrons.

Exercise 3

The atomic number gives the number of protons and so the number of electrons in an atom. The atomic number of argon is 18, therefore there are 18 electrons in an argon atom.

2 electrons will go into the 1st shell, which leaves 18 – 2 = 16 electrons.

8 electrons will go into the 2nd shell, which leaves 16 – 8 = 8 electrons that will go into the 3rd shell.

The electron configuration of an argon atom is therefore 2,8,8.

Exercise 4

The atomic number gives the number of protons and thus the number of electrons in an atom.

The atomic number of magnesium is 12, therefore there are 12 electrons in a magnesium atom.

When a magnesium ion, ${}_{12}\mathrm{Mg}^{2+}$, is formed from a magnesium atom, 2 electrons are removed, so there are 12 – 2 = 10 electrons in a magnesium ion.

2 electrons will go into the 1st shell, which leaves 10 – 2 = 8 electrons that will go into the 2nd shell.

The electron configuration of magnesium ion, ${}_{12}\mathrm{Mg}^{2+}$, is therefore 2,8.

Exercise 5

The atomic number gives the number of protons and so the number of electrons in an atom.

The atomic number of phosphorus is 15, therefore there are 15 electrons in a phosphorus atom.

When a phosphide ion, P^{3-}, is formed from a phosphorus atom, 3 electrons are gained, so there are 15 + 3 = 18 electrons in a phosphide ion.

2 electrons will go into the 1st shell, which leaves 18 – 2 = 16 electrons.

8 electrons will go into the 2nd shell, which leaves 16 – 8 = 8 electrons that will go into the 3rd shell.

The electron configuration of a phosphide ion, P^{3-}, is therefore 2,8,8.

Exercise 6

There are two peaks, so there are two isotopes: ${}^{35}_{17}\mathrm{Cl}$ and ${}^{37}_{17}\mathrm{Cl}$

The heights of the two peaks are in the ratio of 3 : 1.

So in a group of 400 atoms, 300 will be ${}^{35}_{17}\mathrm{Cl}$ and 100 will be ${}^{37}_{17}\mathrm{Cl}$.

Therefore in a group of 100 atoms, 75 will be ${}^{35}_{17}\mathrm{Cl}$ and 25 will be ${}^{37}_{17}\mathrm{Cl}$.

Exercise 7

Bromine is a diatomic molecule, Br_2.

The peaks at m/z values 79 and 81 are formed by single Br^+ ions. As the peaks are the same height, these two isotopes have equal abundances.

The percentage abundances are: 50% ${}^{79}_{35}\mathrm{Br}$ and 50% ${}^{81}_{35}\mathrm{Br}$

The peaks at m/z values 158, 160 and 162 are formed by Br^{2+} molecular ions.

There are four ways for the two isotopes to combine and form a molecule of bromine:

$${}^{79}_{35}\mathrm{Br} — {}^{79}_{35}\mathrm{Br}$$

$${}^{79}_{35}\mathrm{Br} — {}^{81}_{35}\mathrm{Br}$$

$${}^{81}_{35}\mathrm{Br} — {}^{79}_{35}\mathrm{Br}$$

$${}^{81}_{35}\mathrm{Br} — {}^{81}_{35}\mathrm{Br}$$

There are two ways of obtaining a Br^{2+} molecular ion with a mass of 160, so this is twice as abundant as the other two molecular ions.

Exercise 8

Taking the sample of boron to be 100 atoms, 20 will have a mass of 10 and 80 will have a mass of 11.

$$A_r\ (\text{B}) = \left(\frac{20}{100}\times 10\right) + \left(\frac{80}{100}\times 11\right)$$

$$A_r\ (\text{B}) = \frac{200}{100} + \frac{880}{100}$$

$$A_r\ (\text{B}) = \frac{1080}{100} = 10.8$$

Exercise 9

If we take the values on the y-axis of the mass spectrum to be the number of copper atoms then there are 35 with a mass of 63 and 15 with a mass of 65.

Total number of atoms = 35 + 15 = 50

$$A_r\ (\text{Cu}) = \left(\frac{35}{50}\times 63\right) + \left(\frac{15}{50}\times 65\right)$$

$$A_r\ (\text{Cu}) = \frac{2205}{50} + \frac{975}{50}$$

$$A_r\ (\text{Cu}) = \frac{3180}{50} = 63.6$$

C2. The Periodic Table
(IUPAC conventions, Groups are labelled as 1-18)

C2.1 Know that Periods are horizontal rows and Groups are vertical columns.

C2.2 Know that the elements are arranged in the order of increasing atomic number.

C2.3 Recall the position of metals and non-metals in the Periodic Table: alkali metals (Group 1), alkaline earth metals (Group 2), common non-metals in Group 16, the halogens (Group 17), the noble gases (Group 18) and the transition metals.

C2.4 Know and use the relationship between the position of an atom in the Periodic Table (Group and Period) and the electron configuration of the atom.

C2.5 Understand that elements in the same Group have similar chemical properties and that down a metal Group, reactivity increases and down a non-metal Group, reactivity decreases.

The Periodic Table is an arrangement of the elements in which they are sequenced in order of increasing atomic number.

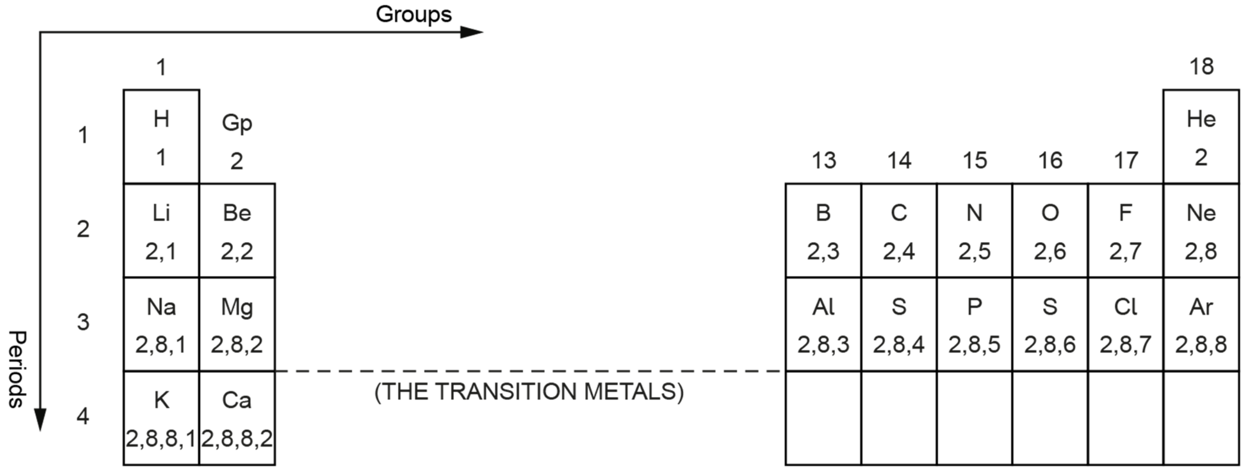
						1											2
3	4											5	6	7	8	9	10
11	12											13	14	15	16	17	18
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36

The sequence is broken at regular intervals to give a table of columns and rows. The horizontal rows are called Periods and the vertical columns are called Groups.

- The number of a Period indicates the outermost filled shell of electrons for the atoms of the elements in that Period.
- The elements in the same Group have a similarity in the chemical behaviour of the electrons in their outermost shell.

In the following shortened and simplified version of the table, the electron configurations have been included to illustrate these patterns.

Shortened Periodic Table



Periods	1	Gp 2	13	14	15	16	17	18
1	H 1							He 2
2	Li 2,1	Be 2,2	B 2,3	C 2,4	N 2,5	O 2,6	F 2,7	Ne 2,8
3	Na 2,8,1	Mg 2,8,2	Al 2,8,3	S 2,8,4	P 2,8,5	S 2,8,6	Cl 2,8,7	Ar 2,8,8
4	K 2,8,8,1	Ca 2,8,8,2						

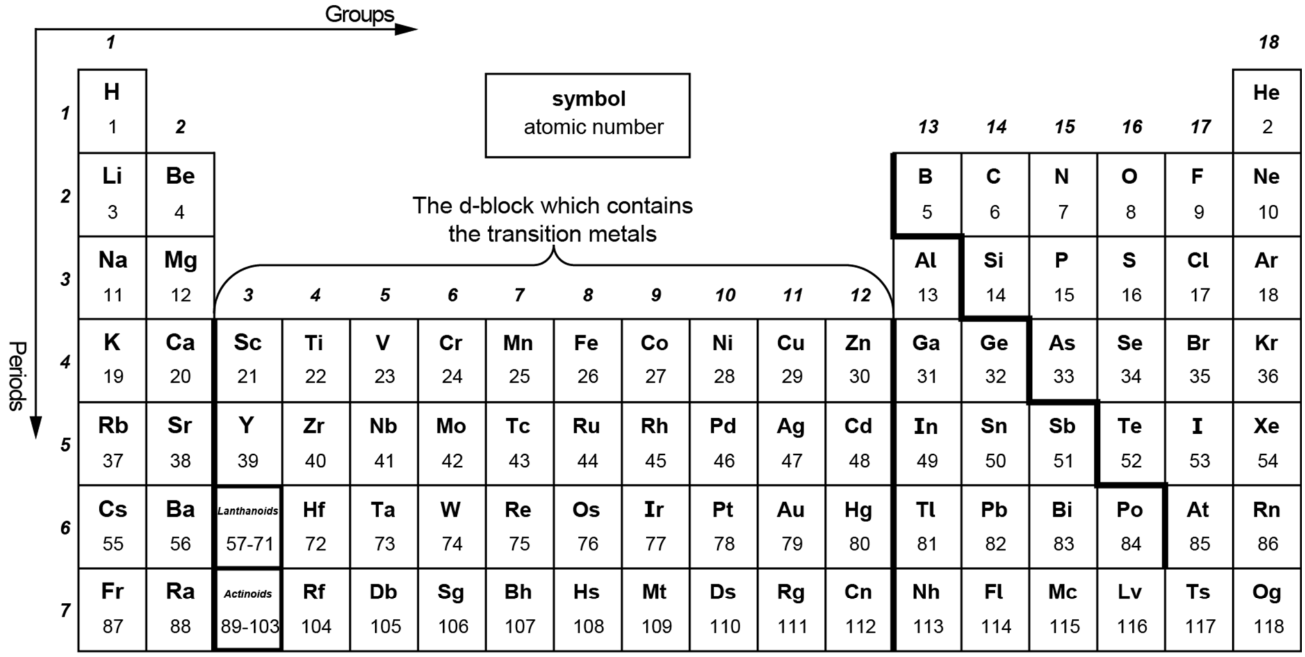
Note the following:

- The Group 1 elements, called the 'alkali metals', have one electron in their outermost shell.
- The Group 2 elements, called the 'alkaline earth metals', have two electrons in their outermost shell.
- The Group 16 elements have six electrons in their outermost shell.
- The Group 17 elements, called the 'halogens', have seven electrons in their outermost shell.
- The Group 18 elements, called the 'noble gases', have a complete outermost shell of electrons.

Arising from this similarity in the outermost shell electron arrangement for elements in the same Group is a similarity in the chemical properties of the elements themselves. Two further trends can then also be noted:

- When a metal Group (e.g. Groups 1 and 2) is descended, the elements become more reactive.
- When a non-metal Group (e.g. Groups 16 and 17) is descended, the elements become less reactive.

A complete and more usual version of the Periodic Table



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**H** 1																	**He** 2
2	**Li** 3	**Be** 4											**B** 5	**C** 6	**N** 7	**O** 8	**F** 9	**Ne** 10
3	**Na** 11	**Mg** 12											**Al** 13	**Si** 14	**P** 15	**S** 16	**Cl** 17	**Ar** 18
4	**K** 19	**Ca** 20	**Sc** 21	**Ti** 22	**V** 23	**Cr** 24	**Mn** 25	**Fe** 26	**Co** 27	**Ni** 28	**Cu** 29	**Zn** 30	**Ga** 31	**Ge** 32	**As** 33	**Se** 34	**Br** 35	**Kr** 36
5	**Rb** 37	**Sr** 38	**Y** 39	**Zr** 40	**Nb** 41	**Mo** 42	**Tc** 43	**Ru** 44	**Rh** 45	**Pd** 46	**Ag** 47	**Cd** 48	**In** 49	**Sn** 50	**Sb** 51	**Te** 52	**I** 53	**Xe** 54
6	**Cs** 55	**Ba** 56	**Lanthanoids** 57-71	**Hf** 72	**Ta** 73	**W** 74	**Re** 75	**Os** 76	**Ir** 77	**Pt** 78	**Au** 79	**Hg** 80	**Tl** 81	**Pb** 82	**Bi** 83	**Po** 84	**At** 85	**Rn** 86
7	**Fr** 87	**Ra** 88	**Actinoids** 89-103	**Rf** 104	**Db** 105	**Sg** 106	**Bh** 107	**Hs** 108	**Mt** 109	**Ds** 110	**Rg** 111	**Cn** 112	**Nh** 113	**Fl** 114	**Mc** 115	**Lv** 116	**Ts** 117	**Og** 118

Lanthanoids	**La** 57	**Ce** 58	**Pr** 59	**Nd** 60	**Pm** 61	**Sm** 62	**Eu** 63	**Gd** 64	**Tb** 65	**Dy** 66	**Ho** 67	**Er** 68	**Tm** 69	**Yb** 70	**Lu** 71
Actinoids	**Ac** 89	**Th** 90	**Pa** 91	**U** 92	**Np** 93	**Pu** 94	**Am** 95	**Cm** 96	**Bk** 97	**Cf** 98	**Es** 99	**Fm** 100	**Md** 101	**No** 102	**Lr** 103

The similarity in chemical properties and reactivity trend of elements within a Group can be illustrated by the reaction of the Group 1 metals with water:

- Lithium reacts quite slowly with cold water. It floats, but does not melt, and gradually dissolves to produce an alkaline solution of lithium hydroxide. Hydrogen gas is given off and burns with a crimson red flame when ignited.
- Sodium reacts more strongly with cold water. It moves around the surface, melts and quickly dissolves to produce an alkaline solution of sodium hydroxide. Hydrogen gas is given off and burns with a yellow-orange flame when ignited.
- Potassium reacts vigorously with water. It moves rapidly on the surface and very quickly dissolves to produce an alkaline solution of potassium hydroxide. Hydrogen gas is given off and self-ignites to burn with a lilac flame.

Exercise 10

An ion X^- has 18 electrons. Use this information to work out the position of element X in the Periodic Table.

Exercise 11

An atom of element Y has two electrons in its outermost shell and is the least reactive element in its Group. Use this information to work out the position of element Y in the Periodic Table.

Solutions to Exercises 10 and 11

Exercise 10

Ion X^- has 18 electrons. An atom of X must therefore have 17 electrons.

An atom with 17 electrons will have the electron arrangement 2,8,7.

X's outermost shell is its third and hence it will be in Period 3.

X has seven electrons in its outer shell and so will be in Group 17.

Exercise 11

An atom of Y has two electrons in its outermost shell and hence element Y must be in Group 2.

Group 2 is a metal group – reactivity increases down a metal group, and hence Y must be at the top of Group 2. The top element in Group 2 is in Period 2.

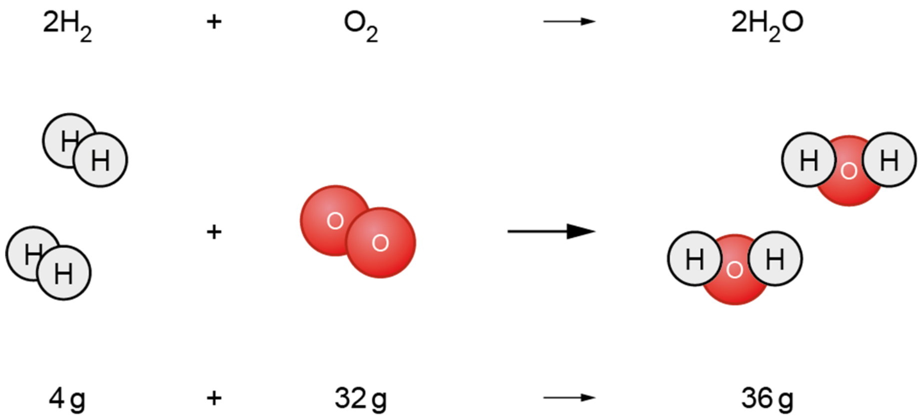
So Y is in Period 2 and Group 2 of the Periodic Table.

C3. Chemical reactions, formulae and equations

C3.1 Understand that in a chemical reaction, new substances are formed by the rearrangement of atoms and their electrons, but no nuclei are destroyed or created.

In all chemical reactions, the atoms in the reactants are rearranged to make new substances called the products. For example, when hydrogen reacts with oxygen, the atoms in the hydrogen and oxygen molecules rearrange to form molecules of the new substance, water.

No atoms are created or destroyed in a chemical reaction. This means that the total mass of all the reactants will equal the total mass of all the products. For example, when 4 g of hydrogen reacts with 32 g of oxygen, the atoms rearrange to make 36 g of water.



Exercise 12

When 2.47 g of green copper carbonate is heated, 1.59 g of black copper oxide remains. Which of the following statements is/are correct?

1) A chemical reaction has occurred
2) 0.88 g of copper carbonate has melted
3) 0.88 g of carbon dioxide has been released
4) 0.88 g of carbon dioxide has vaporised
5) 0.88 g of atoms have been destroyed

C3.2 Know the chemical formulae of simple, common ionic and covalent compounds.

Covalent compounds

The following formulae of common covalent compounds should be learned.

name	**formula**
ammonia	NH_3
carbon dioxide	CO_2
carbon monoxide	CO
methane	CH_4
nitrogen dioxide	NO_2
nitrogen monoxide	NO
sulfur dioxide	SO_2
sulfur trioxide	SO_3
water	H_2O

Ionic compounds

The formula of ionic compounds that contain common ions can be worked out. The tables below show the charge of common ions. Some of these, as shown, are linked to their position in the Periodic Table.

	Group 1 ions		Group 2 ions		Group 13 ions		other positive ions	
positive ions	Li^+	lithium	Mg^{2+}	magnesium	Al^{3+}	aluminium	NH_4^+	ammonium
	Na^+	sodium	Ca^{2+}	calcium			Cu^{2+}	copper(II)
	K^+	potassium	Ba^{2+}	barium			H^+	hydrogen
							Fe^{2+}	iron(II)
							Fe^{3+}	iron(III)
							Ag^+	silver
							Zn^{2+}	zinc

	Group 16 ions		Group 17 ions		other negative ions	
negative ions	O^{2-}	oxide	F^-	fluoride	CO_3^{2-}	carbonate
	S^{2-}	sulfide	Cl^-	chloride	OH^-	hydroxide
			Br^-	bromide	NO_3^-	nitrate
			I^-	iodide	SO_4^{2-}	sulfate

In an ionic compound, the total number of positive charges must equal the total number of negative charges.

Example 1 – sodium oxide:

- contains Na^+ and O^{2-} ions
- there must be two Na^+ ions (2+) for every one O^{2-} ion (2–) to balance the charges
- therefore, the formula is Na_2O

Example 2 – aluminium oxide:

- contains Al^{3+} and O^{2-} ions
- there must be two Al^{3+} ions (6+) for every three O^{2-} ion (6–) to balance the charges
- therefore, the formula is Al_2O_3

Example 3 – ammonium bromide:

- contains NH_4^+ and Br^- ions
- there must be one NH_4^+ ion (1+) for every one Br^- ion (1–) to balance the charges
- therefore, the formula is NH_4Br

Example 4 – calcium hydroxide:

- contains Ca^{2+} and OH^- ions
- there must be one Ca^{2+} ion (2+) for every two OH^- ions (2–) to balance the charges
- therefore, the formula is $Ca(OH)_2$

Example 5 – iron(III) nitrate:

- contains Fe^{3+} and NO_3^- ions
- there must be one Fe^{3+} ion (3+) for every three NO_3^- ions (3–) to balance the charges
- therefore, the formula is $Fe(NO_3)_3$

Note: If there is more than one of an ion that is made from more than one element (i.e. NH_4^+, CO_3^{2-}, OH^-, NO_3^-, SO_4^{2-}) in a formula, then that compound ion is shown in a bracket in the formula.

Common acids

The formulae for the following common acids should be learned.

name	formula
hydrochloric acid	HCl
nitric acid	HNO_3
sulfuric acid	H_2SO_4
ethanoic acid	CH_3COOH

Covalent elements

These formulae of common covalent elements should also be learned.

name	formula
bromine	Br_2
buckminsterfullerene (a form of carbon)	C_{60}
chlorine	Cl_2
fluorine	F_2
hydrogen	H_2
iodine	I_2
nitrogen	N_2
oxygen	O_2

Which of the following substances has/have the correct formula?

1) magnesium oxide, MgO_2
2) potassium bromide, KBr_2
3) ammonia, NH_4
4) sodium fluoride, NaF
5) iron(III) nitrate, $Fe(NO_3)_3$
6) sodium carbonate, $NaCO_3$
7) methane, CH_4
8) ammonium fluoride, NH_4F_4
9) magnesium hydroxide, $MgOH_2$
10) potassium sulfide, K_2SO_4

C3.3 Know and use state symbols: solid (s), liquid (l), gas (g), aqueous solution (aq).

State symbols are often written in balanced equations to show which state each substance is in.

symbol	**state**
s	solid
l	liquid
g	gas
aq	aqueous (dissolved in water)

Example:

$$\underset{\substack{\uparrow\\ \text{solid}}}{CaCO_3(s)} + \underset{\substack{\uparrow\\ \text{aqueous}}}{2HCl(aq)} \rightarrow \underset{\substack{\uparrow\\ \text{aqueous}}}{CaCl_2(aq)} + \underset{\substack{\uparrow\\ \text{liquid}}}{H_2O(l)} + \underset{\substack{\uparrow\\ \text{gas}}}{CO_2(g)}$$

Exercise 14

When magnesium metal reacts with sulfuric acid, hydrogen is given off and a solution of magnesium sulfate is formed.

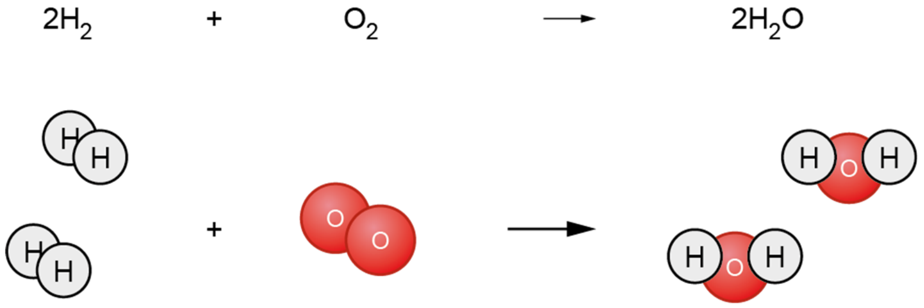
Write a balanced equation for this reaction including state symbols.

C3.4 Be able to construct and balance a chemical equation, including ionic and half-equations.

Balanced equations

Balanced equations are used to show how many particles of each substance are involved in a reaction.

For example, this equation shows that two molecules of H_2 react with one molecule of O_2 to form two molecules of H_2O.



$$2H_2 + O_2 \rightarrow 2H_2O$$

In a balanced equation, the total number of atoms of each element on both sides of the equation must be the same.

In this equation, there are 4 H atoms and 2 O atoms on each side of the equation.

For example, for the complete combustion of methane, in order to write a balanced equation:

Step 1	Write the formula of each substance in the equation.	$CH_4 + O_2 \rightarrow CO_2 + H_2O$
Step 2	Count the number of atoms of each element on each side of the equation. If they are the same, then the equation is balanced.	$CH_4 + O_2 \rightarrow CO_2 + H_2O$ reactants products C = 1 C = 1 H = 4 H = 2 O = 2 O = 3 *Neither the H nor the O are balanced.*

Step 3	If the equation is not balanced, then add in more of the substance that provides the missing atoms. The formula of a substance must never be changed (for example, here the formula of water cannot be changed to make the equation balance as water is always H_2O). However, more of each substance can be added. Keep doing this until the equation is balanced.	*Add another H_2O on the right to balance the H atoms:* $CH_4 + O_2 \rightarrow CO_2 + \mathbf{2}H_2O$ reactants products C = 1 C = 1 H = 4 H = 4 O = 2 O = 4 *The C and H atoms are now balanced but the O atoms are not. We can add another O_2 on the left to balance the O atoms.* $CH_4 + \mathbf{2}O_2 \rightarrow CO_2 + \mathbf{2}H_2O$ reactants products C = 1 C = 1 H = 4 H = 4 O = 4 O = 4 *The equation is now balanced.*

Ionic equations

When an ionic compound dissolves in water, the ions separate from each other and act independently. In reactions involving ionic compounds in solution, some of the ions do not take part in the reaction. An ionic equation can be written that leaves out any ions that do not take part in the reaction. State symbols in ionic equations are often included.

a) Reactions of acids with bases

For example, when hydrochloric acid reacts with sodium hydroxide solution:

full equation: $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

showing ions: $H^+(aq) + \mathbf{Cl^-(aq)} + \mathbf{Na^+(aq)} + OH^-(aq) \rightarrow \mathbf{Na^+(aq)} + \mathbf{Cl^-(aq)} + H_2O(l)$

leaving out ions that do not react: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

This is the simplest ionic equation when any acid reacts with any alkali.

The following table shows some common ionic equations for reactions of acids.

reaction	ionic equation
acid + alkali	$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
acid + carbonate	$2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2O(l) + CO_2(g)$
acid + ammonia	$H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq)$

b) Reactions of acids with metals

For example, when hydrochloric acid reacts with magnesium:

full equation: $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

showing ions: $Mg(s) + 2H^+(aq) + \mathbf{2Cl^-(aq)} \rightarrow Mg^{2+}(aq) + \mathbf{2Cl^-(aq)} + H_2(g)$

leaving out ions that do not react: $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$

c) Precipitation reactions

When solutions of ionic compounds are mixed together, precipitates are sometimes formed. For example, a blue precipitate of copper(II) hydroxide is formed when a solution of sodium hydroxide is added to a solution containing copper(II) ions. This is used as a test for the presence of copper(II) ions in aqueous solutions. In precipitation reactions, only the ions required to form the precipitate need to be shown.

Ionic equation: $Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$

Half-equations

In redox reactions, including displacement reactions and electrolysis, two half-equations can be written to show the reduction and oxidation processes separately. These half-equations show the gain or loss of electrons.

a) Electrolysis

For example, in the electrolysis of molten aluminium oxide: Al^{3+} ions gain electrons to become Al, and O^{2-} ions lose electrons to become O_2.

Al^{3+} to Al
Each Al^{3+} ion gains 3 electrons: $Al^{3+} + 3e^- \rightarrow Al$

O^{2-} to O_2
Two O^{2-} ions are needed to make O_2 and each O^{2-} ion loses 2 electrons: $2O^{2-} \rightarrow O_2 + 4e^-$

b) Displacement reactions

For example, when copper displaces silver from a solution of silver nitrate: the copper atoms lose electrons to form copper ions and the silver ions in silver nitrate gain electrons to form silver. The nitrate ions do not react.

Ag^+ to Ag Each Ag^+ ion gains 1 electron: $Ag^+ + e^- \rightarrow Ag$

Cu to Cu^{2+} Each Cu atom loses 2 electrons: $Cu \rightarrow Cu^{2+} + 2e^-$

Exercise 15

Write a balanced equation for the reaction of sodium with oxygen to form sodium oxide.

Exercise 16

Write an ionic equation for the precipitation of silver iodide when silver nitrate solution is mixed with sodium iodide solution.

Exercise 17

Write half-equations for the electrolysis of molten sodium chloride.

C3.5 Understand that often chemical reactions can be reversible and do not go to completion. All of the reactants do not turn fully into the products but the reaction reaches a state of equilibrium in a closed system.

a. Know the factors that can affect the position of an equilibrium (concentration of reactants/products, temperature, overall pressure).

b. Predict the effect of changing these factors on the position of equilibrium.

Many chemical reactions are reversible. This means that the products of the reaction can turn back into the reactants.

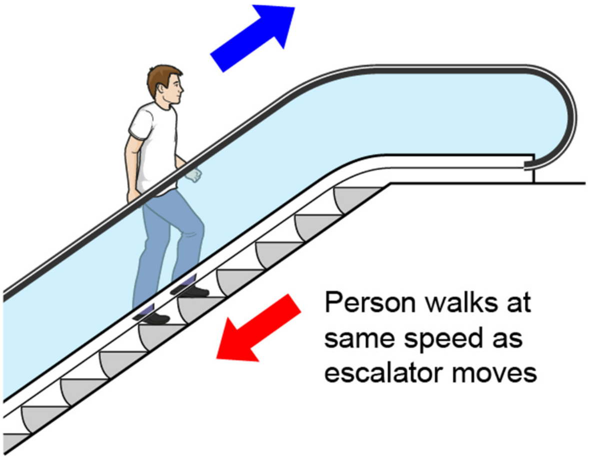
For example, hydrogen gas reacts with nitrogen gas to form ammonia gas. Ammonia also decomposes to re-form hydrogen and nitrogen.

$$3H_2 + N_2 \rightleftharpoons 2NH_3$$

In a closed system, where no chemicals can get in or out, reversible reactions can reach a state of dynamic equilibrium. At this point, both the forwards and reverse reaction are taking place simultaneously and at the same rate.

An everyday example of a dynamic equilibrium is someone walking up a down escalator. When the person walks up at the same speed as the escalator moves down, they are in dynamic equilibrium. The person stays in the same position part way up the escalator.

Dynamic equilibrium



If the position of an equilibrium lies 'to the left', it means that there are more of the reactants than the products in the equilibrium mixture, although both reactions are taking place simultaneously and at the same rate. If the position of the equilibrium lies 'to the right', it means that there are more of the products than reactants in the equilibrium mixture.

If the conditions of a system in a state of dynamic equilibrium are changed, the position of the equilibrium moves to oppose that change.

1) Changing the concentration of reactants/products

add more reactants	**remove some reactants**	**add more products**	**remove some products**
equilibrium position moves right to remove some of the added reactants	equilibrium position moves left to replace some of the reactants	equilibrium position moves left to remove some of the added products	equilibrium position moves right to replace some of the products

For example, yellow $CrO_4^{2-}(aq)$ ions react with $H^+(aq)$ ions to form orange $Cr_2O_7^{2-}(aq)$. The reaction reaches a state of dynamic equilibrium.

$$\underset{\text{yellow}}{2CrO_4^{2-}(aq)} + 2H^+(aq) \rightleftharpoons \underset{\text{orange}}{Cr_2O_7^{2-}(aq)} + H_2O(l)$$

If an acid is added to the equilibrium mixture, the position of the equilibrium moves right to remove some of the added $H^+(aq)$ ions and the mixture becomes more orange as more $Cr_2O_7^{2-}(aq)$ is formed.

If an alkali is added to the equilibrium mixture, it removes $H^+(aq)$ ions. The position of the equilibrium moves left to replace some of the lost $H^+(aq)$ ions and the mixture becomes more yellow as more $CrO_4^{2-}(aq)$ is formed.

2) Changing the temperature

If the energy change for the forward reaction is exothermic, then the energy change for the reverse reaction is endothermic. If the energy change for the forward reaction is endothermic, then the energy change for the reverse reaction is exothermic.

Exothermic reactions have a negative energy change value (ΔH) and release heat to their surroundings, increasing the temperature. Endothermic reactions have a positive value for ΔH and take in heat from the surroundings, decreasing the temperature.

If the temperature of a reaction at equilibrium is changed, the position of the equilibrium moves to oppose that change. If the temperature is increased, the equilibrium moves in the direction of the endothermic reaction to lower the temperature. If the temperature is decreased, the equilibrium moves in the direction of the exothermic reaction to increase the temperature.

For example, sulfur dioxide (SO_2) reacts with oxygen (O_2) to form sulfur trioxide (SO_3). The reaction reaches a state of dynamic equilibrium. The forward reaction is exothermic.

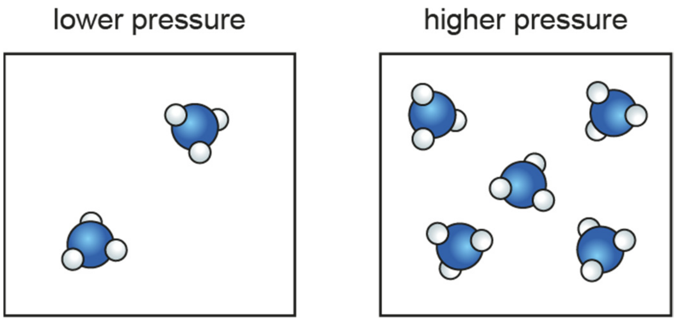
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

If the temperature is increased, the position of the equilibrium moves left, in the endothermic direction, to lower the temperature. As the position of equilibrium moves to the left, the amount of sulfur trioxide present at equilibrium decreases.

If the temperature is increased, the position of the equilibrium moves left, in the endothermic direction, to lower the temperature. As the position of equilibrium moves to the left, the amount of sulfur trioxide present at equilibrium decreases.

2) Changing the pressure

In a fixed volume, the more gas molecules that are present, the higher the pressure.



If the pressure of a system at equilibrium is increased, the position of the equilibrium moves to the side with fewer total number of gas molecules to lower the pressure.

If the pressure of a system at equilibrium is decreased, the position of the equilibrium moves to the side with more total number of gas molecules to increase the pressure.

For example, sulfur dioxide (SO_2) reacts with oxygen (O_2) to form sulfur trioxide (SO_3). The reaction reaches a state of dynamic equilibrium.

$$2SO_2(g) \ + \ O_2(g) \ \rightleftharpoons \ 2SO_3(g)$$

If the pressure is increased, the position of the equilibrium moves right to the side, with fewer gas molecules, to lower the pressure. As the position of equilibrium moves to the right, the amount of sulfur trioxide present at equilibrium increases.

Exercise 18

Nitrogen reacts with hydrogen to make ammonia and reaches a state of dynamic equilibrium. The forwards reaction is exothermic.

$$N_2(g) \ + \ 3H_2(g) \ \rightleftharpoons \ 2NH_3(g)$$

Explain how the amount of ammonia present at equilibrium is affected by:

a) an increase in temperature
b) an increase in pressure.

Exercise 19

Methane reacts with steam to make hydrogen and reaches a state of dynamic equilibrium. The forwards reaction is endothermic.

$$CH_4(g) + H_2O(g) \rightleftharpoons 3H_2(g) + CO(g)$$

Explain how the equilibrium yield of hydrogen is affected by:

a) an increase in temperature

b) an increase in pressure.

Exercise 20

Pink $Co(H_2O)_6^{2+}(aq)$ ions react with chloride ions to form blue $CoCl_4^{2-}(aq)$ ions. The reaction reaches a state of dynamic equilibrium.

$$\underset{\text{pink}}{Co(H_2O)_6^{2+}(aq)} + 4Cl^-(aq) \rightleftharpoons \underset{\text{blue}}{CoCl_4^{2-}(aq)} + 6H_2O(l)$$

If water is added to an equilibrium mixture, would the colour become more pink or more blue?

Solutions to Exercises 12 to 20

Exercise 12

The answer is 1) and 3).

The copper carbonate is decomposing when it is heated in a chemical reaction – it does not melt or vaporise.

2.47 g of copper carbonate breaks down into 1.59 g of copper oxide and 0.88 g of carbon dioxide which escapes as it is a gas.

Exercise 13

The answer is 4), 5) and 7).

The correct formula of each substance is shown below.

1) magnesium oxide, MgO (contains Mg^{2+} and O^{2-} ions)
2) potassium bromide, KBr (contains K^{+} and Br^{-} ions)
3) ammonia, NH_3
4) sodium fluoride, NaF (contains Na^{+} and F^{-} ions)
5) iron(III) nitrate, $Fe(NO_3)_3$ (contains Fe^{3+} and NO_3^{-} ions)
6) sodium carbonate, Na_2CO_3 (contains Na^{+} and CO_3^{2-} ions)
7) methane, CH_4
8) ammonium fluoride, NH_4F (contains NH_4^{+} and F^{-} ions)
9) magnesium hydroxide, $Mg(OH)_2$ (contains Mg^{2+} and OH^{-} ions)
10) potassium sulfide, K_2S (contains K^{+} and S^{2-} ions)

Exercise 14

The formula of each substance and its state symbol is:

magnesium solid = $Mg(s)$

sulfuric acid = $H_2SO_4(aq)$

magnesium sulfate solution = $MgSO_4(aq)$

hydrogen gas = $H_2(g)$

The balanced equation is:

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

Exercise 15

The formula of each substance is:

sodium = Na

oxygen = O_2

sodium oxide = Na_2O (containing Na^+ and O^{2-} ions)

The unbalanced equation is:

$Na + O_2 \rightarrow Na_2O$

reactant atoms: 1 Na + 2 O

product atoms: 2 Na + 1 O

Add another Na_2O on the right to balance the O atoms:

$Na + O_2 \rightarrow \mathbf{2}Na_2O$

reactant atoms: 1 Na + 2 O

product atoms: 4 Na + 2 O

Add three more Na (to give four in total) on the left to balance the Na atoms:

$\mathbf{4}Na + O_2 \rightarrow \mathbf{2}Na_2O$

reactant atoms: 4 Na + 2 O

product atoms: 4 Na + 2 O

The equation is now balanced: $4Na + O_2 \rightarrow 2Na_2O(s)$

Exercise 16

Silver iodide is made up from silver ions (Ag^+) and iodide ions (I^-). The formula of silver iodide is therefore AgI.

The ionic equation is: $Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$

Exercise 17

Each sodium ion (Na^+) gains an electron to form a sodium atom (Na): $Na^+ + e^- \rightarrow Na$

Two chloride ions (Cl^-) lose an electron each to form a chlorine molecule (Cl_2): $2Cl^- \rightarrow Cl_2 + 2e^-$

Exercise 18

a) If the temperature is increased, the position of the equilibrium moves left, in the endothermic direction, to lower the temperature. As the position of equilibrium moves to the left, the amount of ammonia present at equilibrium decreases.

b) If the pressure is increased, the position of the equilibrium moves right to the side, with fewer gas molecules, to lower the pressure. As the position of equilibrium moves to the right, the amount of ammonia present at equilibrium increases.

Exercise 19

a) If the temperature is increased, the position of the equilibrium moves right, in the endothermic direction, to lower the temperature. As the position of equilibrium moves to the right, the amount of hydrogen present at equilibrium increases.

b) If the pressure is increased, the position of the equilibrium moves left to the side, with fewer gas molecules, to lower the pressure. As the position of equilibrium moves to the left, the amount of ammonia present at equilibrium decreases.

Exercise 20

If water is added, the equilibrium position moves to the left to remove some added water. This forms more $Co(H_2O)_6^{2+}(aq)$ ions which are pink. The colour becomes more pink.

C4. Quantitative chemistry

C4.1 Use A_r values to calculate the relative molar mass, M_r.

C4.2 Know that Avogadro's number gives the number of particles in one mole of a substance.

C4.3 Know that one mole of a substance is the A_r or M_r in grams, and perform conversions of grams to moles and *vice versa* (including working in tonnes and kilograms). Know that the amount of a substance corresponds to the number of moles of a substance.

Reactions that are carried out in the laboratory or in an industrial process involve many millions of atoms/ions/molecules. Because these particles are very small, they are counted by weighing them.

Avogadro's constant, N_A, is the conversion factor between the atomic and macroscopic scales. It gives the number of particles in 1 mole (unit: mol) of a substance and has a value (to 4 significant figures) of 6.022×10^{23} mol^{-1}.

The amount of a substance is the number of moles of that substance.

Just as a collection of 12 eggs is called 1 dozen eggs, 6.022×10^{23} atoms of hydrogen is 1 mol of H atoms and 6.022×10^{23} molecules of H_2O is 1 mol of water.

Exercise 21

A balloon contains 0.200 mol of helium. How many atoms of helium are contained in the balloon? [$N_A = 6.022 \times 10^{23}$ mol^{-1}]

Some elements and all compounds exist as groups of atoms that are bonded together. The relative molar mass (also sometimes called the relative molecular or formula mass), M_r, of these substances is calculated by adding together the relative atomic masses, A_r, of all the atoms or ions present in 1 molecule or formula unit of the substance.

Because relative atomic masses, and therefore relative molar masses, are ratios of masses, they do not have any units.

Exercise 22

Calculate the relative molar masses of the following substances:

a) oxygen, O_2

b) glucose, $C_6H_{12}O_6$

c) barium nitrate, $Ba(NO_3)_2$

d) hydrated copper sulfate, $CuSO_4 \cdot 5H_2O$

[A_r values: H = 1.0; C = 12.0; N = 14.0; O = 16.0; S = 32.0; Cu = 63.5; Ba = 137]

The mass of 1 mol of atoms of an element, its molar mass (unit: g mol^{-1}), has the same numerical value as the A_r of the element in grams.

The mass of 1 mol of a substance, its molar mass (unit: g mol^{-1}), has the same numerical value as the M_r of the substance in grams.

The relationship between the molar mass A_r or M_r in grams) of a substance, the mass of the substance and the amount (number of moles) of the substance is given by the expression:

$$\text{(amount) number of moles} = \frac{\text{mass (in g)}}{\text{molar mass (g mol}^{-1}\text{)}}$$

Looking at the units:

$$\text{Amount} = \frac{\text{g}}{\text{g mol}^{-1}} = \text{mol}$$

This means that the amount of a substance (or the number of atoms/molecules/ions) in a given mass of the substance can be calculated, or the amount of substance can be used to calculate the mass of a substance.

Exercise 23

What is the mass of 0.010 mol of magnesium?

If the mass is given (or required) in kilograms or tonnes, then the conversion to (or from) grams must be made.

Exercise 24

a) How many moles of aluminium is formed if 5.4 tonnes are produced?

b) What is the mass, in kg, of 100 mol of sodium hydroxide?

[A_r values: H = 1.0; O = 16.0; Na = 23.0; Al = 27.0]

C4.4 Calculate the percentage composition by mass of a compound using given A_r values.

C4.5 Know that the *empirical formula* is the simplest integer ratio of atoms in a compound. Find the empirical formula of a compound from a variety of data, such as the percentage composition by mass of the elements present or reacting masses. Find the molecular formula from the empirical formula if given the M_r value.

The mass of an element or compound is comprised of the masses of the atoms/ions in the substance.

In 1 mol of calcium carbonate, $CaCO_3$, there is: 1 mol of calcium ions, 1 mol of carbon atoms and 3 mol of oxygen atoms.

1 mol of calcium ions has a mass of 40 g

1 mol of carbon atoms has a mass of 12 g

3 mol of oxygen atoms have a mass of 3 × 16 = 48 g

The total mass of 1 mol of $CaCO_3$ = 40 + 12 + 48 = 100 g

Of that total, 40 g is due to the calcium ions present therefore the percentage Ca = $\frac{40}{100} \times 100 = 40\%$

12 g is due to the carbon atoms present, therefore percentage C = $\frac{12}{100} \times 100 = 12\%$

48 g is due to the oxygen atoms present, therefore percentage O = $\frac{48}{100} \times 100 = 48\%$

As 40, 12 and 16 are the A_r values of Ca, C and O, respectively, and 100 is the M_r value of $CaCO_3$, an expression for calculating the percentage composition by mass of the elements in a compound is:

$$\%\ \text{element} = \frac{A_r \times \text{number of atoms of element in formula of compound}}{M_r \text{ of compound}} \times 100$$

Exercise 25

What is the percentage by mass of carbon in glucose, $C_6H_{12}O_6$?

[A_r values: H = 1.0; C = 12.0; O = 16.0]

The percentage of water in a hydrated compound can also be calculated in a similar manner.

Exercise 26

What is the percentage by mass of water in crystals of sodium sulfide-9-water, $Na_2S{\cdot}9H_2O$?

[*Mr* values: Na2S·9H2O = 240; H2O = 18]

The empirical formula of a compound is the simplest whole number ratio of atoms of each element present in the compound.

The empirical formula can be determined from the percentage composition of mass of the elements present in the compound.

Exercise 27

What is the empirical formula of a compound that is 36% beryllium and 64% oxygen?

[A_r values: Be = 9.0; O = 16.0]

The empirical formula can also be found from the reacting masses of elements.

Exercise 28

What is the empirical formula of a compound that is 36% beryllium and 64% oxygen?

[A_r values: Be = 9.0; O = 16.0]

The molecular formula of a compound is the actual number of atoms of each element present in one molecule of the compound.

The molecular formula is a multiple of the empirical formula and can be found if the M_r of the compound is given.

Exercise 29

The empirical formula of a compound is CHO_2 and its M_r is 90.0.

What is the molecular formula of the compound?

[A_r values: H = 1.0; C = 12.0; O = 16.0]

C4.6	Use balanced chemical equations to calculate the masses of reactants and products, including if there is a limiting reactant present.
C4.7	Be able to construct balanced chemical equations from reacting masses or gas volumes data.
C4.8	Understand that (for an ideal gas) one mole of a gas occupies a set volume at a given temperature and pressure (for example, 24 dm^3 at room temperature and pressure (rtp)), and perform conversions of volumes to number of moles, and *vice versa*.

A balanced chemical equation gives the molar quantities of the reacting substances and products formed.

For example, the equation for the reaction of magnesium with oxygen gas:

$$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$$

states that 1 mol Mg reacts with ½ mol O_2 to form 1 mol MgO.

This means that the amount of a substance participating in, required for or produced by a reaction can be calculated if the balanced chemical equation is known.

Exercise 30

What is the maximum mass of magnesium oxide that can be formed if 0.12 g of magnesium is completely burned in excess oxygen?

[A_r values: O = 16; Mg = 24]

In the previous example it was stated that one of the reactants (oxygen) was in excess. This information was given so that it was known that all the magnesium reacted – the magnesium was the limiting reactant.

In other cases, the amounts of reactants have to be calculated and compared to the equation in order to determine which, if any, is in excess.

Exercise 31

In the manufacture of calcium carbide:

$CaO(s) + 3C(s) \rightarrow CaC_2(s) + CO(g)$

What is the maximum mass of calcium carbide that can be obtained from 11.2 kg of calcium oxide and 11.2 kg of carbon?

[A_r values: C = 12.0; O = 16.0; Ca = 40.0]

The volume of gas molecules is very small compared to the volume occupied by the gas (this is one of the assumptions of an 'ideal gas') and is considered negligible.

A consequence of this is that the volume of a gas depends on the conditions of temperature and pressure, and not the identity of the gas.

This means that equal volumes of gases, when measured under the same conditions of temperature and pressure, contain the same number of moles (and molecules) of gas.

Exercise 32

A car engine burns octane, C_8H_{18} :

$$2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$$

What is the minimum volume of oxygen that is required to ensure complete combustion of 1 dm^3 of octane vapour (all volumes measured at the same conditions of temperature and pressure)?

When the temperature and pressure of a gas is given, its molar volume has a specific value. At room temperature and pressure (rtp), this is often quoted as 24 dm^3.

This means that the amount of a gas in a given volume of the gas can be calculated, or the amount of gas can be used to calculate the volume of the gas if the molar volume is given.

The relationship between the molar gas volume, the volume of the gas and the amount (number of moles) of the gas is given by the expression:

$$\text{Number of moles of gas} = \frac{\text{volume}}{\text{molar volume}} \quad \text{(both volumes in the same unit)}$$

Exercise 33

Calculate the mass of ammonium chloride required to produce 1.20 dm^3 of ammonia, at room temperature and pressure, in the reaction

$$2NH_4Cl(s) + Ca(OH)_2(s) \rightarrow 2NH_3(g) + CaCl_2(s) + 2H_2O(g)$$

(Assume that one mole of any gas has a volume of 24.0 dm^3 at room temperature and pressure.)

[A_r values: H = 1.0; N = 14.0; Cl = 35.5]

Exercise 34

What is the volume of hydrogen obtained when 3.25 g of zinc reacts with an excess of dilute sulfuric acid at room temperature and pressure?

(Assume that one mole of any gas has a volume of 24.0 dm^3 at room temperature and pressure.)

[A_r value: Zn = 65]

Balanced chemical equations can be constructed from both reacting mass and reacting gas volume data.

Exercise 35

100 cm^3 of a gaseous alkane required 500 cm^3 of oxygen for complete combustion, all volumes being measured at the same conditions of temperature and pressure.

What is the equation for this complete combustion reaction?

Exercise 36

1.12 g of a metal hydroxide, M_r = 56, is required to exactly neutralise a solution containing 0.98 g of sulfuric acid.

Using Q as the symbol for the metal, determine the chemical equation for the reaction between Q hydroxide and sulfuric acid.

[A_r values: H = 1.0; O = 16.0; S = 32.0]

C4.9 Solutions:

a. Understand that concentration can be measured in $mol\,dm^{-3}$ or $g\,dm^{-3}$, and be able to calculate the concentration given the number of moles (or mass) of solute and the volume of solution.

b. Know the term *saturated solution*, be able to calculate solubility and interpret solubility data.

C4.10 Use the concentrations of solutions (or find the concentrations from given data) and the reacting ratio of reactants from the balanced equation to perform titration calculations.

Solutions: their concentration, amount of substance present and dilution

The concentration of a solution is a measure of the number of solute particles in a given volume of solution.

Because the absolute number of solute particles is usually very large, the concentration of a solution is often given as:

the amount in moles of a solute present in $1\,dm^3$ of solution, unit: $mol\ dm^{-3}$

or

the mass of solute in $1\,dm^3$ of solution, unit: $g\ dm^{-3}$

(Note that concentration in either unit is ‘in $1\,dm^3$ of solution’ and not ‘in $1\,dm^3$ of solvent’ because when a solute dissolves in a solvent, there is a volume change.)

Exercise 37

What is the concentration, in $g\,dm^{-3}$, of a solution of 8.0 g sodium hydroxide dissolved in $5.0\,dm^3$ of solution?

If the volume of solution is given in cm^3, then the volume has to be converted into dm^3.

The expression can be rearranged to calculate the mass of solute required to make a certain volume of a specified concentration.

Exercise 38

Normal saline is an aqueous solution of NaCl with a concentration of 9.0 g dm^{-3}.

Calculate the mass of sodium chloride required to make 250 cm^3 of a normal saline solution.

Or a calculation might use mol dm^{-3} as the unit.

Exercise 39

What mass of $NaHCO_3(s)$ must be used in order to prepare 750 cm^3 of 0.100 mol dm^{-3} $NaHCO_3(aq)$?

[A_r values: H = 1.0; C = 12.0; O = 16.0; Na = 23.0]

Data might be provided in grams but the concentration in mol dm^{-3} is required.

Exercise 40

What is the concentration, in mol dm^{-3}, of a solution formed when 5.6 g potassium hydroxide is dissolved in a total volume of 500 cm^3?

[A_r values: H = 1; O = 16; K = 39]

If the volume of solution and its concentration are given, the amount of solute contained in that volume can be calculated by rearranging the expression:

$$\text{amount of solute (in mol)} = \text{volume of solution (in dm}^3\text{)} \times \text{concentration (in mol dm}^{-3}\text{)}$$

Exercise 41

Determine the amount of solute present in the following solutions:

a. dm^3 of hydrochloric acid of concentration 0.020 mol dm^{-3}

b. 10 cm^3 of a 0.25 mol dm^{-3} solution of sodium hydroxide

Likewise, if the amount of solute and the concentration of the solution are given, the volume that contains the specified amount of solute can be calculated by a further rearrangement.

$$\text{Volume of solution (in dm}^3\text{)} = \frac{\text{amount of solute (in mol)}}{\text{concentration (in mol dm}^{-3}\text{)}}$$

Exercise 42

Calculate the volumes of the following solutions that contain the stated amount of solute.

a. 0.1 mol from a 0.05 mol dm^{-3} solution

b. 2.0×10^{-3} mol from a 0.080 mol dm^{-3} solution

Combinations of these calculations are used in determining the volumes of concentrated solutions required to give more dilute solutions and in volumetric analysis, such as in acid-base titrations.

Exercise 43

What volumes of the following concentrated solutions are required to give the stated volumes of the more dilute solutions?

a. 4.00 dm^3 of 0.250 mol dm^{-3} H_2SO_4(aq) from 2.00 mol dm^{-3} H_2SO_4(aq)

b. 250 cm^3 of 2.00 mol dm^{-3} KOH(aq) from 2.50 mol dm^{-3} KOH(aq)

Titration calculations

Exercise 44

25.0 cm^3 of an aqueous solution of sodium hydroxide required 20.0 cm^3 of 0.100 mol dm^{-3} hydrochloric acid for neutralisation. What is the concentration of the sodium hydroxide solution?

Exercise 45

What volume of aqueous 0.200 mol dm^{-3} sodium hydroxide is required to exactly neutralise 50.0 cm^3 of 0.100 mol dm^{-3} sulfuric acid?

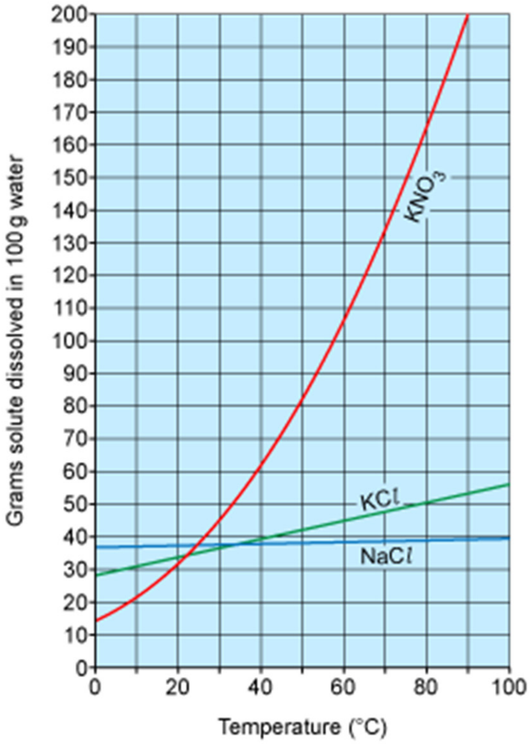
Exercise 46

What volume of an aqueous solution of sodium hydroxide of concentration 20.0 g dm^{-3} is required to exactly neutralise 25.0 cm^3 of 0.1 mol dm^{-3} hydrochloric acid?

Saturated solutions

A saturated solution is one in which no more solute will dissolve at a given temperature.

Solubility in water of three salts



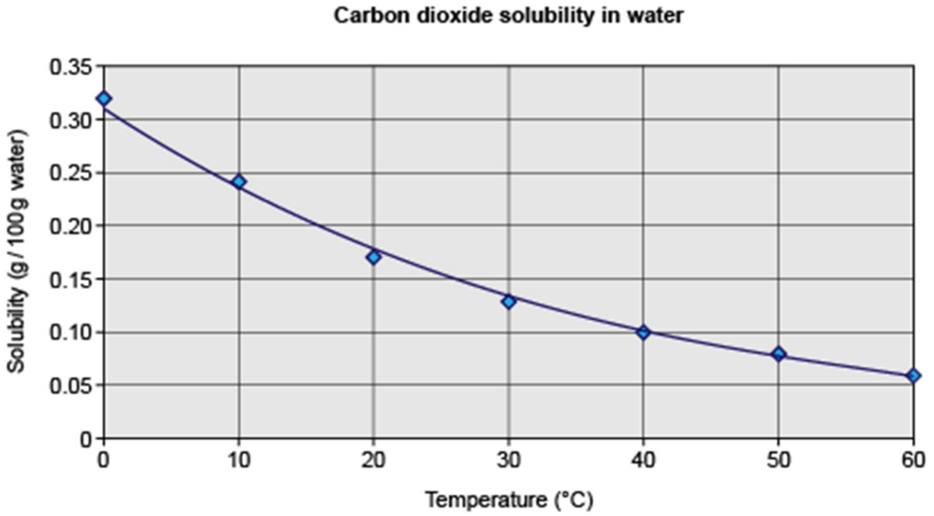
This graph shows how the solubility in water of three salts: potassium nitrate, potassium chloride and sodium chloride, vary with temperature.

The unit for solubility is usually g of solute per 100 g of solvent.

Any point on the solubility curve line represents a saturated solution.

(The reasons why solubility varies with temperature are complex and are not covered in this specification.)

Not all substances become more soluble as the temperature of the solution increases. For example, gases become less soluble as temperature increases as shown by this graph of the solubility of carbon dioxide.



Exercise 47

What is the maximum mass of copper(II) chloride that will dissolve in 250 cm^3 water at 20 °C?

[Solubility of $CuCl_2$ at 20 °C is 73 g / 100 g H_2O]

[Density of water at 20 °C is 1.0 g cm^{-3}]

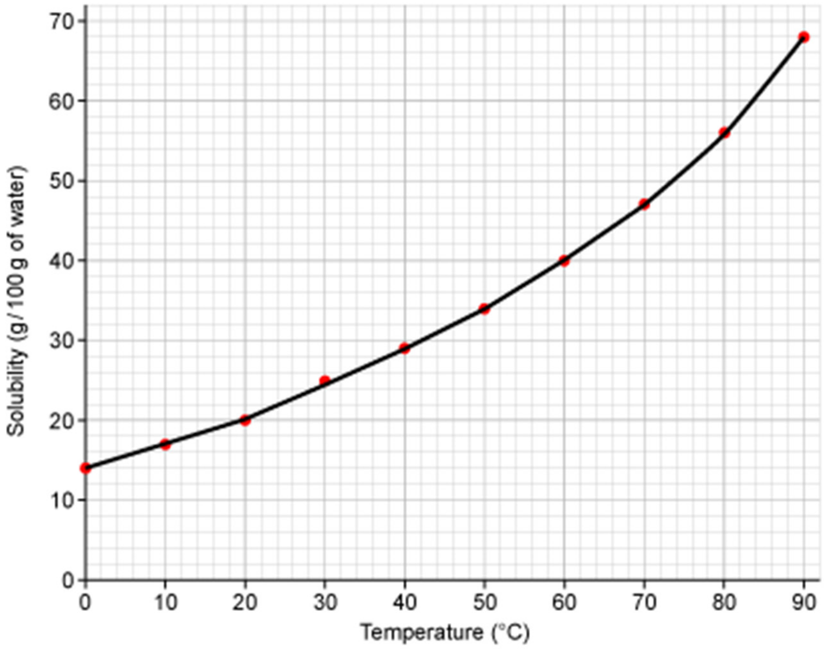
The solubility curves show why cooling a hot concentrated solution results in a precipitate forming for many salts.

A solubility graph can be used to calculate the mass of a salt that will precipitate out as a hot saturated solution is cooled.

Exercise 48

Using the following solubility curve, what mass of copper(II) sulfate will be precipitated out if a saturated solution, made with 50 g water, at 74 °C is cooled to 24 °C?

Solubility curve for copper(II) sulfate (solute) in water (solvent)



C4.11 Calculate the percentage yield of a reaction using the balanced chemical equation and the equation:

$$\text{percentage yield} = \frac{\text{actual yield (g)}}{\text{predicted yield (g)}} \times 100$$

Even though no atoms are gained or lost in a chemical reaction, it is not always possible to obtain the predicted mass of a product because:

- the reaction will not go to completion if it is reversible
- some of the product may be lost when it is separated from the reaction mixture
- some of the reactants may also react in ways different to the expected reaction.

The mass of a product obtained is known as the yield.

When the actual mass obtained is compared with the predicted mass as a percentage, it is called the percentage yield.

Exercise 49

25.0 g of ethanoic acid, CH_3COOH, are formed from the oxidation of 23.0 g of ethanol, CH_3CH_2OH.

$$CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$$

What is the percentage yield of this reaction?

[A_r values = H = 1.0; C = 12.0; O = 16.0]

The percentage yield can be used to calculate the mass of product formed, or amount of reactant required by a reaction.

Exercise 50

Ammonia is formed by the reaction of nitrogen with hydrogen:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Under certain reaction conditions the percentage yield is 15%.

What mass of ammonia is formed when 2.8 g of nitrogen reacts with an excess of hydrogen under these conditions?

[A_r values: H = 1.0; N = 14.0]

Exercise 51

Ethyl ethanoate is formed by the reaction of ethanol with ethanoic acid in the presence of concentrated sulfuric acid.

$$CH_3CH_2OH + CH_3COOH \rightarrow CH_3COOCH_2CH_3 + H_2O$$

If the percentage yield for this reaction is 50%, what mass of ethanol must be reacted with excess ethanoic acid to form 4.4 g ethyl ethanoate?

[A_r values: H = 1.0; C = 12.0; O = 16.0]

Solutions to Exercises 21 to 51

Exercise 21

N_A gives the number of particles in 1 mol of a substance.

Therefore, 0.2 mol is $6.022 \times 10^{23} \times 0.200 = 1.204 \times 10^{23}$ particles.

So there are 1.204×10^{23} He atoms in the balloon.

Exercise 22

a) $M_r(O_2) = 2 \times A_r(O) = 2 \times 16.0 = 32.0$

b) $M_r(C_6H_{12}O_6) = (6 \times A_r(C)) + (12 \times A_r(H)) + (6 \times A_r(O))$

$= (6 \times 12.0) + (12 \times 1.0) + (6 \times 16.0)$

$= 72.0 + 12.0 + 96.0 = 180$

c) $M_r(Ba(NO_3)_2) = A_r(Ba) + 2 \times \{A_r(N) + (3 \times A_r(O))\}$

$= 137 + 2 \times \{14.0 + (3 \times 16.0)\}$

$= 137 + 2 \times \{14.0 + 48.0\}$

$= 137 + 2 \times \{62.0\} = 261$

d) $M_r(CuSO_4{\cdot}5H_2O) = A_r(Cu) + A_r(S) + (4 \times A_r(O)) + 5 \times \{(2 \times A_r(H)) + A_r(O)\}$

$= 63.5 + 32.0 + (4 \times 16.0) + 5 \times \{(2 \times 1) + 16.0\}$

$= 63.5 + 32.0 + 64.0 + 5 \times \{18.0\} = 249.5$

Exercise 23

One mole of magnesium has a mass of 24.3 g (A_r in grams).

Therefore, 0.010 mol of magnesium has a mass of $0.01 \times 24.3 = 0.243$ g

Exercise 24

a) 10^6 g $= 10^3$ kg $=$ 1 tonne

number of moles of aluminium $= \frac{mass\ (in\ g)}{molar\ mass} = \frac{5.4\times10^6}{27.0}$ as there are 10^6 g in a tonne = 200 000 mol

b) $M_r(NaOH) = 23.0 + 16.0 + 1.0 = 40.0$

number of moles $= \frac{mass\ (in\ g)}{molar\ mass}$

$100 = \frac{mass}{40.0}$

mass $= 100 \times 40.0 = 4000$ g $= 4$ kg, as there are 10^3 g in 1 kg.

Exercise 25

$M_r(C_6H_{12}O_6) = (6 \times 12.0) + (12 \times 1.0) + (6 \times 16.0) = 180$

percentage C $= \frac{(12.0\times6)}{180} \times 100 = \frac{72}{180} \times 100 = \frac{8}{20} \times 100 = 40\%$

Exercise 26

percentage water $= \frac{9\times18}{240} \times 100 = \frac{162}{240} \times 100 = \frac{27}{40} \times 100 = 67.5\%$

Exercise 27

The compound must be composed of beryllium and oxygen only as 36% + 64% = 100%

	Be	**O**
mass of 100 g of compound	36	64
÷ by relative molar mass	$\frac{36}{9.0}$	$\frac{64}{16}$
amount (number of moles)	4	4
÷ by 4 to get the simplest ratio	1	1

Empirical formula is BeO

Exercise 28

Mass of chlorine that reacts = 16.25 – 5.60 = 10.65 g

	Fe	**Cl**
mass of 16.25 g iron chloride	5.60	10.65
÷ by relative molar mass	$\frac{5.60}{56.0}$	$\frac{10.65}{35.5}$
amount (number of moles)	0.1	0.3
× by 10 to get the simplest ratio	1	3

Empirical formula is $FeCl_3$

Exercise 29

Empirical formula mass = 12.0 + 1.0 + 32.0 = 45.0

M_r = n × empirical formula mass

90.0 = n × 45.0

n = 2

The molecular formula is $C_2H_2O_4$

Exercise 30

$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$

M_r (MgO) = 24 + 16 = 40

Number of moles of Mg reacting = $\frac{\text{mass}}{\text{molar mass}} = \frac{0.12}{24}$ = 0.005 mol

From the equation 1 mol Mg forms 1 mol MgO, therefore the maximum amount of MgO that can be formed from 0.0050 mol Mg is 0.005 mol.

Mass of MgO = amount × molar mass = 0.0050 × 40 = 0.20 g

Exercise 31

M_r (CaO) = 40.0 + 16.0 = 56.0

Number of moles of CaO = $\frac{\text{mass}}{\text{molar mass}} = \frac{11200}{56.0}$ = 200 mol

From the equation, 200 mol CaO react with 3 × 200 = 600 mol of C

Mass of C required to react = amount × molar mass = 600 × 12 = 7200 g = 7.2 kg

The mass of C provided is 11.2 kg which is greater than 7.2 kg, so the C is in excess and the CaO is the limiting reactant (all of it will be used up).

M_r (CaC_2) = 40.0 + 24.0 = 64.0

From the equation, 1 mol CaO forms 1 mol CaC_2.

Mass of 200 mol CaC_2 = 200 × 64.0 = 12 800 g = 12.8 kg

Exercise 32

The equation states that 2 volumes of octane vapour require 25 volumes of oxygen for complete combustion.

2 volumes is equivalent to 1 dm^3

therefore, 25 volumes $= \frac{1}{2} \times 25 = 12.5\,dm^3$

12.5 dm^3 oxygen are required to ensure complete combustion of the octane.

Exercise 33

Number of moles of $NH_3 = \frac{\text{volume}}{\text{molar volume}} = \frac{1.2}{24} = 0.050\,mol$

From the equation, 1 mol NH_4Cl forms 1 mol NH_3 (2 : 2 in the equation)

Therefore, 0.050 mol NH_4Cl is required.

M_r $(NH_4Cl) = 14.0 + (1.0 \times 4) + 35.5 = 53.5$

Mass of NH_4Cl required = 0.050 × 53.5 = 2.68 g

Exercise 34

$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$

Number of moles of Zn reacted $= \frac{3.25}{65} = 0.050\,mol$

From the equation, 1 mol Zn forms 1 mol H_2

Volume of H_2 produced = 0.050 × 24.0 = 1.20 dm^3

Exercise 35

The ratio of gases alkane : oxygen is 100 : 500, or 1 : 5

Therefore, 1 mol alkane requires 5 mol O_2 for complete combustion.

Let the alkane be C_nH_{2n+2}, then the equation becomes:

Balancing the number of oxygen atoms on both sides of the equation:

$10 = 2n + \frac{2n+2}{2} = 2n + n + 1$

$9 = 3n$

$3 = n$

The equation is: $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

Exercise 36

Number of moles of Q hydroxide = $\frac{1.12}{56}$ = 0.020 mol

M_r (H_2SO_4) = (2 × 1.0) + 32.0 + (4 × 16.0) = 98.0

Number of moles of H_2SO_4 = $\frac{0.98}{98.0}$ = 0.010 mol

The reacting ratio of Q hydroxide : H_2SO_4 is 0.020 : 0.010, or 2 : 1

Therefore, Q hydroxide is monobasic and has the formula QOH and the equation is:

$$2QOH + H_2SO_4 \rightarrow Q_2SO_4 + 2H_2O$$

Exercise 37

Concentration (in $g\,dm^{-3}$) = $\frac{\text{mass of solute (in g)}}{\text{volume of solution (in dm}^3\text{)}}$ = $\frac{8.0}{5.0}$ = 1.6 $g\,dm^{-3}$

Exercise 38

Mass of solute (in g) = concentration (in $g\,dm^{-3}$) × volume of solution (in dm^3)

= 9.0 × $\frac{250}{1000}$ as there are 1000 cm^3 in 1 dm^3

Mass of NaCl required = 2.25 g

Exercise 39

Number of moles of $NaHCO_3$ = $\frac{750}{1000}$ × 0.100 = 0.0750 mol

M_r ($NaHCO_3$) = 23.0 + 1.0 + 12.0 + (3 × 16.0) = 84.0

Mass of $NaHCO_3$ required = 84.0 × 0.0750 = 6.30 g

Exercise 40

M_r (KOH) = 39 + 16 + 1 = 56

Amount of KOH = $\frac{5.6}{56}$ = 0.10 mol

Concentration (in $mol\,dm^{-3}$) = $\frac{\text{amount of solute (in mol)}}{\text{volume of solution (in dm}^3\text{)}}$ = $\frac{0.10 \times 1000}{500}$

Concentration of KOH = 0.20 $mol\,dm^{-3}$

Exercise 41

a. Number of moles of HCl $= 1.00 \times 0.020 = 0.020\,\text{mol}$

b. Number of moles of NaOH $= \frac{10}{1000} \times 0.25$ (divided by 1000 to convert to dm^3) $= 2.5 \times 10^{-3}\,\text{mol}$

Exercise 42

a. Volume of solution (in dm^3) $= \frac{0.1}{0.05} = 2\,\text{dm}^3$

b. Volume of solution (in dm^3) $= \frac{2.0 \times 10^{-3}}{0.080} = \frac{0.2}{8} = 0.025\,\text{dm}^3$ (or $25\,\text{cm}^3$)

Exercise 43

Both the concentrated and more dilute solutions contain the same amount of solute.

a. Number of moles of $H_2SO_4(aq)$ in dilute solution $= 4.00 \times 0.250\,\text{mol}$

Volume of concentrated solution required $= \frac{1.00}{2.00} = 0.500\,\text{dm}^3$ (or $500\,\text{cm}^3$)

b. Number of moles of KOH(aq) in dilute solution $= \frac{250}{1000} \times 2.00 = 0.500\,\text{mol}$

Volume of concentrated solution required $= \frac{0.500}{2.50} = 0.200\,\text{dm}^3$ (or $200\,\text{cm}^3$)

(Note: As the volume change when preparing one dilute solution from another is very small, it can be ignored in this type of calculation.)

Exercise 44

Number of moles of HCl(aq) $= \frac{20.0}{1000} \times 0.100 = 2 \times 10^{-3}\,\text{mol}$

From the equation, amount of NaOH(aq) = amount of HCl(aq) $= 2 \times 10^{-3}\,\text{mol}$

Concentration NaOH(aq) $= \frac{2\times10^{-3} \times 1000}{25.0} = \frac{2}{25.0} = 0.080\,\text{mol}\,\text{dm}^{-3}$

Exercise 45

The balanced chemical equation for the reaction is:

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

Number of moles of H_2SO_4(aq) = $\frac{50.0}{1000} \times 0.100 = 5 \times 10^{-3}$ mol

From the equation, number of moles of NaOH(aq) = 2 × number of moles of H_2SO_4(aq)

= $2 \times 5 \times 10^{-3} = 10 \times 10^{-3}$ mol

Concentration NaOH(aq) = $\frac{10 \times 10^{-3} \times 1000}{0.200} = \frac{10}{0.200} = 50.0\ cm^3$

Exercise 46

M_r (NaOH) = 23.0 + 16.0 + 1.0 = 40.0

Number of moles of NaOH in 1.0 dm^3 = $\frac{20.0}{40.0}$ = 0.50 mol

Therefore, the concentration is 0.50 mol dm^{-3}

The balanced chemical equation for the reaction is:

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

Number of moles of HCl(aq) = $\frac{25.0}{1000} \times 0.100 = 2.5 \times 10^{-3}$ mol

From the equation, number of moles of NaOH(aq) = number of moles of HCl(aq) = 2.5×10^{-3} mol

Volume of NaOH(aq) required = $\frac{2.5 \times 10^{-3}}{0.50} = 5.0 \times 10^{-3}\ dm^3$ (or 5.0 cm^3)

Exercise 47

Density = $\frac{\text{mass}}{\text{volume}}$

Mass of water = 250 × 1.0 = 250 g

If 100 g water will dissolve 73 g $CuCl_2$

then 250 g water will dissolve $\frac{73 \times 250}{100} = 73 \times 2.5 = 182.5$ g $CuCl_2$

Exercise 48

At 74 °C, the solubility of copper(II) sulfate is 50 g / 100 g water.

Therefore, $\frac{50}{2}$ = 25 g copper(II) sulfate will saturate 50 g water.

At 24 °C, the solubility of copper(II) sulfate is 22 g / 100 g water.

Therefore, $\frac{22}{2}$ = 11 g copper(II) sulfate will saturate 50 g water.

25 – 11 = 14 g of copper(II) sulfate precipitates out.

Exercise 49

The equation shows that 1 mol CH_3CH_2OH is oxidised to form 1 mol CH_3COOH

M_r $CH_3CH_2OH = (2 \times 12.0) + (6 \times 1.0) + 16.0 = 46.0$

M_r $CH_3COOH = (2 \times 12.0) + (4 \times 1.0) + (2 \times 16.0) = 60.0$

So it is predicted that 46.0 g CH_2CH_3OH will form 60.0 g CH_3COOH

Therefore, 23.0 g CH_3CH_2OH is predicted to form $\frac{23.0}{46.0} \times 60.0 = 30.0$ g CH_3COOH

Percentage yield of CH3COOH $= \dfrac{\text{actual yield (g)}}{\text{predicted yield (g)}} \times 100$

$= \frac{25.0}{30.0} \times 100 = \frac{5}{6} \times 100 = 83.3\%$

Exercise 50

The equation shows that 1 mol N_2 forms 2 mol NH_3

M_r $(N_2) = 2 \times 14.0 = 28.0$

M_r $(NH_3) = 14.0 + (3 \times 1.0) = 17.0$

So, it is predicted that 28.0 g N_2 will form $(2 \times 17.0) = 34.0$ g NH_3

Therefore, 2.8 g N_2 is predicted to form $\frac{2.8}{28.0} \times 34.0 = 3.4$ g NH_3

Actual yield = percentage yield × predicted yield $= \frac{15}{100} \times 3.4 = 0.51$ g NH_3

Exercise 51

If the percentage yield is 50%, the predicted yield $= 4.4 \times \frac{100}{50} = 8.8\,\text{g}$

The equation shows that 1 mol $CH_3COOCH_2CH_3$ is formed from 1 mol CH_3CH_2OH.

$M_r\ (CH_3COOCH_2CH_3) = (4 \times 12.0) + (2 \times 16.0) + (8 \times 1.0) = 88.0$

$M_r\ (CH_3CH_2OH) = (2 \times 12.0) + 16.0 + (6 \times 1.0) = 46.0$

So, it is predicted that 88.0 g $CH_3COOCH_2CH_3$ is formed from 46.0 g CH_3CH_2OH

Therefore, 8.8 g is formed from $46.0 \times \frac{8.8}{88.0} = 4.6\,\text{g}$

C5. Oxidation, reduction and redox

C5.1 Know that on a basic level, oxidation is the gain of oxygen and that reduction is the removal of oxygen.

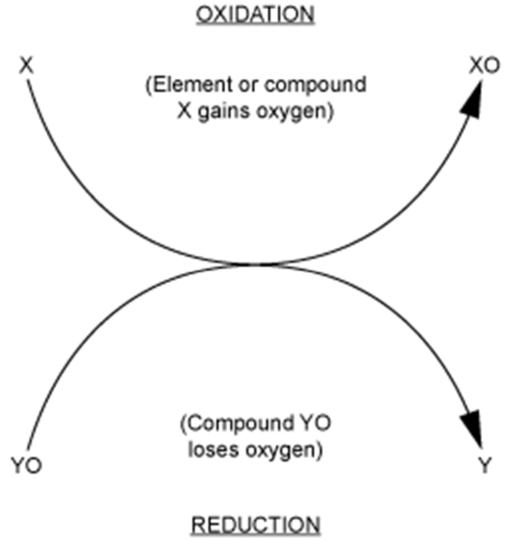
C5.2 Know and be able to use the concept that oxidation and reduction are the transfer of electrons, i.e. reduction is the gain of electrons and oxidation is the loss of electrons.

C5.4 Identify any chemical equation that involves: oxidation only, reduction only, redox (both oxidation and reduction taking place), or no oxidation/reduction.

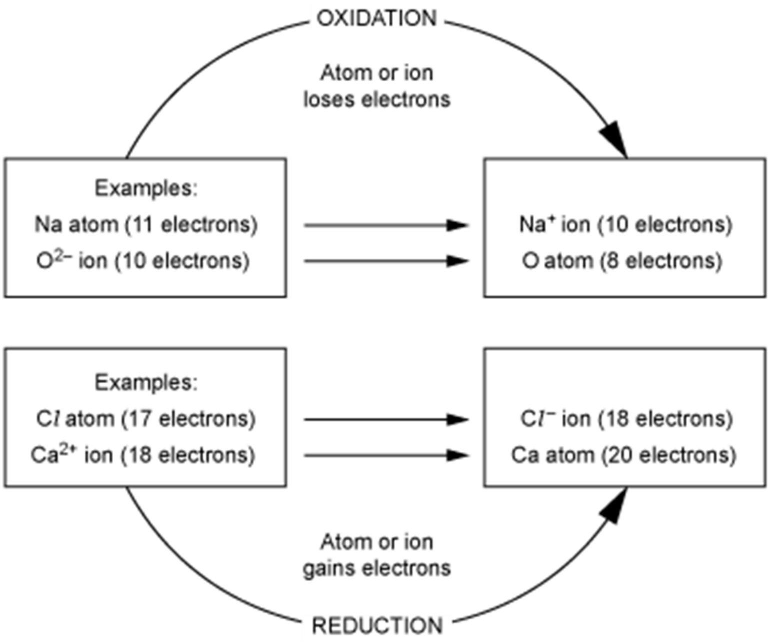
(C5.3 is covered on pages 72 to 76.)

When chemists were trying to classify chemical reactions by type, an easily spotted type of reaction was one that involved a gain of oxygen – combustion reactions being obvious examples of this type. Such reactions were called oxidation reactions, with oxidation being defined as the gain of oxygen.

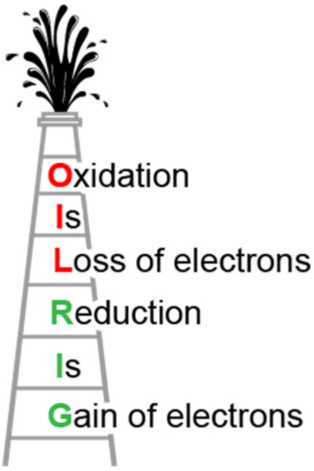
The opposite of this was given the name reduction, with reduction being defined as the loss of oxygen.



Later on, chemists noted that similar reactions happened with other reactive non-metals. For example, the reaction of sodium with chlorine is very similar to the reaction of sodium with oxygen: both reactions involve sodium losing electrons which are then gained by the non-metal element. The definition of oxidation was broadened to include these similar reactions. The sodium is oxidised when it reacts with oxygen, but more generally it loses electrons in its reactions with non-metals. Hence oxidation became to be defined as a loss of electrons, and reduction was defined as a gain of electrons.



A mnemonic to help you remember this is 'OIL RIG':



Many equations will show both oxidation and reduction occurring – such equations are called redox equations.

Spotting oxidation and reduction:

The following examples illustrate the application of the earlier definitions.

1) $H_2O + CO \rightarrow H_2 + CO_2$

   The water has lost oxygen (reduction) and the carbon monoxide has gained oxygen (oxidation). This is an example of a redox equation.

2) Mg + Br2 → MgBr2

   In this reaction an ionic compound, magnesium bromide, has been formed from its elements. Magnesium bromide consists of Mg^{2+} ions and Br^- ions. The magnesium atoms have lost electrons (oxidation) and the bromine atoms in the bromine molecules have gained electrons (reduction). This is an example of a redox equation.

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

   When molten lead(II) bromide is electrolysed, the reaction above occurs at the cathode (negative electrode). The Pb^{2+} ions have gained electrons (reduction). This is an example of a reduction only equation.

4) $2Br^- \rightarrow Br_2 + 2e^-$

   This reaction occurs at the anode (positive electrode) during the electrolysis of molten lead(II) bromide. The Br^- ions have lost electrons (oxidation). This is an example of an oxidation only equation.

5) $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

   Silver chloride is an ionic compound comprising of Ag^+ and Cl^- ions. In this equation nothing has lost or gained electrons and hence there is no oxidation/reduction involved.

Exercise 52

What is being oxidised and what is being reduced in the following equation?

$$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$$

Exercise 53

Which of these equations is an example of an oxidation only equation?

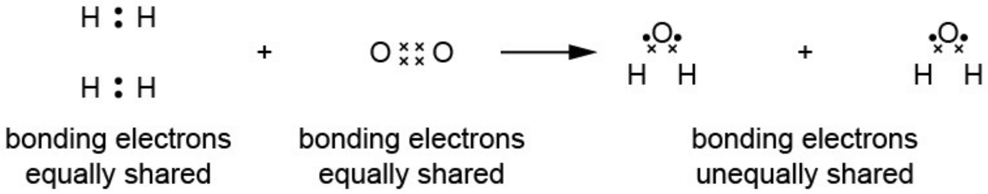
1) $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$
2) $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$
3) $2H^+ + 2e^- \rightarrow H_2$
4) $Pb^{2+} + 2I^- \rightarrow PbI_2$

C5.3 Determine and use the oxidation states of atoms in simple inorganic compounds.

Only in reactions that involve ionic substances are electrons truly lost or gained. However in reactions that involve covalent compounds, the 'degree of sharing' of electrons can change.

For example, in the molecules O_2 and H_2 the bonding electrons are equally shared between the two atoms. However, in the molecule H_2O the bonding electrons in the two O–H bonds are not equally shared – the oxygen has a greater share than the hydrogen.

In the following reaction:



the oxygen has gained an increased share in the bonding electrons, and this can be thought of as reduction. The hydrogen has a lesser share in the bonding electrons, and this can be thought of as oxidation.

To take this partial transfer of electrons into account, and to simplify the idea of oxidation and reduction, the concept of oxidation states (or oxidation numbers) is used.

Rules for assigning oxidation states to atoms

- The oxidation state of an atom in its elemental state is zero, for example the oxidation state of each oxygen atom in O_2 is zero.

- The oxidation state of a monatomic ion is equal to the charge on the ion.

  For example, the oxidation state of chlorine in Cl^- is −1, and the oxidation state of magnesium in Mg^{2+} is +2.

- The sum of the oxidation states of all the atoms in a compound is zero.

  For example, the sum of the oxidation states of the two hydrogen atoms, the one sulphur atom and the four oxygen atoms in H_2SO_4 is equal to zero.

- The sum of the oxidation states of all the atoms in a polyatomic ion is equal to the charge on the ion.

  For example, the sum of the oxidation states of the one carbon atom and the three oxygen atoms in CO_3^{2-} is equal to −2.

- The oxidation state of a Group 1 metal atom in a compound is +1.

  For example, the oxidation state of the sodium atom in NaOH is +1.

- The oxidation state of a Group 2 metal atom in a compound is +2.

  For example, the oxidation state of the magnesium atom in $MgCl_2$ is +2.

- The oxidation state of an oxygen atom in a compound is almost always going to be −2.

  The exceptions are: in peroxides, for example H_2O_2 where the oxygen atoms have an oxidation state of −1; and when combined with fluorine, for example OF_2 where the oxygen atom has an oxidation state of +2.

- The oxidation state of a hydrogen atom in a compound is almost always +1.

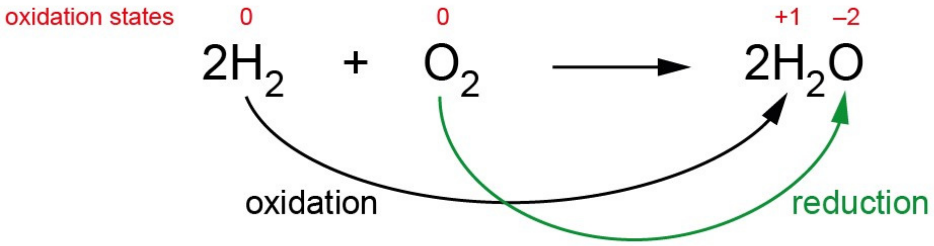
  The exception is when hydrogen is part of a metal hydride, for example MgH_2, and in this case the hydrogen atoms have an oxidation state of −1.

Using oxidation states to spot oxidation and reduction

- If in a reaction an element increases its oxidation state, then it has been oxidised.
- If in a reaction an element decreases its oxidation state, then it has been reduced.

Example 1

$$2H_2 + O_2 \rightarrow 2H_2O$$



The hydrogen and oxygen atoms in H_2 and O_2 have oxidation states of zero because they are in their elemental state.

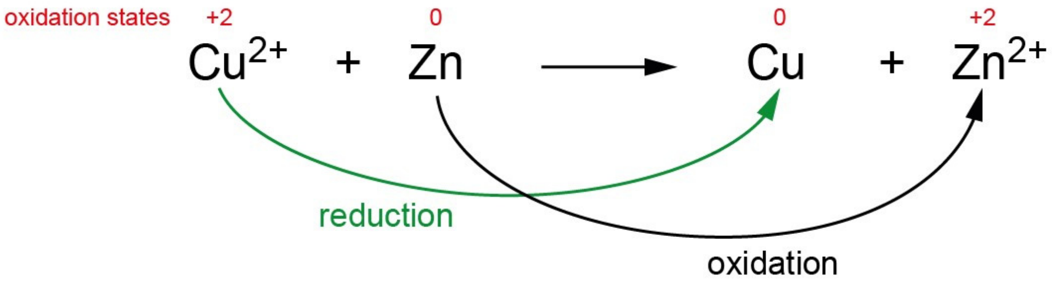
The hydrogen atoms in H_2O have oxidation states of +1, and the oxygen atom in H_2O has an oxidation state of −2. Note that the sum of the oxidation states of all the atoms in H_2O is zero.

The hydrogen atoms have increased their oxidation states from 0 to +1. This is oxidation.

The oxygen atom has decreased its oxidation state from 0 to −2. This is reduction.

Example 2

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$



The Zn and Cu have oxidation states of zero because they are in their elemental state.

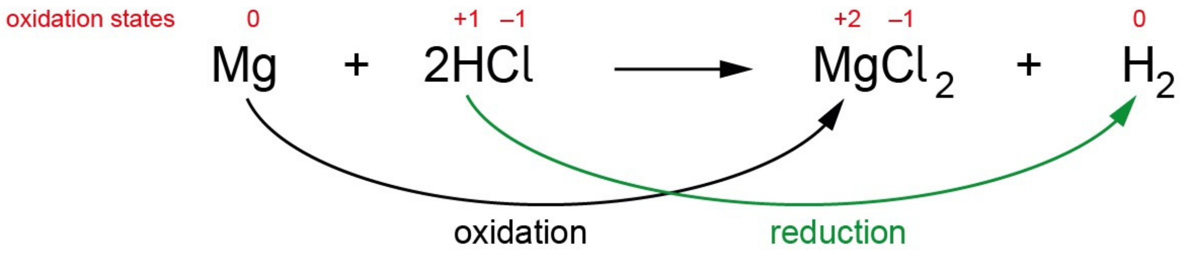
The Cu^{2+} and the Zn^{2+} have oxidation states of +2 because that is the charge on the ions.

The copper ion has undergone a decrease in oxidation state from +2 to 0. This is reduction.

The zinc atom has undergone an increase in oxidation state from 0 to +2. This is oxidation.

Example 3

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$



The Mg atom and the two hydrogen atoms in Mg and H_2 have oxidation states of zero because they are in their elemental states.

The hydrogen atom in HCl has an oxidation state of +1, and to make the sum of oxidation states in HCl equal to zero, the Cl must have an oxidation state of −1.

The oxidation state of Mg in $MgCl_2$ is equal to +2, and to make the sum of the oxidation states in $MgCl_2$ equal to zero, the two Cl must have oxidation states of −1.

The Mg has increased its oxidation state from 0 to +2. This is oxidation.

The hydrogen has decreased its oxidation state from +1 to 0. This is reduction.

Note that the oxidation state of the Cl has not changed and is therefore neither oxidised nor reduced.

Exercise 54

Use oxidation states to work out which species has been oxidised and which species has been reduced in the following reaction:

$$2KI + Br_2 \rightarrow I_2 + 2KBr$$

Exercise 55

In which two of the following species does the nitrogen have the same oxidation state?

NO

NO_2

N_2O

NH_3

HNO_2

NO_3^-

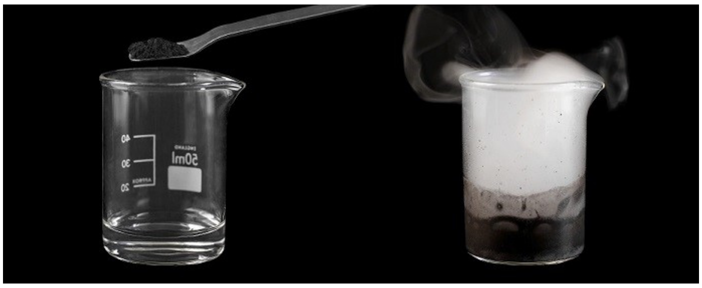
Mg_3N_2

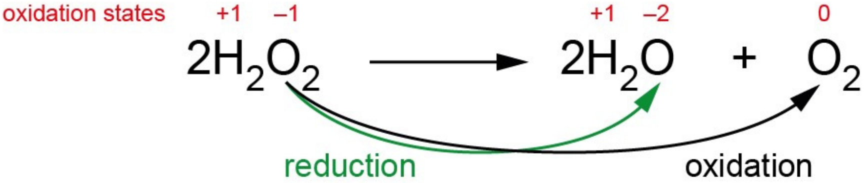
C5.5 Understand the concept of *disproportionation* and recognise reactions (or species) where this occurs.

Disproportionation is a particular type of redox reaction: it is one in which a single species is simultaneously both oxidised and reduced.

An example of disproportionation is the decomposition of hydrogen peroxide:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$





The oxygen in hydrogen peroxide (H_2O_2) has an oxidation state of −1.

The oxygen in water has an oxidation state of −2

The oxygen in elemental oxygen (O_2) has an oxidation state of zero.

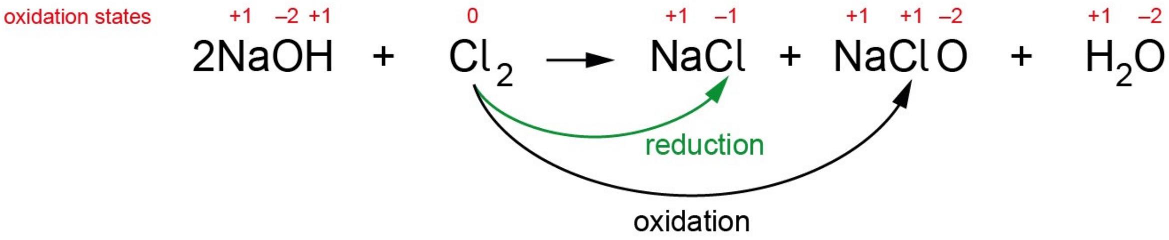
Hence two of the four oxygen atoms in $2H_2O_2$ have had their oxidation state decreased from -1 to -2 in $2H_2O$. This is reduction. The other two oxygen atoms in $2H_2O_2$ have had their oxidation state increased from −1 to 0 in O_2. This is oxidation.

So, the oxygen in hydrogen peroxide has been simultaneously oxidised and reduced. In other words, it has undergone disproportionation.

Further examples of disproportionation

1) The reaction of chlorine with a cold dilute sodium hydroxide solution.

$$2NaOH + Cl_2 \rightarrow NaCl + NaClO + H_2O$$



The oxidation state of the chlorine atoms in Cl_2 is zero, because the chlorine is in its elemental state.

The oxidation state of the chlorine in sodium chloride is −1. The oxidation state of the Na is +1, and hence to give a sum of the oxidation states equal to zero, the Cl must have an oxidation state of −1.

The oxidation state of the Cl in NaClO is +1. The oxidation state of the Na is +1 and that of the O is −2, and hence to give a sum of all the oxidation states equal to zero, the Cl must have an oxidation state of +1.

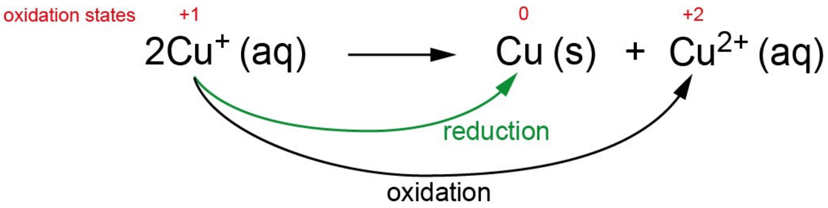
One chlorine atom from Cl_2 has reduced its oxidation state from 0 to −1 in NaCl. This is reduction.

The other chlorine atom in Cl_2 has increased its oxidation state from 0 to +1 in NaClO. This is oxidation.

The chlorine (Cl_2) has therefore been simultaneously oxidised and reduced − it has undergone disproportionation.

2) The disproportionation of Cu^+ ions in aqueous solution.

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



The oxidation states of Cu^+ and Cu^{2+} are +1 and +2, respectively, because the oxidation state of an ion is equal to the charge on the ion.

The oxidation state of elemental copper (Cu) is zero.

One Cu^+ ion has reduced its oxidation state from +1 to 0 (in Cu). This is reduction.

The other Cu^+ ion has increased its oxidation state from +1 to +2 (in Cu^{2+}). This is oxidation.

The Cu^+ ions have therefore undergone simultaneous oxidation and reduction − it has undergone disproportionation.

Exercise 56

By considering oxidation states, interpret the following reaction in terms of oxidation and reduction.

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

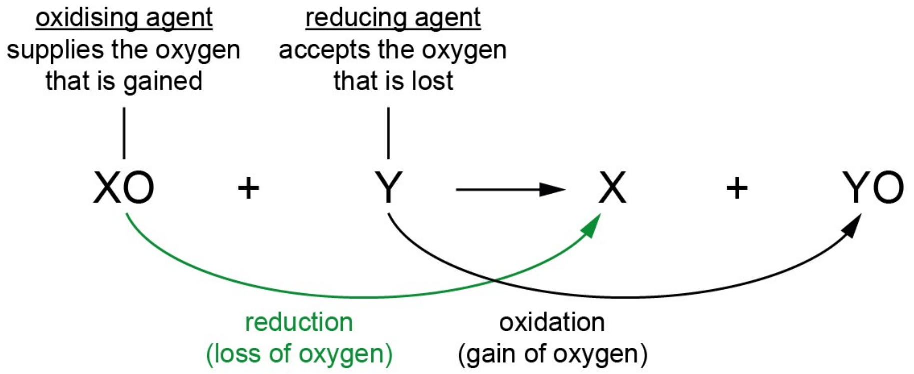
Exercise 57

Show that the reaction between chlorine and a hot aqueous solution of sodium hydroxide is a disproportionation reaction.

$$3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

C5.6 Understand the terms *oxidising agent* and *reducing agent*, and be able to identify them in reactions.

In terms of loss/gain of oxygen:



- Oxidising agents give oxygen to another substance.
- Reducing agents remove oxygen from another substance.

For example, consider the reaction between iron(III) oxide and carbon monoxide.

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

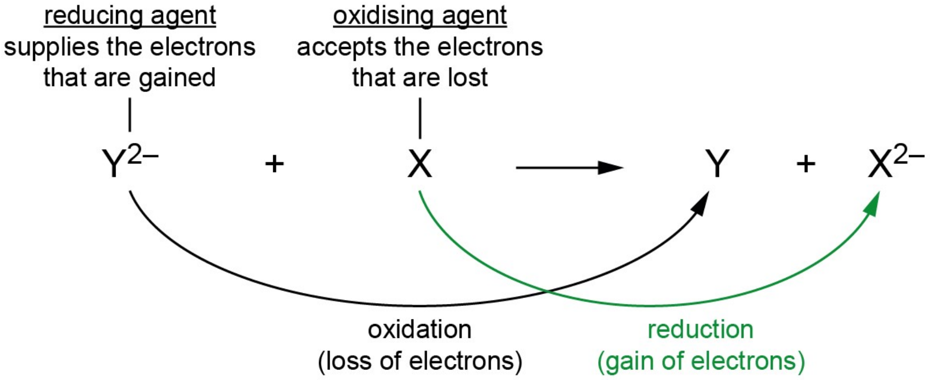
The iron(III) oxide has been reduced (lost oxygen) to iron.

The carbon monoxide has been oxidised (gained oxygen) to carbon dioxide.

The oxidising agent is the substance that supplies the oxygen that is gained: in this case that is the iron(III) oxide.

The reducing agent is the substance that accepts that oxygen, i.e. ‘removes’ the oxygen: in this case that is the carbon monoxide.

In terms of loss/gain of electrons:



An oxidising agent oxidises something else. Oxidation is a loss of electrons, so the oxidising agent must take the electrons that are being lost. Hence the oxidising agent gains electrons and is itself reduced.

A reducing agent reduces something else. Reduction is a gain of electrons, so the reducing agent must supply the electrons that are being gained. Hence the reducing agent loses electrons and is itself oxidised.

For example, consider the reaction between zinc and aqueous copper(II) ions.

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Zn atoms have been oxidised (lost electrons) to form Zn^{2+} ions.

Cu^{2+} ions have been reduced (gained electrons) to form Cu atoms.

The oxidising agent is the substance that has gained the electrons: in this case that is the Cu^{2+} ions.

The reducing agent is the substance that has lost the electrons: in this case that is the Zn atoms.

Identify the oxidising agent and reducing agent in the following redox reaction:

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

The first thing to do is to work out what has been oxidised and what has been reduced.

The two I^- ions have been oxidised: they have lost one electron each to form an I_2 molecule, or alternatively they have increased their oxidation state (from −1 to 0).

The Cl_2 molecule has been reduced: it has gained two electrons to form two Cl^- ions, or alternatively it has decreased its oxidation state (from 0 to −1).

Having established what has been oxidised and what has been reduced, the oxidising agent and the reducing agent can now be identified.

The oxidising agent is the species that is reduced: in this case the oxidising agent is therefore the Cl_2 molecule.

The reducing agent is the species that is oxidised: in this case the reducing agent is therefore the I^- ions.

Exercise 58

Identify the oxidising agent and the reducing agent in the following redox reaction:

$$Mg + 2H^+ \rightarrow Mg^{2+} + H_2$$

Exercise 59

Group 2 elements in their reactions tend to form positive ions. Group 17 elements in their reactions tend to form negative ions.

a) Elements from which of these two groups will make the better oxidising agents?

b) Elements from which of these two groups will make the better reducing agents?

Solutions to Exercises 52 to 59

Exercise 52

$FeCl_2$ comprises Fe^{2+} and Cl^- ions. $FeCl_3$ comprises Fe^{3+} and Cl^- ions.

The Fe^{2+} ions are losing an electron each to form the Fe^{3+} ions. Hence the Fe^{2+} ions are being oxidised.

$$2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$$

The Cl_2 is gaining two electrons to form two Cl^- ions. Hence the Cl_2 is being reduced.

Exercise 53

1) The Cu^{2+} ions are gaining electrons to form Cu atoms (reduction), and the Zn atoms are losing electrons to form Zn^{2+} ions (oxidation). Hence this is a redox reaction.

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad \text{and} \qquad Zn \rightarrow Zn^{2+} + 2e^-$$

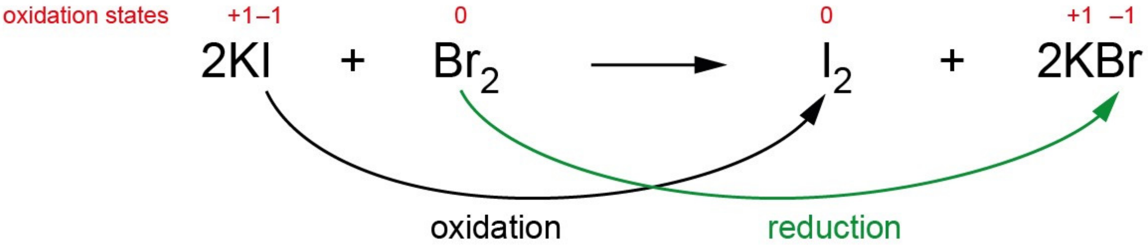
2) The OH^- ions are losing electrons (oxidation). Nothing in the equation is gaining the electrons, and so this is an oxidation only equation.

3) The H^+ ions are gaining electrons (reduction). This is a reduction only equation.

4) PbI_2 is an ionic compound comprising of Pb^{2+} ions and I^- ions. Nothing has lost or gained electrons, and hence this reaction involves no oxidation/reduction.

The correct answer is therefore 2) $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

Exercise 54



The Br_2 and the I_2 have oxidation states of zero because they are in their elemental states.

The oxidation state of K in KI is +1, and hence the oxidation state of I in KI must be −1, in order to make the sum of the oxidation states in the compound equal to zero. Similarly, the oxidation state of Br in KBr must also be −1.

The oxidation state of the iodine has increased from −1 in KI to 0 in I_2. This is oxidation.

The oxidation state of the bromine has decreased from 0 in Br_2 to −1 in KBr. This is reduction.

Hence, the iodide ions (in KI) have been oxidised and the bromine (Br_2) has been reduced.

Exercise 55

NO: the oxidation state of O is −2, and hence the oxidation state of the N must be +2 in order that the sum of the oxidation states equals zero.

NO_2: the oxidation state of each oxygen atom is −2, and hence the oxidation state of the N must be +4 in order that the sum of the oxidation states equals zero.

N_2O: the oxidation state of the oxygen atom is −2, and hence the oxidation state of each N must be +1 in order that the sum of the oxidation states equals zero.

NH_3: the oxidation state of each of the hydrogen atoms is +1, and hence the oxidation state of the N must be −3 in order that the sum of the oxidation states equals zero.

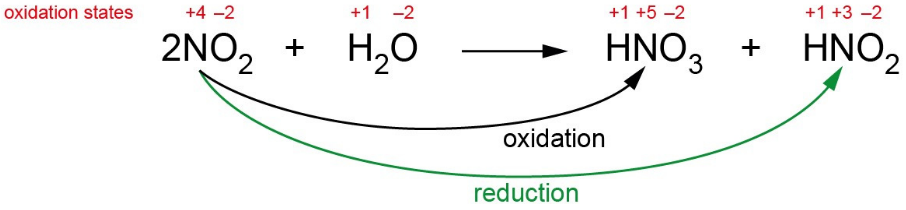
HNO_2: the oxidation state of the hydrogen is +1, and the oxidation state of each of the oxygens is −2. The oxidation state of the N must be +3 in order that the sum of the oxidation states equals zero.

NO_3^-: the oxidation state of each of the oxygen atoms is −2, and hence the oxidation state of the N must be +5 in order that the sum of the oxidation states is equal to the charge on the ion (−1).

Mg_3N_2: the oxidation state of the Group 2 metal Mg is +2, and hence the oxidation state of the N must be −3 $[-(+2 \times \frac{3}{2})]$ in order that the sum of the oxidation states of all the atoms equals zero.

Hence only NH_3 and Mg_3N_2 contain nitrogen in the same oxidation state (−3).

Exercise 56



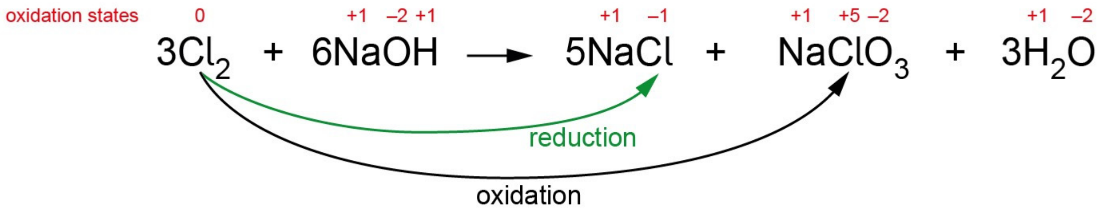
In NO_2, the two oxygens have oxidation states of −2, so in order to make the sum of the oxidation states of all the atoms in the compound equal to zero, the oxidation state of N must equal +4.

In HNO_3, the oxidation state of H is +1 and each oxygen atom has an oxidation state of −2. In order to make the sum of the oxidation states of all the atoms in the compound equal to zero, the oxidation state of the N must equal +5. By similar reasoning, the oxidation state of N in HNO_2 must equal +3.

One nitrogen atom in $2NO_2$ has had its oxidation state increased from +4 to +5 (in HNO_3). This is oxidation.

The other nitrogen atom in $2NO_2$ has had its oxidation state decreased from +4 to +3 (in HNO_2). This is reduction. The nitrogen in $2NO_2$ has been simultaneously oxidised and reduced − it has undergone disproportionation.

Exercise 57



The oxidation state of the elemental chlorine (Cl_2) is zero.

The oxidation state of the Cl in NaCl is −1. The oxidation state of the Na is +1, and so in order for the sum of the oxidation states of the Na and Cl to equal zero, the oxidation state of the Cl must be −1.

The oxidation state of the Cl in $NaClO_3$ is +5. The oxidation state of the Na is +1, and each of the oxygen atoms has an oxidation state of −2. So in order for the sum of the oxidation states of all the atoms in the compound to equal zero, the oxidation state of the Cl must be +5.

No other atom has had its oxidation state changed.

Five Cl atoms in $3Cl_2$ have had their oxidation states reduced from 0 to −1 (in 5NaCl). This is reduction.

The one remaining Cl atom in $3Cl_2$ has had its oxidation state increased from 0 to +5 (in $NaClO_3$). This is oxidation.

Hence this is a disproportionation reaction as the chlorine has been simultaneously oxidised and reduced.

Exercise 58

Identifying which species has been oxidised and which species has been reduced:

The Mg has been oxidised; it has lost electrons. It has increased its oxidation state from 0 to +2.

The two H^+ ions have been reduced; they have each gained an electron. They have decreased their oxidation state from +1 to 0.

Now identifying the oxidising agent and reducing agent:

The oxidising agent is reduced − in this case therefore the oxidising agent is the H^+ ions.

The reducing agent is oxidised − in this case therefore the reducing agent is the Mg.

Exercise 59

Group 2 elements form positive ions, by losing electrons. Losing electrons is oxidation. So when Group 2 elements react, they are being oxidised.

Group 17 elements form negative ions, by gaining electrons. Gaining electrons is reduction. So when Group 17 elements react, they are being reduced.

Oxidising agents are reduced when they oxidise another substance. Hence the better oxidising agents will be the Group 17 elements.

Reducing agents are oxidised when they reduce another substance. Hence the better reducing agents will be the Group 2 elements.

Photos: Science Photo Library

C6. Chemical bonding, structure and properties

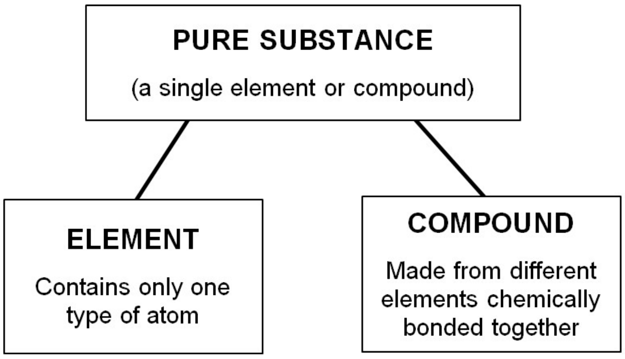
C6.1 Define and understand the differences between elements, compounds and mixtures.

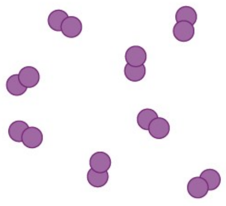
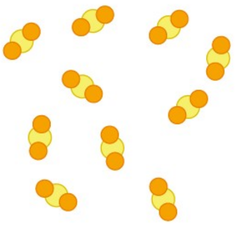
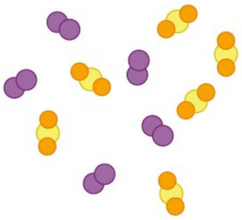
Pure substances contain a single element or compound.

An element is a substance made from only one type of atom. Elements cannot be decomposed into simpler substances by chemical means.

A compound is a substance made from different elements bonded together.

Mixtures (for example, air or tap water) contain more than one element or compound.



Particle diagram			
Pure or mixture?	Pure substance	Pure substance	Mixture
Individual substances	Element	Compound	Element + compound

Exercise 60

Is each of these substances an element or compound?

a) Br_2

b) CO

c) Co

d) Fe_2O_3

e) C_{60}

Exercise 61

Is each of these a pure substance or a mixture of substances?

a) spring water

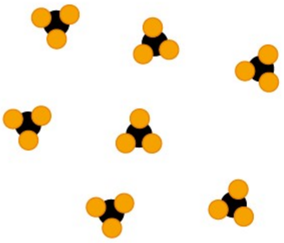
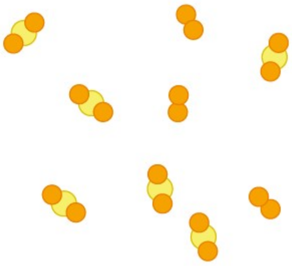
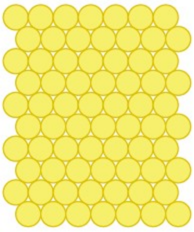
b) steel

c) oxygen

Exercise 62

For each diagram in the following table:

- state whether it is a pure substance or a mixture of substances
- identify whether the component(s) is/are elements or compounds

	i	ii	iii
Particle diagram			

C6.2 Understand that atoms often react to form compounds which have the electron configuration of a noble gas (Group 18). Understand that the type of bonding taking place depends on the atoms involved in the reaction.

The elements of Group 18 are called the noble gases. Each of these elements has a full outermost shell of electrons and include helium (2), neon (2,8) and argon (2,8,8).

When atoms react to form compounds, they transfer or share electrons and obtain their full outermost shell of electrons like one of the noble gases:

- Metal atoms often lose electrons
- Non-metal atoms often gain extra electrons

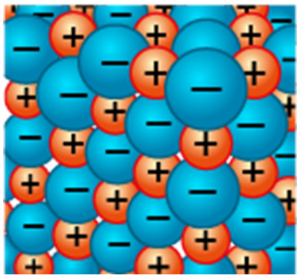
Metals + non-metals

When a metal reacts with a non-metal, there is usually a transfer of electrons. The metal atoms lose electrons and the non-metal atoms gain electrons. The ions formed have the full electron configuration of a noble gas.

When metals react with non-metals in this way, an ionic compound is formed which is made of a giant lattice of positive and negative ions. There is a strong overall electrostatic attraction between the positive and negative ions.

This is known as ionic bonding.

Ionic lattice



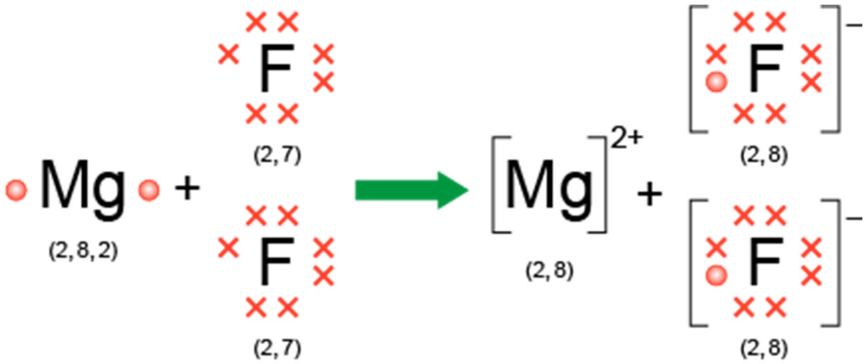
Example: sodium + chlorine

Sodium atoms react with chlorine atoms in the ratio 1:1 to form sodium chloride.

(only electrons involved in bonding are shown)

Example: magnesium + fluorine

Magnesium atoms react with fluorine atoms in the ratio 1:2 to form magnesium fluoride.



(only electrons involved in bonding are shown)

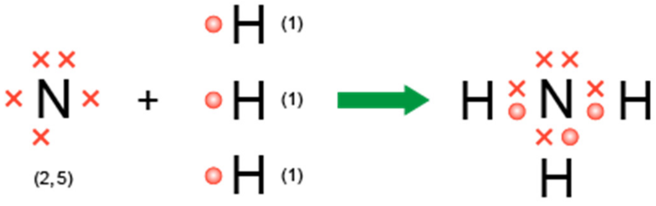
Non-metals + non-metals

When non-metals react with each other, they share electrons. When atoms share electrons they form molecules.

The two shared electrons that join the atoms together in the molecule are called a covalent bond. Covalent bonds are generally strong.

Example: nitrogen + hydrogen

One nitrogen atom shares electrons with three hydrogen atoms to form ammonia.



(only electrons involved in bonding are shown)

Exercise 63

In each of the following situations, does a reaction take place?

If a reaction does take place, are electrons shared or transferred and is an ionic or covalent compound formed?

a) sulfur + oxygen

b) copper + chlorine

C6.3 Ionic bonding:

a. Know that ions are formed by transfer of electrons from atoms of metals to atoms of non-metals, and that these ions (of opposite charge) attract to form ionic compounds.

b. Predict the charge of the most stable ions formed from elements in Groups 1, 2, 16 and 17 and aluminium by consideration of their electron configuration.

c. Know the chemical formulae of common compound ions, e.g. CO_3^{2-} and OH^-.

d. Know that when an element can exist in more than one oxidation state, e.g. Cu, Fe, then Roman numerals are used to denote the one present, e.g. iron(III) chloride for $FeCl_3$.

e. Determine the formulae of ionic compounds from their constituent ions.

f. Understand the general physical properties of ionic compounds, such as melting point and conductivity.

Formation of ionic compounds

When a metal reacts with a non-metal, there is usually the transfer of electrons. The metal atoms lose electrons and the non-metal atoms gain electrons. An ionic compound is formed which is made of a giant lattice of positive and negative ions.

Ion charges

When atoms react to form ions, they gain/lose electrons and obtain the electron configuration of a noble gas. Therefore, the charge of these ions depends on the electron configuration of the atoms. For example, atoms in Group 1 of the Periodic Table have one electron in their outer shell and so lose one electron forming 1+ ions.

The table summarises some of the ions formed by elements:

Group:	Group 1	Group 2	Group 13	Group 16	Group 17
Charge on ions:	1+	2+	3+	2–	1–
Examples:	Li^+ Na^+ K^+	Mg^{2+} Ca^{2+} Ba^{2+}	Al^{3+}	O^{2-} S^{2-}	F^- Cl^- Br^- I^-

Some metals can form ions with different charges. There is a Roman numeral in the names of their compounds so that the charge on the metal ion it contains can be identified. For example, iron(II) oxide contains Fe^{2+} ions and iron(III) oxide contains Fe^{3+} ions.

Combinations of atoms can also exist as overall charged ‘compound ions’.

There are some other common ions whose formulae and charges should learned:

- hydrogen H^+
- ammonium NH_4^+
- hydroxide OH^-
- nitrate NO_3^-
- sulfate SO_4^{2-}
- carbonate CO_3^{2-}
- phosphate PO_4^{3-}

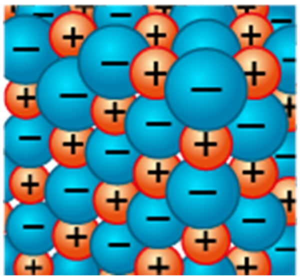
The total number of positive and negative charges in an ionic compound must balance out. This allows the formula of ionic compounds to be worked out.

name	**positive ions**	**negative ions**	**comments**	**formula**
iron(III) bromide	Fe^{3+}	Br^- Br^- Br^-	for every Fe^{3+} ion (3+ charge) there must be three Br^- ions (3− charge overall)	$FeBr_3$
calcium oxide	Ca^{2+}	O^{2-}	for every Ca^{2+} ion (2+ charge) there must be one O^{2-} ion (2– charge)	CaO
potassium sulfide	K^+ K^+	S^{2-}	for every two K^+ ions (2+ charge overall) there must be one S^{2-} ion (2– charge)	K_2S
aluminium oxide	Al^{3+} Al^{3+}	O^{2-} O^{2-} O^{2-}	for every two Al^{3+} ions (6+ charge overall) there must be three O^{2-} ions (6– charge overall)	Al_2O_3
sodium carbonate	Na^+ Na^+	CO_3^{2-}	for every two Na^+ ions (2+ charge overall) there must be one CO_3^{2-} ion (2– charge)	Na_2CO_3
magnesium hydroxide	Mg^{2+}	OH^- OH^-	for every Mg^{2+} ion (2+ charge) there must be two OH^- ions (2– charge overall)	$Mg(OH)_2$
ammonium sulfate	NH_4^+ NH_4^+	SO_4^{2-}	for every two NH_4^+ ions (2+ charge overall) there must be one SO_4^{2-} ion (2– charge)	$(NH_4)_2SO_4$

Properties of ionic compounds

Ionic compounds are generally solids at room temperature. They are made of a giant lattice of positive and negative ions. A lattice is a huge, continuous, regular structure.

There is a strong overall electrostatic attraction between all of the positive and negative ions. This means that ionic compounds have high melting points as it is difficult to overcome the many strong attractions between the positive and negative ions.



Ionic compounds generally do not conduct electricity as solids because the ions cannot move around freely. However, if a compound is melted, it does conduct electricity because the ions can move and carry the charge. Many ionic compounds dissolve in water and will conduct as a solution because the solvated ions can move to carry the charge.

Exercise 64

Which of these compounds are likely to have an ionic structure?

$NaBr$ C_6H_{12} H_2S PF_5 MgO $ZnSO_4$ C_2H_6S

Exercise 65

Give the formula of the following ionic compounds:

a) iron(II) oxide

b) potassium nitrate

c) magnesium fluoride

d) calcium hydroxide

e) aluminium sulfate

Exercise 66

Which of these substances have an ionic structure?

substance	melting point / °C	boiling point / °C	conductivity as solid	conductivity as liquid
A	85	132	insulator	insulator
B	772	1288	insulator	conductor
C	873	1056	conductor	conductor
D	–57	32	insulator	insulator
E	801	1465	insulator	conductor
F	3550	4830	insulator	insulator

C6.4 Covalent bonding:

a. Know that a covalent bond is formed when atoms share one (or more) pair(s) of electrons, generally between non-metals.

b. Understand that covalently bonded substances can be small molecules (e.g. water, ammonia, methane) or giant structures (e.g. diamond, graphite, silicon dioxide).

c. Understand the general physical properties of substances composed of small molecules or of those that exist as giant covalent structures.

Formation of covalent bonds

When non-metals react with each other, they each will gain extra electrons. They can do this by sharing electrons. The two shared electrons that join the atoms together are called a covalent bond.

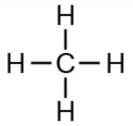
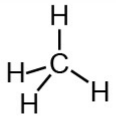
Molecular substances

Most substances that contain covalent bonds are made up of many molecules. Each molecule contains a specific number of atoms joined by covalent bonds.

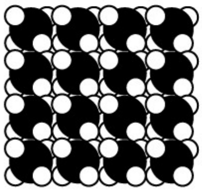
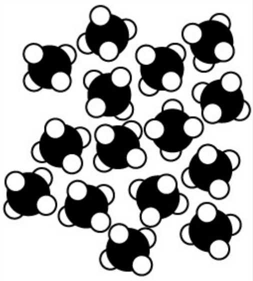
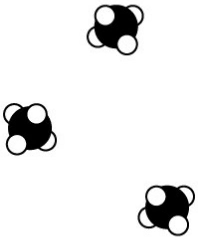
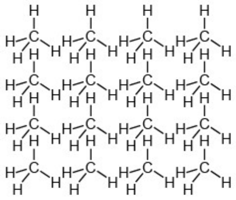
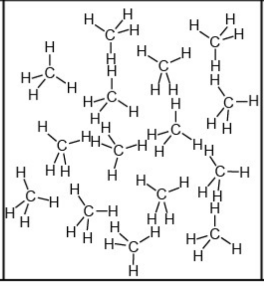
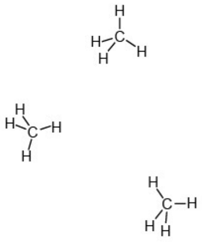
Methane (CH_4) is an example of a substance made of small molecules, with each molecule containing one carbon and four hydrogen atoms.

Glucose ($C_6H_{12}O_6$) is another example of a substance made of molecules, but larger ones containing six carbon, twelve hydrogen and six oxygen atoms.

Molecules can be drawn in different ways, as shown below for methane (CH_4):

2D stick diagram	3D stick diagram	space-filling diagram
		

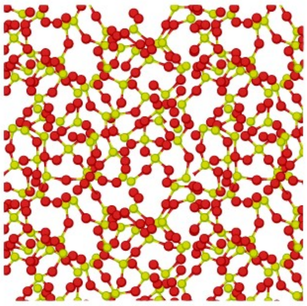
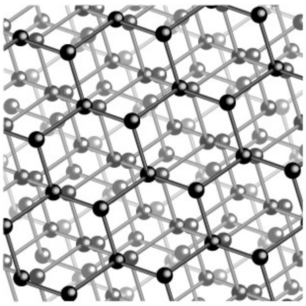
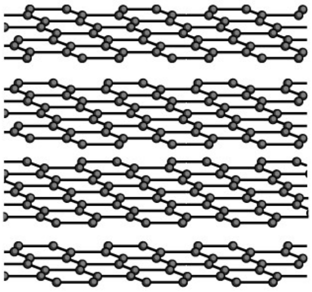
Within each molecule, the atoms are joined by covalent bonds. However, the molecules are not joined to each other. There are only weak attractive forces between molecules. This means that it is easy to overcome the weak forces between the molecules and so molecular substances usually have low melting and boiling points (see in section C15 about intermolecular forces).

state	solid	liquid	gas
space-filling diagrams			
stick diagrams			

Molecular substances do not conduct electricity because they do not contain any mobile ions or delocalised electrons that can carry the charge.

Giant covalent substances

Some covalent substances are made up of a single, giant lattice. Common examples are diamond (C), graphite (C) and silicon dioxide (SiO_2). The lattice is a continuous network of atoms linked by covalent bonds.

		
part of the lattice in silicon dioxide	part of the lattice in diamond	part of the lattice in graphite

Giant covalent substances have very high melting and boiling points because all of the strong covalent bonds have to be broken when they melt and boil.

Graphite conducts electricity because it contains some delocalised electrons that can move along the layers. However, most giant covalent substances do not conduct electricity because they do not contain any delocalised electrons.

Diamond and silicon dioxide are very hard due to the rigid network of atoms linked by covalent bonds. However, graphite is soft because the layers of covalently bonded atoms are not bonded to each other and so can slide over each other.

Exercise 67

The properties of some substances are shown in the table:

substance	**melting point / °C**	**boiling point / °C**	**conductivity as solid**	**conductivity as liquid**
A	–183	–161	insulator	insulator
B	3550	4830	insulator	insulator
C	842	1494	conductor	conductor
D	114	183	insulator	insulator
E	1414	3265	insulator	insulator
F	661	1304	insulator	conductor

a) Which of these substances are made up of small covalent molecules?

b) Which of these substances have giant covalent structures?

Exercise 68

Ethane (C_2H_6) is a molecular substance with a low boiling point.

Which of the following is a correct explanation of this?

A. The forces between the C and H atoms in the molecules are weak.
B. The bonds between the C and H atoms in the molecules are weak.
C. There are no double bonds in the molecules.
D. The forces between the molecules are weak.

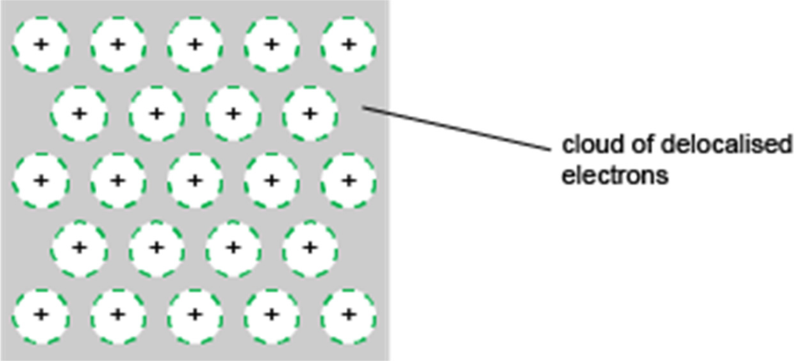
C6.5 Metallic bonding:

a. Understand that solid metals exist as a giant structure of positively charged ions surrounded by delocalised (free) electrons.

b. Understand the general physical properties of metals, such as melting point and conductivity.

Metallic bonding

In metals (as solids and liquids), the outer shell electrons are delocalised (free) and can move throughout the metal. This means that solid metals effectively consist of a lattice of positively charged ions surrounded by delocalised electrons.

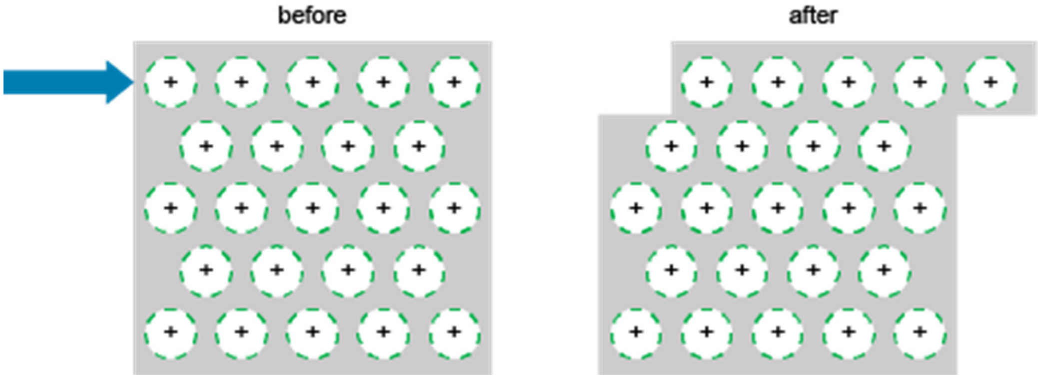


Properties of metals

Most metals have high melting points because the metallic bonding is strong. This is because there is a strong overall attraction between the positive metal ions and the negative delocalised electron cloud.

Metals conduct electricity because the outer shell electrons are delocalised and can carry charge through the metal.

Metals are malleable (can be hammered into shape) because the metal ions can move relative to each other while maintaining the metallic bonding.



Exercise 69

Which of the following substances have a metallic structure?

substance	melting point / °C	boiling point / °C	conductivity as solid	conductivity as liquid
A	747	1396	insulator	conductor
B	650	1091	conductor	conductor
C	–39	357	conductor	conductor
D	1414	3265	insulator	insulator
E	2572	2850	insulator	conductor
F	3422	5555	conductor	conductor

Exercise 70

Iron is a metal with a high melting point.

Which of the following is the best explanation of this?

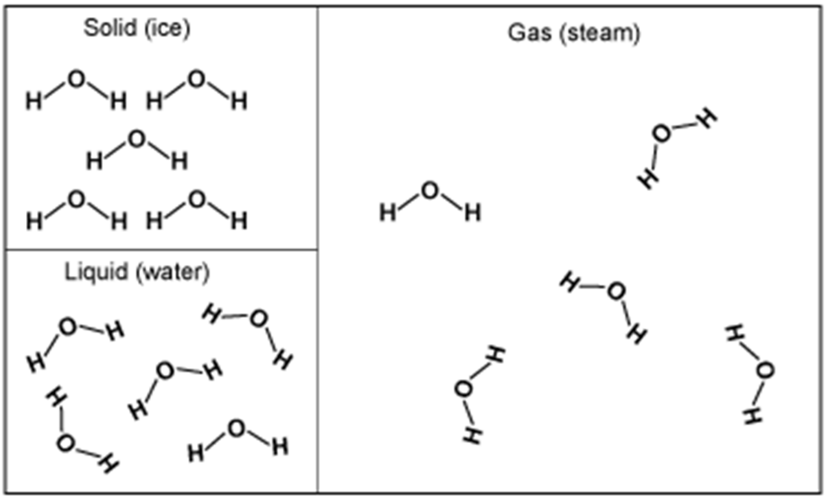
A. The forces between atoms are strong.
B. The forces between the metal ions are strong.
C. The covalent bonds between the atoms are strong.
D. The forces between the metal ions and delocalised electrons are strong.

C6.6 Understand that intermolecular forces can exist between molecules, and that these forces must be overcome in melting and boiling.

The atoms within molecules are joined by covalent bonds which are very strong. However, there are no bonds between molecules, just weak attractive forces called intermolecular forces.

When molecular substances melt or boil, it is the weak forces between molecules that are overcome. The covalent bonds within the molecules do not break.

For example, when ice melts to form water and water boils to form steam, the covalent bonds in the H_2O molecules do not break. If the covalent bonds did break, then it would no longer be H_2O when it melts or boils.



C6.7 Be able to relate structure and bonding to physical properties, such as melting point and conductivity.

Bonding:	**Ionic**	**Covalent**		**Metallic**
Structure type:	**Ionic**	**Molecular**	**Giant covalent**	**Metallic**
Description of structure:	Giant lattice of positive and negative ions. There is a strong electrostatic attraction between the positive and negative ions.	Many separate molecules. Each molecule contains two or more atoms joined by strong covalent bonds. There are only weak forces between molecules.	Giant lattice of atoms linked by strong covalent bonds.	Giant lattice of positive metal ions surrounded by delocalised outer shell electrons. There is a strong attraction between the positive metal ions and the negative delocalised electrons.
Melting and boiling points:	HIGH due to the strong attraction between the positive and negative ions.	LOW due to weak forces between molecules.	VERY HIGH as the strong covalent bonds need to be broken.	HIGH as the attraction between the positive metal ions and negative delocalised electrons is strong.
Conductivity:	Not a conductor as solid (ions cannot move). Conductor when molten or dissolved (as ions can move to carry charge).	Not a conductor (does not contain any mobile ions or delocalised electrons).	Not a conductor (does not contain any mobile ions or delocalised electrons) except for graphite (which contains delocalised electrons).	Conductor (as delocalised electrons can move to carry charge).

Exercise 71

The properties of some substances are shown in the table.

substance	melting point / °C	boiling point / °C	conductivity as solid	conductivity as liquid
A	711	1250	insulator	conductor
B	3550	4830	insulator	insulator
C	–57	125	insulator	insulator
D	44	281	insulator	insulator
E	1085	2562	conductor	conductor
F	2072	2977	insulator	conductor

a) Which of these substances are made of covalent molecules?

b) Which of these substances have giant covalent structures?

c) Which of these substances have a metallic structure?

d) Which of these substances have an ionic structure?

Solutions to Exercises 60 to 71

Exercise 60

a) bromine molecule - element
b) carbon monoxide - compound
c) cobalt - element
d) iron(III) oxide - compound
e) buckminsterfullerene (carbon allotrope) - element

Exercise 61

a) mixture (of water and dissolved salts)

b) mixture (of iron and carbon)

c) pure

Exercise 62

i) pure, compound

ii) mixture, element + compound

iii) pure, element

Exercise 63

a) There is a reaction. Electrons are shared. Covalent compound formed.

b) There is a reaction. Electrons are transferred. Ionic compound formed.

Exercise 64

$NaBr$, MgO, $ZnSO_4$

Exercise 65

a) FeO
b) KNO_3
c) MgF_2
d) $Ca(OH)_2$
e) $Al_2(SO_4)_3$

Exercise 66

The answer is B and E

Exercise 67

a) The answer is substances A and D.

b) The answer is substances B and E.

Exercise 68

The answer is option D.

Exercise 69

The answer is substances B, C and F.

Exercise 70

The answer is option D.

Exercise 71

a) substances C and D

b) substance B

c) substance E

d) substances A and F

C7. Group chemistry

C7.1 Know the physical and chemical properties of the alkali metals (Group 1), the halogens (Group 17) and the noble gases (Group 18).

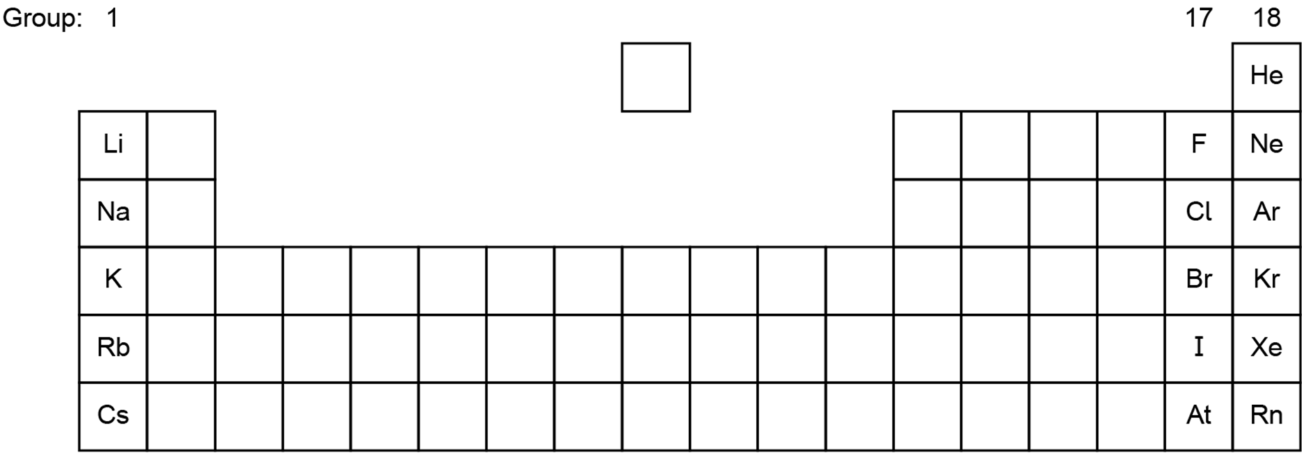
C7.2 Describe the trends in chemical reactivity and physical properties of the alkali metals (Group 1) and make predictions based on those trends. This includes knowledge of the relative positions of lithium, sodium and potassium in Group 1.

C7.3 The halogens (Group 17):

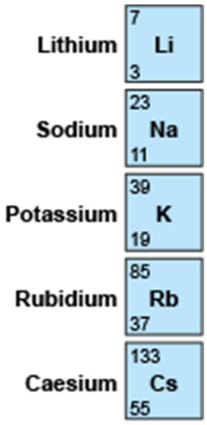
a. Describe the trends in chemical reactivity and physical properties of the halogens and make predictions based on those trends. This includes knowledge of the relative positions of fluorine, chlorine, bromine and iodine in Group 17.

b. Explain what is meant by a displacement reaction, in terms of reactivity competition, between halogens and halide ions.

Groups 1, 17 and 18



Group 1 – the alkali metals



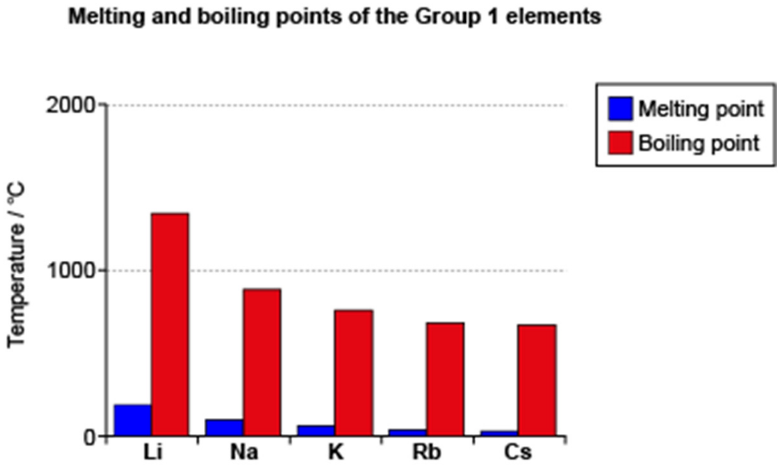
Physical properties of Group 1

The alkali metals are shiny metallic solids at room temperature.

- Melting and boiling points – are low for metals and decrease down the group.
- Densities – are low for metals and generally increase down the group.
- Hardness – they are soft and they become softer down the group.
- Conductivity – they are good conductors of heat and electricity.

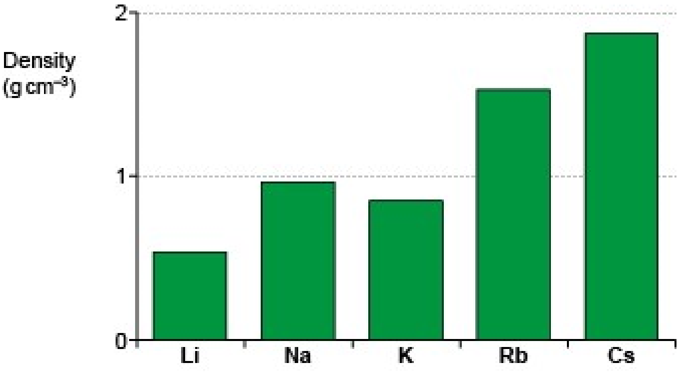
Melting and boiling points decrease as the group is descended due to a decrease in the strength of metallic bonding.

Melting and boiling points of Group 1 elements



Each element in the group has the same number of electrons available for delocalisation, one per atom. As the group is descended, the distance of the delocalised electrons to the 1+ ion core within the metallic solid will increase as the ions get larger, causing a decrease in the metallic bond strength.

Densities of the Group 1 elements



The densities of Group 1 elements generally increase down the group due to the increasing masses of the individual ion cores within the metallic solids as the group is descended.

The Group 1 elements become softer and easier to cut with a knife as the group is descended due to the decreasing strength of metallic bonding within the solid structures.

Chemical properties of Group 1

As the alkali metals all have one electron in their outermost shell, they react by losing that electron, forming 1+ ions.

- The alkali metals are very reactive. The elements have to be stored in oil to prevent them from reacting with oxygen and water in the air.
- When freshly cut and exposed to the air, the shiny metals will quickly react with oxygen and tarnish, forming the metal oxide.
- The alkali metals react with non-metals to form ionic compounds.
- As Group 1 is descended, the elements become more reactive.

Reaction with water:

- When lithium, sodium or potassium are added to cold water, they visibly react.
- Lithium, sodium and potassium float on water, moving around on the surface and fizzing.
- Hydrogen gas is produced, which burns with a ‘squeaky pop’ sound when ignited.
- Potassium reacts so exothermically that the hydrogen produced spontaneously ignites and burns with a lilac flame, characteristic of potassium ions.
- A soluble metal hydroxide is also formed, so the resultant solution will be alkaline and have a high pH, which would turn universal indicator blue or purple.

The reaction equation for all alkali metals with water will be similar. For example, sodium with water:

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

Sodium reacting with water

Reaction with oxygen:

In combustion reactions or when tarnishing due to oxygen in the air, the reaction equation to form the simple oxides will be similar, for example, lithium and oxygen:

$$2Li(s) + O_2(g) \rightarrow Li_2O(s)$$

Reaction with chlorine:

The alkali metals react vigorously with non-metals such as chlorine gas, producing metal chlorides. For example, potassium and chlorine:

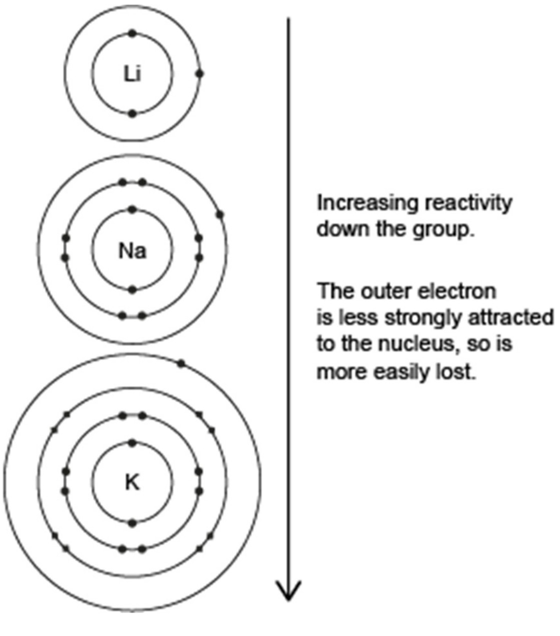
$$2K(s) + Cl_2(g) \rightarrow 2KCl(s)$$

The alkali metals react with other halogens in a similar way to produce metal halide salts.

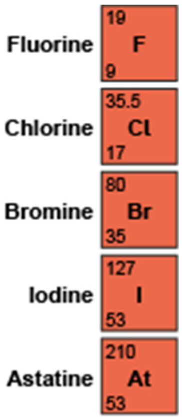
The trend of increasing reactivity as Group 1 is descended is consistent for all reactions.

As the group is descended, the alkali metals become more reactive due to less energy being required to remove an electron from the atoms of the elements.

- The atomic radii increase as the group is descended.
- The outermost electron is an increased distance from the nucleus.
- The attraction between the outermost electron and the nucleus decreases as the group is descended.
- This is despite there being an increase in nuclear charge.



Group 17 – the halogens



Physical properties of Group 17 (F to I)

The halogens are all non-metals with coloured vapours, having properties typical of non-metals:

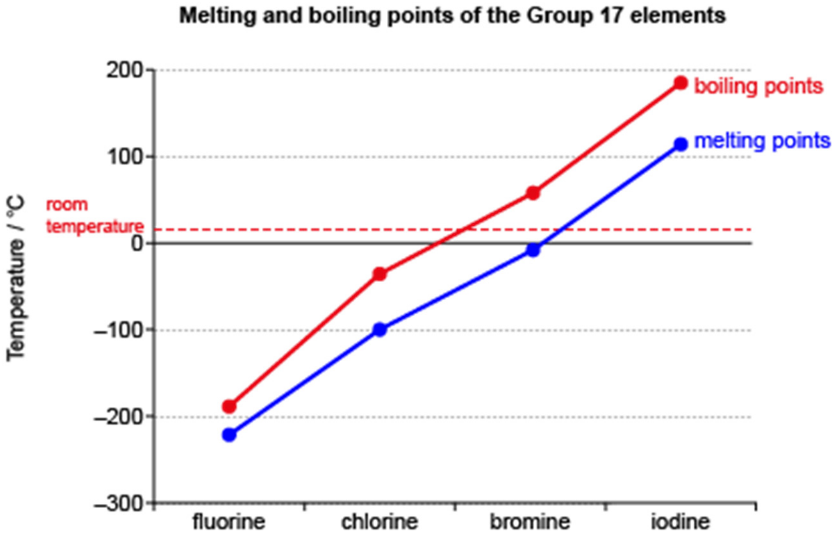
- Low melting and boiling points, which increase down the group.
- Poor conductors of heat and electricity.

The halogens exist as diatomic molecules (two atoms per molecule).

halogen	**formula**	**description** (at room temperature and pressure)	**melting point / °C**	**boiling point / °C**
fluorine	F_2	pale yellow gas	−220	−188
chlorine	Cl_2	yellow-green gas	−101	−35
bromine	Br_2	red-brown volatile liquid with orange vapour	−7	59
iodine	I_2	grey shiny solid, gives a purple vapour on heating	114	184

Melting and boiling points increase as the group is descended due to an increase in the strength of intermolecular forces between the molecules.

Melting and boiling points of Group 17 elements



As the halogen molecules get larger down the group, with increasing numbers of electrons within the molecules, the strength of their intermolecular forces increases.

This means that a greater amount of energy is required to break the intermolecular forces and change state. Hence the melting and boiling points increase down Group 17.

Chemical properties of Group 17

The halogen atoms all have seven electrons in their outermost shell and so can gain one more electron leading to a full shell. They can react with metals to form ionic compounds, gaining one electron to form 1− ions, or with non-metals by sharing a pair of electrons and forming one covalent bond per atom, forming covalent compounds.

The reactivity of the halogens decreases as the group is descended.

Reaction with alkali metals:

The halogens react vigorously with heated alkali metals to form metal halide salts. For example, the reaction between potassium and bromine:

$$2K(s) + Br_2(g) \rightarrow 2KBr(s)$$

Displacement reactions between halogens:

A more reactive halogen will displace a less reactive halogen from solutions of its salts.

This reactivity provides evidence for the trend in reactivity, which decreases down the group.

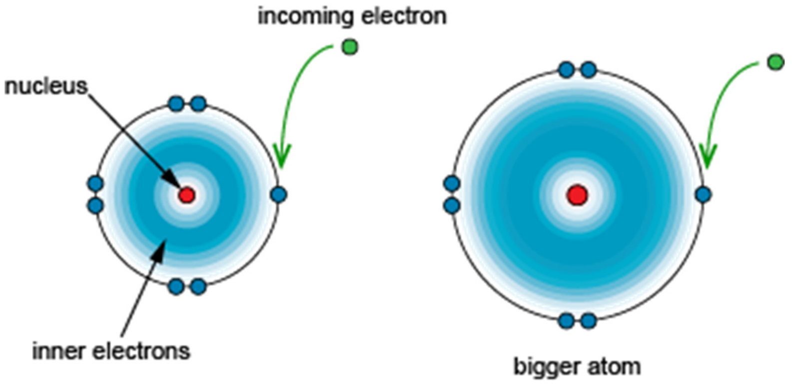
For example, chlorine can displace bromine or iodine from aqueous solutions of their salts (bromides or iodides); bromine will displace iodine from solutions of iodides.

	potassium **chloride** solution: $KCl(aq)$ colourless solution	potassium **bromide** solution: $KBr(aq)$ colourless solution	potassium **iodide** solution: $KI(aq)$ colourless solution
chlorine water colourless solution	no observable reaction -	orange solution of Br_2 formed $Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$	brown solution of I_2 formed $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$
bromine water orange solution	no observable reaction -	no observable reaction -	brown solution of I_2 formed $Br_2 + 2I^- \rightarrow 2Br^- + I_2$
iodine solution brown solution	no observable reaction -	no observable reaction -	no observable reaction -

The results of these displacement reactions confirm that:

- Chlorine is more reactive than bromine or iodine. Chlorine can remove an electron from (oxidise) a bromide or iodide ion.
- Bromine is more reactive than iodine. Bromine can remove an electron from (oxidise) an iodide ion.

When the halogens react, their atoms gain an electron. They get less reactive down the group because as the group is descended the atoms get larger, meaning that the incoming electron joins a shell that is at a greater distance from the nucleus. This new electron does not feel as strong a force of attraction to the nucleus despite nuclear charge increasing down the group.



The net effect is that the larger the halogen atom, the less energy is released on gaining an electron compared to the energy put in to remove it from its previous location.

Group 18 – the noble gases

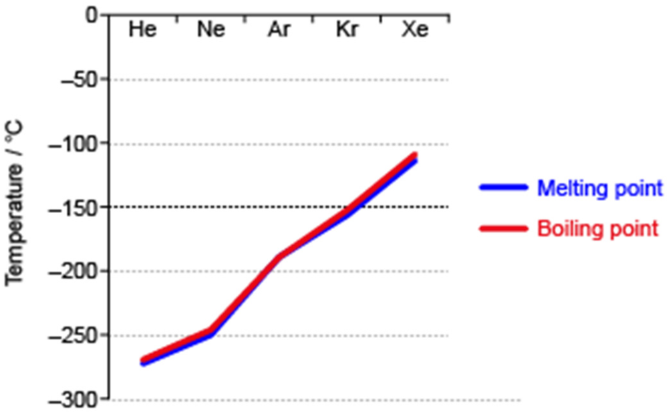
Physical properties of Group 18

The noble gases are all colourless gases at room temperature and pressure and have physical properties typical of gaseous non-metals.

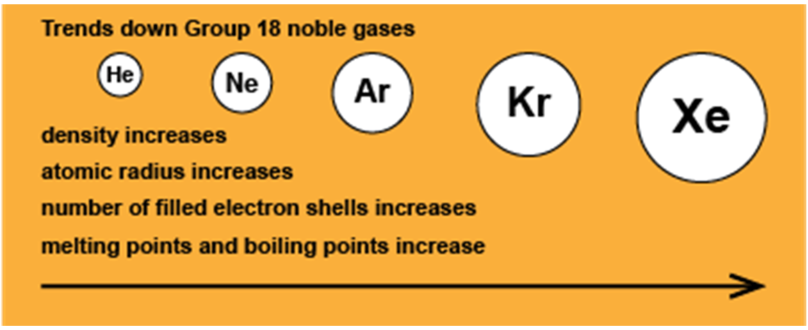
- Very low melting and boiling points, which increase down the group.
- The densities of the noble gases increase down the group.

Melting and boiling points increase as Group 18 is descended due to the size of the "intermolecular" forces that exist between its atoms. The size of the noble gas atoms, and the numbers of electrons present in the atoms, increase down the group, leading to stronger forces between the atoms in the solid or liquid phase. These forces require more energy to be overcome and so the melting/boiling points increase.

Melting and boiling points of Group 18



The densities of the gases also increase down the group due to the increasing mass of the atoms.



Chemical properties of Group 18

The noble gases have a complete outer shell of electrons, making the atoms very unreactive.

This electron configuration also explains why the elements exist as single atoms (monatomic).

The inert nature of the noble gases gives them a variety of uses such as providing an inert atmosphere in old fashioned electric filament lamps, food packaging and 3D printing.

Some compounds of noble gases towards the bottom of the group have been manufactured, such as XeF_4, XeO_2 and KrF_2, but only with the most reactive of the non-metal elements.

Exercise 72

Write balanced equations for the reactions of rubidium with:

a) water

b) oxygen

c) chlorine

Exercise 73

For the Group 17 elements (the halogens), state the trend going down the group in:

a) boiling points

b) reactivity

Exercise 74

Sodium chloride solution is tested in three separate test tubes: one with chlorine water, one with bromine water and one with a solution of iodine.

In which test tubes, if any, would there be evidence that a reaction takes place?

Solutions to Exercises 72 to 74

Exercise 72

General equations:

a) metal + water → metal hydroxide + hydrogen

b) metal + oxygen → metal oxide

c) metal + chlorine → metal chloride.

Simple ionic compounds of alkali metals contain a 1+ ion. The formulae of the compounds are determined and equations are then balanced.

a) $2Rb(s) + 2H_2O(l) \rightarrow 2RbOH(aq) + H_2(g)$

b) $4Rb(s) + O_2(g) \rightarrow 2Rb_2O(s)$

c) $2Rb(s) + Cl_2(g) \rightarrow 2RbCl(s)$

Exercise 73

As the group is descended, the size of the diatomic molecules increases, as does the number of electrons present in these molecules. This causes the intermolecular forces to increase, meaning more energy is required to break them, which is necessary to change the state from liquid to gas. Hence, there is an increase in boiling points as the group is descended.

The halogens react by gaining an electron. As the group is descended the size of the atoms increase, so an incoming electron joins an electron shell at a distance further from the nucleus. Hence, more energy is released when an electron joins a smaller halogen atom. As the group is descended, the reactivity of the halogens decreases.

Exercise 74

A more reactive halogen will displace a less reactive halogen from a solution of its salts.

As the salt is sodium chloride, a salt of chlorine, there will be no reaction with chlorine, bromine or iodine as none of these halogens are more reactive than chlorine.

There would be no evidence of a chemical reaction in any of the three test tubes.

Photos: Science Photo Library

C8. Separation techniques

C8.1 Know that chemical processes are required to displace constituent elements from their compounds.

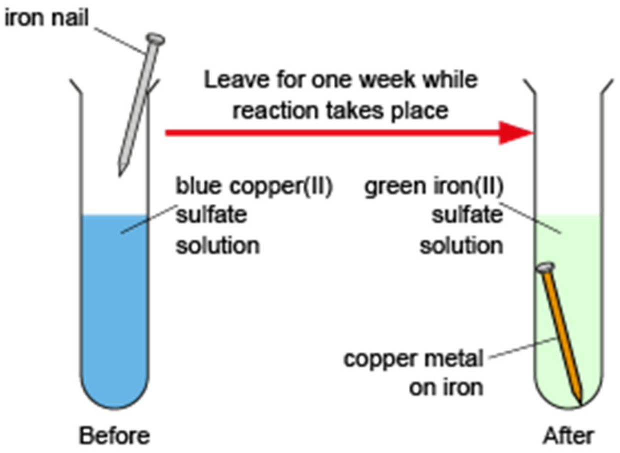
Very few substances can be found in a pure form in nature. To obtain a pure substance, one or more separation techniques need to be used. These techniques involve either chemical or physical processes.

Chemical processes are often used to extract individual elements from their compounds. In chemical processes, a chemical reaction occurs.

Displacement

The displacement reaction or redox reaction can be used to extract an element from a compound. An example is the reaction between magnesium and copper(II) sulfate solution. In this reaction, the more reactive magnesium acts as a reducing agent. The dissolved copper(II) ions are reduced to solid copper metal. The magnesium is oxidised to Mg^{2+} and the ions dissolve into solution. The solid copper metal can then be removed from the mixture by filtration.

If an iron nail is added to copper(II) sulfate solution, a displacement reaction will happen and the nail will become coated in a layer of copper metal.



Electrolysis

Electrolysis is the breakdown of an ionic compound using electricity. For electrolysis to occur, the ions need to be mobile. This can be done either by dissolving the ionic compound in water or by melting it. The mixture containing mobile ions is called the electrolyte. A direct current is then applied through the electrolyte using two electrodes.

Positive ions are attracted to the negative electrode (the cathode) and negative ions are attracted to the positive electrode (the anode).

Reduction occurs at the cathode and oxidation occurs at the anode.

Electrolysis of molten binary ionic compounds

In molten electrolytes, the cation and the anion of the compound are discharged. For example, sodium chloride will produce sodium at the cathode and chlorine at the anode. Sodium and chlorine are reactive elements and so inert, unreactive electrodes (such as platinum) are used.

Exercise 75

Which of the following could *not* precipitate silver ions from a solution of silver nitrate:
$HCl(aq)$, $NaNO_3(aq)$, $NaOH(aq)$?

C8.2 Know that physical processes are required to separate mixtures, including miscible/immiscible liquids and dissolved/insoluble solids.

C8.3 Know when to apply the following separation techniques: simple/fractional distillation, paper chromatography (including use of R_f values), use of a separating funnel, centrifugation, dissolving, filtration, evaporation and crystallisation.

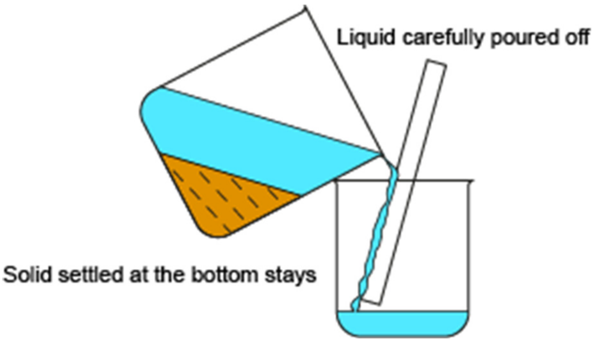
C8.4 Know how to establish the purity of a substance using chromatography.

Physical processes

Physical processes are used when separating individual elements or compounds from a mixture. All of the techniques rely on there being a difference in a physical property between the substances being separated. These properties could include differences in solubility, melting/boiling points, particle size or mass.

Decanting

Decanting is a quick and simple way to separate a solid and a liquid or solution. If the mixture is left, the solid will settle to the bottom of the container. All that is required is a steady hand to carefully pour the liquid or solution away without disturbing the solid.



Filtration

Filtration is used to separate a liquid (or solution) from an insoluble solid. The solid particles are larger and are trapped by the mesh of the filter paper. The smaller liquid particles are able to pass through the filter paper into the collection vessel. This separated liquid is known as the filtrate and the solid is the residue.

Using a separating funnel

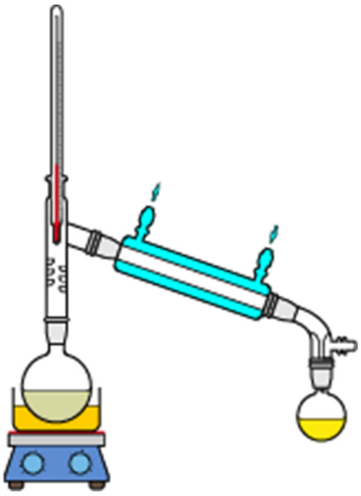
A separating funnel is used to separate two immiscible liquids. When two immiscible liquids are added to a separating funnel, they form two layers. The upper layer has the lower density. When the tap is opened, the lower layer can be poured out. The narrowing walls of the separating funnel make it easier to close the tap the moment the last drop of the lower layer has passed through.

Distillation

Distillation (sometimes called simple distillation) is used to separate two substances with differing boiling points.

Simple distillation is typically used to separate the solvent from a solution, leaving the solute behind.

The mixture is heated to above the boiling point of the solvent. The solvent becomes a vapour and starts to spread out through the apparatus. As the vapour hits the condenser it cools and condenses as droplets which run down the condenser to the collection vessel. The higher boiling point solute remains in the heated flask. If the solute is stable to heating, it can also be collected once the solvent has been removed.



The condenser used is often an active cooling Liebig condenser. Cold water is passed through the condenser in an outer jacket which maintains a cooling atmosphere for the vapours to pass through. When water is flowed through this jacket, it is always added at the bottom to ensure that there is always cold water in the jacket and that condensation occurs all the way along the condenser.

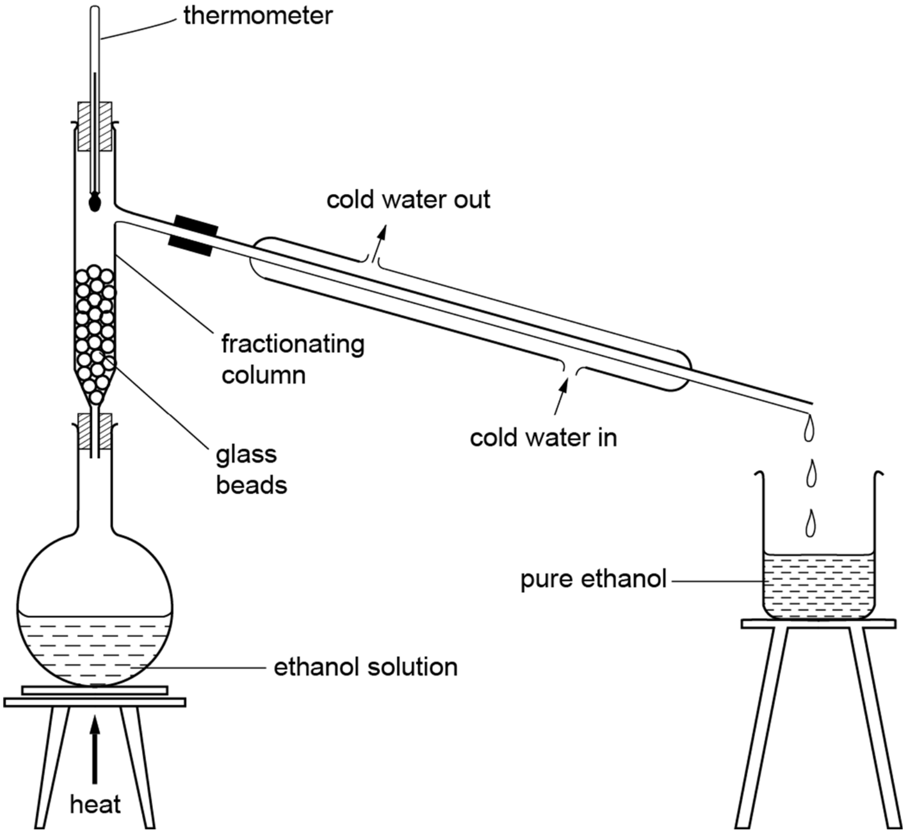
Fractional distillation

Fractional distillation is used to separate miscible liquids (ones soluble in each other) from a mixture. Like simple distillation, fractional distillation requires each liquid to have a different boiling point. In the separation of larger mixtures such as the hydrocarbons in crude oil, the separation can be into groups of compounds with similar boiling points, or it can be used to separate individual components.

During the distillation, the mixture is heated. When the temperature of the mixture reaches the boiling point of the component with the lowest boiling point, the temperature no longer rises and the first component boils. This lowest boiling point component rises up the fractionating column towards the condenser where it is condensed and collected. The thermometer at the entrance to the condenser monitors the boiling point of the component being distilled.

Once the first component has boiled away, the remaining mixture then rises in temperature until the boiling point of the next lowest component is reached. This then boils away to be condensed and collected.

When separating the two liquids, a thermometer is used to monitor the temperature of the vapour that is being condensed.



When separating liquids, the fractionating column provides a surface for condensing. The higher boiling point liquid is more likely to condense on the glass beads in the column. As the vapours rise, there is continual evaporation and condensing on the glass beads, with the higher boiling point substance condensing and falling back to the mixture all the way up the condenser leaving only the lower boiling point substance to escape to the condenser. The separation of the two liquids therefore occurs all the way up the fractionating column.

Evaporation and crystallisation

This technique is also used to separate the solvent from a solute and uses the difference in boiling point and/or volatility to separate the mixture. In this separation method, it is the solute rather than the solvent that is wanted and so a condenser is not used to collect the solvent as it evaporates or boils away.

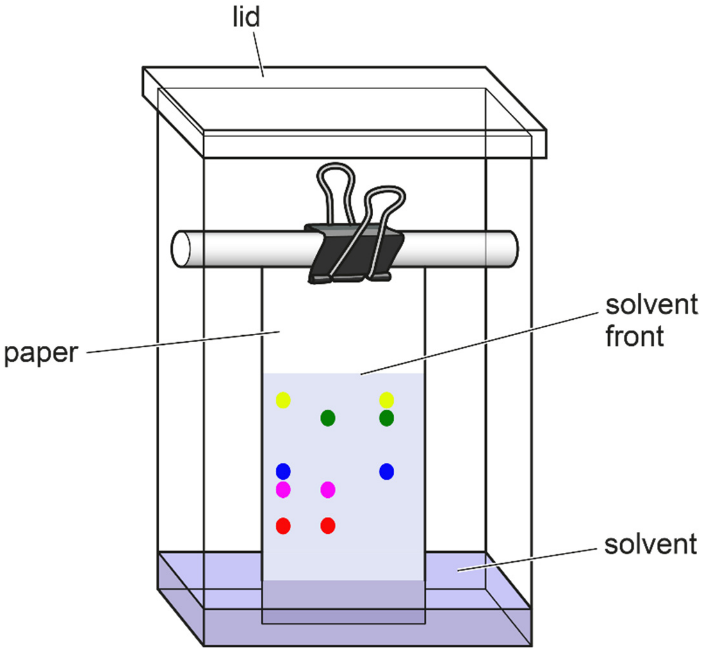
To separate the solute, the solution is heated gently until crystals just begin to appear. This is the crystallising point. The remaining concentrated solution is then left to evaporate. It’s not sensible to heat to dryness because some solids may decompose if heated too strongly.

Chromatography

Chromatography is used to separate mixtures of different solutes, such as dyes in ink, or it can be used to separate mixtures of different liquids.

In chromatography, differences in the relative affinity to the stationary phase of the chromatogram to the mobile phase (the solvent) lead to the separation of the substances.

In paper chromatography, a small sample of the mixture is spotted on to a piece of chromatography paper. This paper is then placed into a tank or beaker which contains a solvent at the bottom and the lid is replaced. The solvent then rises up the paper by capillary action and through the mixture. The different components each have a different tendency to adsorb to the paper. If the component adsorbs more strongly to the paper (the stationary phase) then it does not travel up as readily.



To make comparisons between different chromatograms, an R_f value (retention factor) is calculated. This is a measure of how far the sample, seen as a spot, travels up the paper compared to have far the solvent travels.

It is calculated using the formula:

$$R_f = \frac{\text{distance travelled by sample}}{\text{distance travelled by solvent}}$$

Key points in running the chromatogram:

- The sample must be placed above the solvent in the tank so that it spreads up with the rising solvent rather than dissolves in the solvent at the bottom.
- The position of the sample is marked with a pencil line. Pencil is used because it does not dissolve in most solvents and so does not move. It gives a clear fixed start position for measuring R_f values.
- The solvent front should not reach the top of the paper.
- A lid is kept on the tank to ensure that the atmosphere in the tank has a saturated solvent vapour. This prevents the solvent evaporating from the paper rather than rising.

Centrifugation

Centrifugation is used to separate heterogeneous mixtures based on their differences in particle mass. It can be used to separate mixtures of gases but it is more commonly used to separate solids from liquids or solutions.

If a liquid is mixed with a solid, the solid particles to settle to the bottom of a container as they are more dense than the liquid. When the solid is small or finely divided, random motion and collisions of the particles causes them to settle much more slowly and in some cases they do not settle to the bottom.

Centrifugation encourages settling by spinning the mixture at high speed in a horizontal circle. As the mixture is spun, the heavier particles are brought to the end of the tube. The heaviest particles settle out first, becoming a pellet at the bottom of the tube.

The remaining liquid may be pure, a solution or still contain small solid particles. The remainder, called the supernatant may be decanted into a new tube and spun again at a higher speed to separate the smaller particles.

Centrifugation is used in medicine for the separation of blood components such as red blood cells and platelets from the remaining plasma.

Choosing the right physical technique

Physical techniques do not change the chemicals. They separate by using a difference in the physical properties between the components of the mixture.

The key to choosing the right technique is in identifying the main differences between the components.

If the liquid component of a solid-liquid mixture is wanted, distillation is often used. If the single solid component is wanted, decantation, filtration or centrifugation can be used.

The separating funnel is specific to immiscible liquid-liquid mixtures.

Gas-gas mixtures can be separated by centrifugation or cryogenic distillation.

If the mixture is more complicated, different techniques can be used one after another to extract the desired substance.

Using techniques to test purity

In addition to separating mixtures, some techniques allow the purity of samples to be checked.

In chromatography, the R_f value of a substance using a constant stationary phase and solvent is always the same.

Chromatography can check whether a mixture contains that component and, if there are spots present with different R_f values, these would indicate an impurity. However, it should be noted that an impurity might have the same R_f value as a desired compound by coincidence and/or not be coloured/visible. Therefore it is not possible to be 100% sure of purity after analysis by this type of chromatography.

Distillation can also be used to indicate whether there is an impurity. During the boiling of a liquid, the boiling point can be found. If a liquid starts to boil off at a higher temperature than expected at a particular pressure, this indicates the presence of an impurity.

A similar change occurs at the freezing point when an impurity is present in a liquid. In this case, the freezing point is lowered.

In general, pure substances have definite, sharp melting and boiling points whereas impure substances melt and boil over a range of temperatures.

Evaporation can be used to check for dissolved impurities. If a solution is evaporated to dryness, any solid residue is a dissolved impurity.

Exercise 76

How could a mixture of common salt, sand and water be separated, collecting each component separately?

Exercise 77

Which techniques could be used to collect a solid precipitate suspended in an aqueous salt solution?

Exercise 78

Which of the following values cannot be an R_f value: 0.15, 0.55, 0.95, 1.05?

Solutions to Exercises 75 to 78

Exercise 75

The answer is $NaNO_3(aq)$.

Compounds containing silver ions are generally insoluble except for silver nitrate.

The HCl provides chloride ions and NaOH provides hydroxide ions. In the presence of dissolved silver ions, silver chloride and silver hydroxide would both precipitate. Adding silver nitrate provides more nitrate ions which would not cause the silver ions to precipitate.

Exercise 76

There is a mixture of an insoluble solid and a solution. There is also a difference in particle size.

The sand can be separated using filtration, leaving a salt solution. This is a mixture of a dissolved solid and the solvent.

There is a difference in boiling point, therefore distil to collect the water solvent leaving the salt behind.

Exercise 77

A precipitate is a solid and so there is a difference in particle size between the solid and the remaining solution.

Filter the mixture and wash the residue with distilled water or simply decant the solution away. A centrifuge could also be used to force the solid to the bottom of the tube and pour the supernatant liquid away.

Distillation could not be used in this case because the solid is being collected. As the solvent of the solution evaporates, the remaining solid would be a mixture of the precipitate required and the dissolved salt.

Exercise 78

The R_f value is calculated by dividing the distance travelled by the sample by the distance travelled by the rising solvent.

The sample cannot overtake the solvent and so all R_f values must be between 0 and 1.

The value that cannot be an R_f value is 1.05.

C9. Acids, bases and salts

C9.1 Acids:

a. Define an acid as a substance that can form $H^+(aq)$ ions or that is an H^+ donor.

b. Describe reactions with metals, carbonates, metal hydroxides and metal oxides in which salts are formed.

c. Understand the terms *strong*, *weak*, *dilute* and *concentrated*.

d. Know that some oxides of non-metals react with water to form acidic solutions.

e. Recall that pH is a measure of H^+ ion concentration, and recall that a change of 1 on the pH scale corresponds to a change by a factor of 10 in H^+ ion concentration.

f. Know that one mole of some acidic substances is able to form/donate more than one mole of H^+ ions, including the use of the terms *mono*-, *di*-, *tri*-, and *polyprotic*.

An acid can be defined as a substance which has the ability to donate H^+ ions. When dissolved in water, acids will form $H^+(aq)$ ions.

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

Acids can react with a variety of chemicals to produce salts.

A salt is a general name for a compound formed when the hydrogen ions in an acid are replaced by metal ions (or other cations).

Consequently, the name of a salt can be derived from the name of the acid from which it can be formed and the ion which has replaced some or all of the hydrogen ions in the acid.

acid name	acid formula	sodium salt name	sodium salt formula
hydrochloric acid	HCl	sodium chloride	$NaCl$
sulfuric acid	H_2SO_4	sodium sulfate or sodium hydrogensulfate	Na_2SO_4 or $NaHSO_4$
nitric acid	HNO_3	sodium nitrate	$NaNO_3$
ethanoic acid	CH_3COOH	sodium ethanoate	CH_3COONa

Exercise 79

Give the name and formulae of the magnesium salts of the following acids:

a) hydrochloric acid

b) sulfuric acid

c) propanoic acid

Metals and acids

metal + acid → salt + hydrogen

The reaction produces hydrogen gas as well as a salt, hence effervescence of a colourless gas will be observed.

Reactions between metals and acids will only occur if the metal is more reactive than hydrogen.

For example, iron will react with dilute acids, but gold will not.

If a metal is very reactive, the reaction may be too violent to be carried out safely.

The reaction of a metal and an acid is an example of a redox reaction – the metal atoms are oxidised (lose electrons) and hydrogen ions are reduced (gain electrons).

Exercise 80

Explain why silver sulfate cannot be prepared by adding silver metal to dilute sulfuric acid.

Exercise 81

Explain why sodium chloride should not be prepared in the laboratory by reacting sodium metal with dilute hydrochloric acid.

Exercise 82

Write the formula equation for the reaction between:

a) calcium and sulfuric acid

b) magnesium and ethanoic acid

Exercise 83

Consider the reaction between magnesium and hydrochloric acid.

a) Write a balanced symbol equation, including state symbols.

b) Write the ionic equation, including state symbols.

c) Write the half-equations, to show electron transfer and explain why this is a redox process.

Metal carbonates and acids

metal carbonate + acid → salt + water + carbon dioxide

Metal carbonates react with acids to produce a salt, water and carbon dioxide gas, so effervescence of a colourless gas will be observed.

The reaction between calcium carbonate and hydrochloric acid can be shown as:

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

This neutralisation reaction is not a redox reaction.

Exercise 84

Consider the reaction between solid potassium carbonate and dilute nitric acid.

a) Write a balanced symbol equation, including state symbols.

b) Write the ionic equation, including state symbols.

Metal hydroxides and acids

metal hydroxide + acid → salt + water

Metal hydroxides react with acids to form a salt and water only.

The reactions between acids and soluble metal hydroxides are commonly seen neutralisation reactions and used in laboratory techniques such as titration.

The reaction between sodium hydroxide and hydrochloric acid can be shown as:

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

This neutralisation reaction is not a redox reaction.

Exercise 85

Consider the reaction between dilute potassium hydroxide and dilute sulfuric acid.

a) Write a balanced symbol equation, including state symbols.

b) Write the ionic equation, including state symbols.

Metal oxides and acids

metal oxide + acid → salt + water

Metal oxides react with acids to form a salt and water only.

Metal oxides are bases, so these are neutralisation reactions. They are not redox reactions.

An example would be the formation of copper(II) sulfate from the reaction between copper(II) oxide and sulfuric acid:

$$CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$$

Exercise 86

Consider the reaction between solid zinc oxide (ZnO) and dilute sulfuric acid.

c) Write the balanced equation.

d) Calculate the mass of zinc salt that would be formed if excess zinc oxide was reacted with 20 cm^3 of 2.0 $mol\,dm^{-3}$ sulfuric acid.

[Ar values: O = 16.0, Zn = 65.4, S = 32.1]

Strong acid

An acid that undergoes full dissociation in water, forming its constituent ions.

$$HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$$

The → arrow to indicates that the reaction goes to completion.

Common laboratory acids, such as hydrochloric acid, sulfuric acid and nitric acid, are strong acids.

Weak acid

An acid that only slightly dissociates into its constituent ions in solution.

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

The ⇌ arrow indicates that an equilibrium exists in aqueous solution between the undissociated (covalently bonded) acid molecules and the ions formed on dissociation.

Carboxylic acids are weak acids.

If two acids of equal aqueous concentration are considered, HCl (a strong acid) and CH_3COOH (a weak acid), the HCl solution will have a higher concentration of $H^+(aq)$ ions than the CH_3COOH solution. Hence, the HCl solution has a lower pH and will react more rapidly with a compound such as a metal carbonate, when compared to the CH_3COOH solution.

Concentrated and dilute acids

These terms refer to the ratio of the amount of moles to volume, or 'concentrations' in mol dm^{-3}, of the solutions of acids. For example,

2.0 mol dm^{-3} is considered 'dilute'.

6.0 mol dm^{-3} is considered 'concentrated'.

There is no specific 'cut-off' value between 'dilute' and 'concentrated' as descriptions of acids and they can be considered as relative terms.

In understanding these terms, it is clearly possible to have a 'concentrated weak acid' and a 'dilute strong acid'.

Exercise 87

Equal quantities of sodium carbonate are added to beakers containing aqueous solutions of ethanoic acid and nitric acid of equal concentrations. Describe and explain how observations of the reactions in each beaker would differ.

Oxides of non-metals

Whilst metal oxides are basic in nature, some non-metal oxides react with water to produce acidic solutions.

Examples include oxides of sulfur and nitrogen, involved in the production of ‘acid rain’:

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

$$2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$$

Carbon dioxide also reacts with water to produce carbonic acid:

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$$

Exercise 88

Phosphorus(V) oxide, P_4O_{10}, reacts with water to produce phosphoric(V) acid. Write the balanced equation for this reaction.

How pH values are related to the concentration of H^+(aq) ions pH is a measure of hydrogen ion concentration in aqueous solution.

All acids are able to contribute H^+(aq) ions to a solution. The higher the concentration of H^+(aq) ions, the lower the pH value of the solution and the more acidic that solution.

The relationship between concentration of H^+(aq) and pH can be quantified:

concentration of H^+(aq) ions in mol dm^{-3}		pH value at 25 °C
0.10	1.0×10^{-1}	1.0
0.01	1.0×10^{-2}	2.0
0.001	1.0×10^{-3}	3.0
0.0001	1.0×10^{-4}	4.0

As the concentration of H^+(aq) ions decreases by a factor of 10, the pH value increases by one unit.

A change of 1 on the pH scale corresponds to a change by a factor of 10 in H^+(aq) ion concentration.

Exercise 89

3.65 g of HCl gas is completely dissolved in 10 dm^3 of distilled water.

1.0 cm^3 of this solution is transferred into a large volumetric flask and made up to 1.0 dm^3 using distilled water.

What is the pH of this solution in the volumetric flask?

[A_r values: H = 1.0, Cl = 35.5]

Monoprotic, diprotic and triprotic acids

Depending on the formula of an acid, one mole of an acidic substance may be able to form or donate more than one mole of H^+(aq) ions into an aqueous solution.

HCl, HNO_3 and CH_3COOH are examples of monoprotic acids, in that that they are only able to donate one acidic H^+ (aq) ion per acid molecule.

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

H_2SO_4 is an example of a diprotic acid, in that it can donate two acidic H^+(aq) ions per acid molecule.

$$H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$$

H_3PO_4 is an example of a triprotic acid, in that it can donate three acidic H^+(aq) ions per acid molecule.

$$H_3PO_4(aq) \rightarrow 3H^+(aq) + PO_4^{3-}(aq)$$

Exercise 90

It was found that 21.5 cm^3 of sulfuric acid neutralised 25.0 cm^3 of a 2.0 mol dm^{-3} solution of sodium hydroxide.

Calculate the concentration of the sulfuric acid.

C9.2 Bases:

a. Define a base as a substance that can form $OH^-(aq)$ ions or that is an H^+ acceptor.

b. Understand the terms strong, weak, dilute and concentrated.

c. Know that some oxides and hydroxides of metals react with water to form alkaline solutions.

A base is the chemical opposite of an acid. Some bases are soluble in water, and these are sometimes called alkalis.

The definition of a base is a substance that can accept H^+ ions, or one that has the ability to form $OH^-(aq)$ in solution.

Strong base

A base (alkali) which undergoes full dissociation in water, forming its constituent ions.

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$

The → arrow indicates that the reaction goes to completion.

Common laboratory alkalis, such as sodium hydroxide and potassium hydroxide, are strong bases.

Weak base

A base that only partially forms ions in solution.

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

Ammonia is a weak base.

Concentrated and dilute bases (alkalis)

These terms refer to the ratio of moles to volume, or ‘concentrations’ in mol dm^{-3}, of the solutions of soluble bases (alkalis).

2.0 mol dm^{-3} would be considered ‘dilute’.

6.0 mol dm^{-3} would be considered ‘concentrated’.

There is no specific ‘cut-off’ value between ‘dilute’ and ‘concentrated’, as with descriptions of acids, and so they can be considered as relative terms.

In understanding these terms, it is clearly possible to have a ‘concentrated weak base’ and a ‘dilute strong base’.

Reactions of some metal oxides and metal hydroxides with water to form alkaline solutions

Aqueous hydroxide ions, $OH^-(aq)$, are found in alkaline solutions.

Some metal hydroxides dissolve in water to form alkaline solutions:

$$NaOH(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq)$$

$$Ca(OH)_2(s) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$

There are other metal hydroxides which are insoluble (such as $Cu(OH)_2$), so whilst basic, they are not able to from alkaline solutions.

Some metal oxides react with water to produce $OH^-(aq)$ ions and therefore alkaline solutions:

$$Na_2O(s) + H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq)$$

$$BaO(s) + H_2O(l) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$$

Other metal oxides, such as CuO, do not react with water and so do not form alkaline solutions.

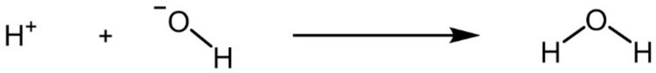
C9.3 Know that the reaction of an acid with a base can lead to neutralisation and is often exothermic.

When an acid reacts with a base, the reaction is described as a neutralisation reaction.

Neutralisation reactions are often exothermic, in that they release heat to the surroundings.

In a simple neutralisation of an acidic solution ($H^+(aq)$ ions) with an alkaline solution ($OH^-(aq)$ ions), this can be illustrated by the following equation as it is a bond forming process.

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



Bond forming releases energy. As there is no bond breaking (endothermic) in this process, this simple neutralisation is an exothermic process.

Solutions to Exercises 79 to 90

Exercise 79

a) magnesium chloride, $MgCl_2$

b) magnesium sulfate, $MgSO_4$

c) magnesium propanoate, $(CH_3CH_2COO)_2Mg$

Exercise 80

Silver is less reactive than hydrogen, so no reaction will take place under standard conditions.

Exercise 81

The reaction is likely to be too violent and therefore unsafe.

Exercise 82

a) $Ca(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + H_2(g)$

b) $Mg(s) + 2CH_3COOH(aq) \rightarrow (CH_3COO)_2Mg(aq) + H_2(g)$

Exercise 83

a) $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

b) $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$

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

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

The magnesium atoms lose two electrons and therefore are oxidised. The hydrogen ions gain electrons and therefore are reduced. The process involves electron transfer and is a redox process.

Exercise 84

a) $K_2CO_3(s) + 2HNO_3(aq) \rightarrow 2KNO_3(aq) + H_2O(l) + CO_2(g)$

b) $K_2CO_3(s) + 2H^+(aq) \rightarrow 2K^+(aq) + H_2O(l) + CO_2(g)$

Exercise 85

a) $2KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$

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

Note: This is the simplest ionic equation for all reactions between an aqueous acid and an aqueous alkali.

Exercise 86

a) $ZnO(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2O(l)$

b) Number of moles of H_2SO_4 = concentration × volume = $2.0 \times \frac{20}{1000} = 0.04\,\text{mol}$

Number of moles of $ZnSO_4$ = number of moles of H_2SO_4 = 0.04 mol (as a 1 : 1 mole ratio)

Mass $ZnSO_4$ = number of moles × M_r = $0.04 \times 161.5 = 6.46\,\text{g}$

Exercise 87

In both cases, effervescence of a colourless gas would be observed as each acid will react with the sodium carbonate to produce a soluble sodium salt, water and carbon dioxide gas. However, the rate at which the gas will be produced in the beaker containing the nitric acid (a strong acid) will be higher than that in the beaker containing the ethanoic acid (a weak acid). This is because, although the concentrations of the acids are equal, the concentration of the H^+ (aq) ions will be higher in the strong acid solution than in the weak acid solution, so the strong acid will react more quickly and vigorously.

Note that both acids would eventually produce the same volume of carbon dioxide gas. It is only the rate of reaction that would differ.

Exercise 88

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

Exercise 89

Number of moles of HCl originally $= \dfrac{\text{mass}}{M_r} = \dfrac{3.65}{36.5} = 0.10\,\text{mol}$

Concentration of HCl in original solution $= \dfrac{\text{number of moles}}{\text{volume}} = 0.010 \times \dfrac{1}{100} = 0.000010\,\text{mol}\,\text{dm}^{-3}$

Concentration of new solution $= \dfrac{\text{number of moles}}{\text{volume}} = \dfrac{0.000010}{1} = 0.000010\,\text{mol}\,\text{dm}^{-3}$
$= 1.0 \times 10^{-5}\,\text{mol}\,\text{dm}^{-3}$

pH of new solution = 5.0

Exercise 90

The equation for the reaction is: $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

Sulfuric acid is diprotic, so the mole ratio of (sulfuric acid) **:** (sodium hydroxide) is 1 **:** 2

Number of moles of NaOH = concentration × volume $= 2.0 \times \dfrac{25.0}{1000} = 0.050\,\text{mol}$

Number of moles of H_2SO_4 $= \dfrac{1}{2} \times$ number of moles of NaOH $= 0.025\,\text{mol}$

Concentration of H_2SO_4 $= \dfrac{\text{number of moles}}{\text{volume}} = \dfrac{0.025}{\left(\frac{21.5}{1000}\right)} = 1.16\,\text{mol}\,\text{dm}^{-3}$

C10. Rates of Reaction

C10.1	Describe the qualitative effects on a rate of reaction of concentration, temperature, particle size, a catalyst and, for gases, pressure.
C10.2	Know that the rate of reaction can be found by measuring the loss of a reactant or the gain of a product, or by measurement of a physical property over time, and be able to identify which of these measurements can be used in a given situation.
C10.3	Interpret data in graphical form concerning the rate of a reaction.
C10.4	Use collision theory to explain changes in the rate of a reaction.
C10.5	Understand that particles must have sufficient energy when they collide to react, and that this energy is called the activation energy (E_a). Identify the activation energy on an energy level diagram.
C10.6	Know that catalysts: a. are not used up in a reaction. b. are chemically unchanged at the end of a reaction. c. provide an alternative route (reaction mechanism) with a lower activation energy, and interpret this effect on an energy level diagram. d. do not affect the position of an equilibrium.

Rates of reaction

In a reaction, reactants form products. How quickly the reaction takes place is known as the rate of reaction. For the reaction to be monitored, either the rate at which one of the reactants is used up or the rate at which one of the products is formed, needs to be measured.

Being able to measure rates of reaction is important in the chemical industry to ensure that chemical reactors are safe and that industrial processes run as economically as possible. Monitoring rates of reaction can also help determine how enzymes (biological catalysts) function and how organic mechanisms proceed.

Reactions may be monitored in a number of ways:

- In a reaction where a gas is produced, for example:

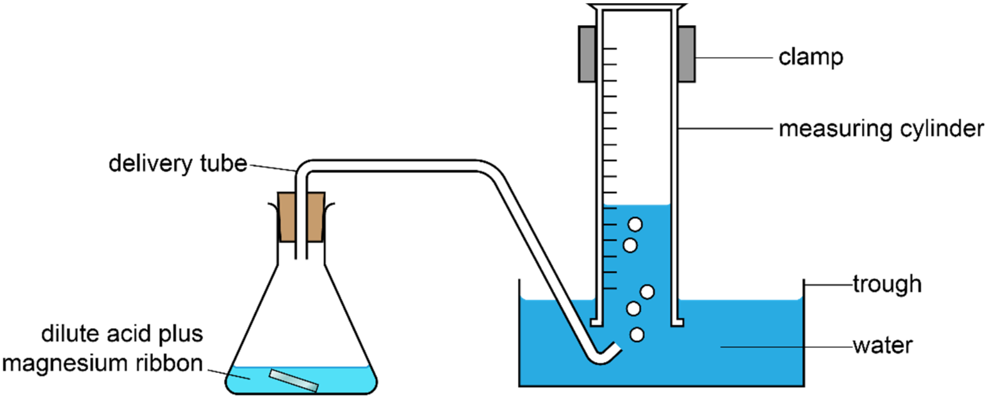
metal + acid → hydrogen

metal + carbonate → carbon dioxide

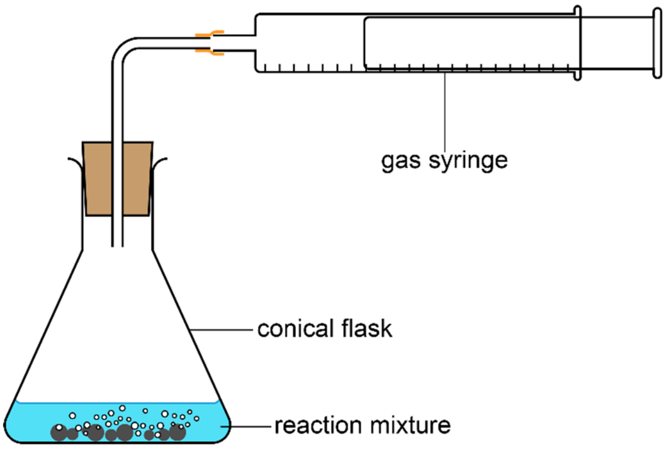
the gas may be collected either over water in an inverted measuring cylinder, or in a gas syringe. The rate of gas release ('evolution') can then be measured over the course of the reaction.

Diagrams of these two methods are shown below:

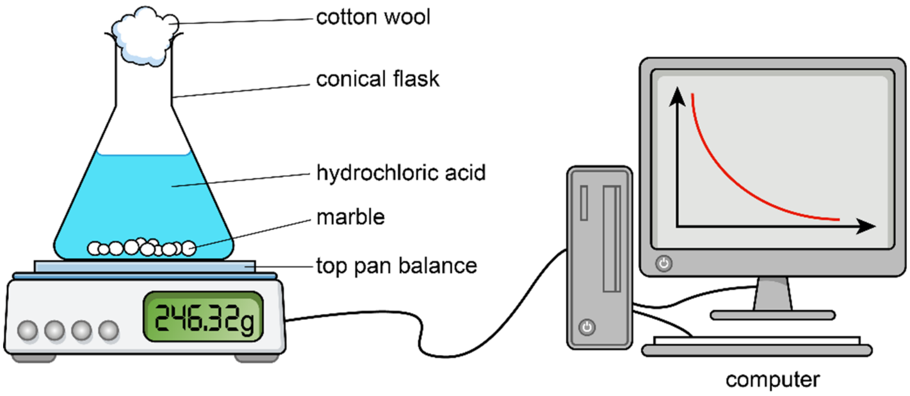
Using an inverted measuring cylinder



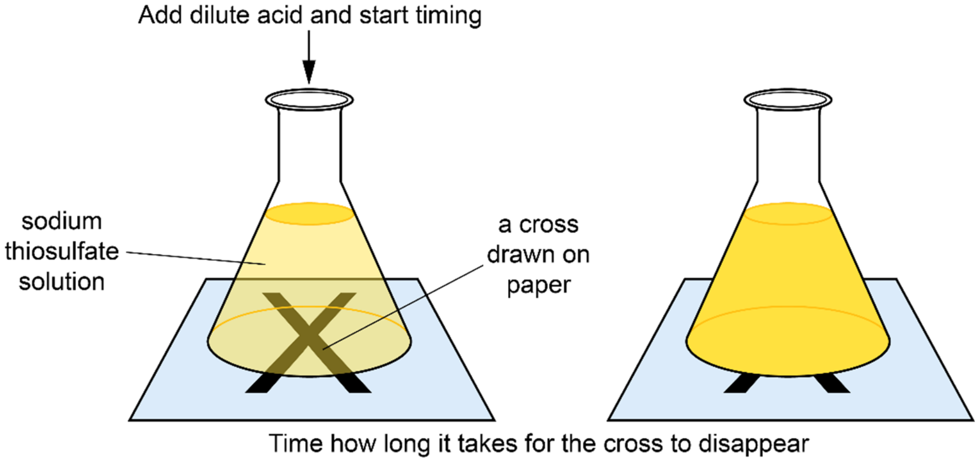
Using a gas syringe



- In a reaction where a gas is produced, an alternative method involves allowing the reaction to proceed in an open container placed on an electronic balance. The gas is allowed to escape and the consequent mass loss can be measured against time over the course of the reaction, as shown below:

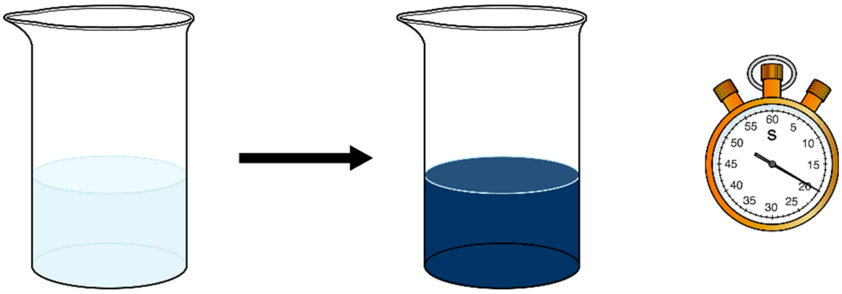


- In a reaction where a precipitate is formed, for example the reaction between hydrochloric acid and sodium thiosulfate forming a yellow precipitate of sulfur, the time taken for a fixed amount of sulfur (product) that causes a cross to disappear can be measured. This is proportional to the initial rate of reaction.



- Sometimes a chemical is added that reacts with one of the products when a particular reactant is used up to form a coloured solution, for example iodine clock reactions. The time taken for the starch indicator to form a blue-black colour with iodine, I_2, is measured. Again, this is proportional to the initial rate of reaction.

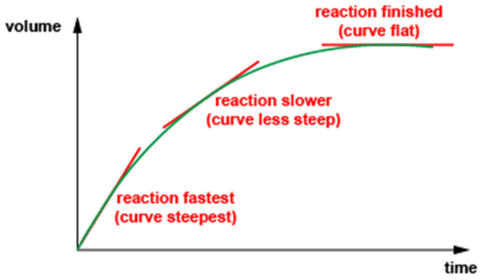
  Iodine clock reaction



- Other physical properties that can be measured to monitor the rate of a chemical reaction include a change in pH, a change in temperature or a change in colour.

Using tangents to calculate rates

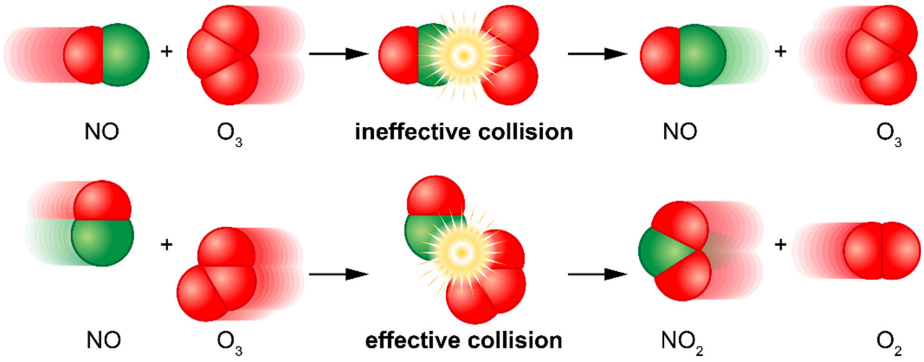
If a graph of the change of reactant or product against time is plotted, then the rate of reaction at any point is equal to the gradient of the tangent to the curve at that point, for example plotting the volume of gas formed against time.



In the example above, it can be seen that the rate of reaction starts off fast and gradually slows as the reactant particles are used up. The reaction is over at the point the curve becomes horizontal.

Collision theory

For two particles to react, they must collide at the correct orientation and have sufficient energy. The activation energy (E_a) is defined as the minimum amount of energy a particle must have to successfully react upon collision. It can be seen in the example below that not all collisions are successful.



Factors which affect rates of reaction

The rate of reaction is determined by the number of successful collisions within a given time. This depends on the following factors:

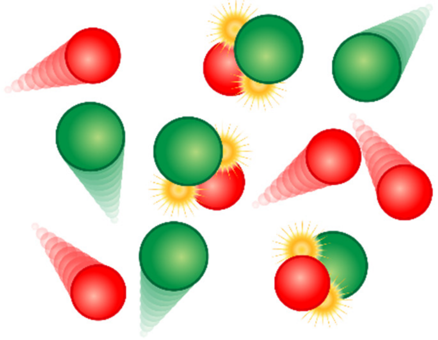
- temperature
- concentration of solutions
- (pressure for gases)
- surface area of solid reactants catalysts

Temperature

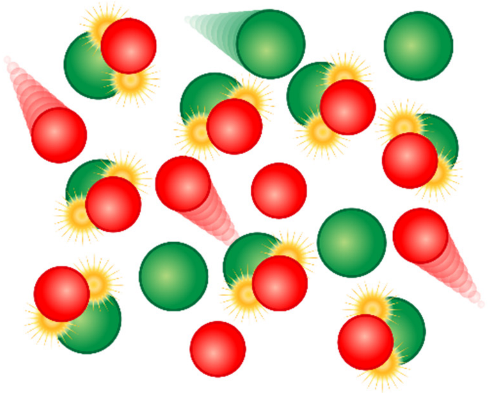
Most reactions are faster at higher temperatures. This is because the particles will have more kinetic energy and will therefore move faster. There will be more frequent collisions and so more frequent successful collisions. As the particles will have more energy at a higher temperature, a greater proportion of the collisions will be successful as many more of the particles will have the required activation energy. In many reactions, an increase in 10 °C will approximately double the rate of reaction as approximately twice as many particles will have sufficient energy to react.

Concentration

At a higher concentration, there will be a greater number of particles in a given volume. It follows that there will be more frequent collisions and so more frequent successful collisions.

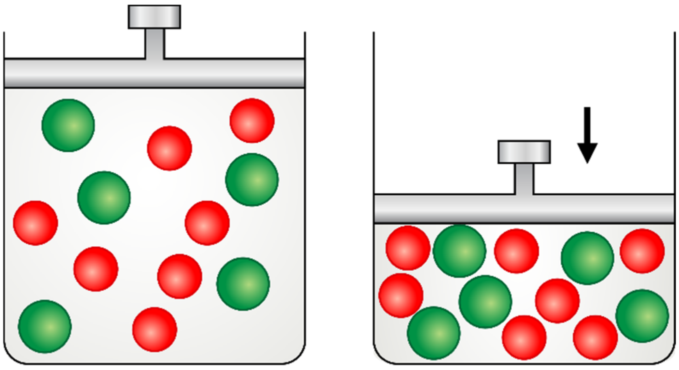


low concentration = few collisions



high concentration = more collisions

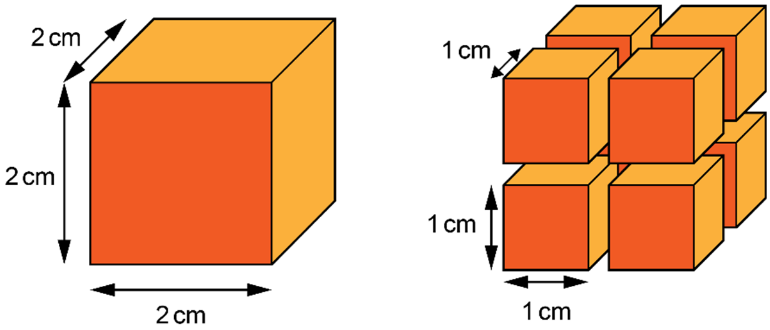
In gaseous reactions, pressure is analogous to concentration in liquids. At a higher pressure there will be a greater number of particles in a given volume and so more frequent collisions and more frequent successful collisions.



As pressure increases, the gas molecules can have more collisions

Surface area

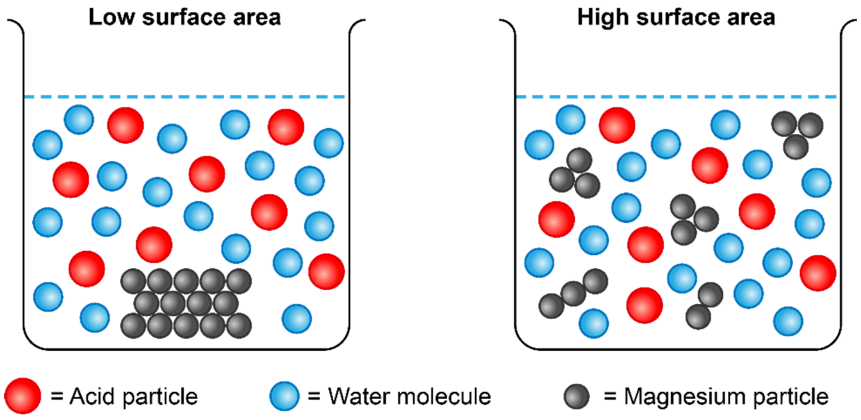
The diagram shows that if a cube of side length 2 cm is cut into smaller cubes of side length 1 cm, the total surface area is doubled. It follows that in a reaction involving a solid, smaller sized pieces will react faster than a larger sized lump.



Surface area =
$6 \times (2 \times 2)\,\text{cm}^2$
$= 24\,\text{cm}^2$

Surface area =
$8 \times (6 \times (1 \times 1))\,\text{cm}^2$
$= 48\,\text{cm}^2$

This is because there will be more particles exposed for reaction with another reactant's particles and so there will be more frequent collisions and more frequent successful collisions. For example, the reaction between magnesium and acid:

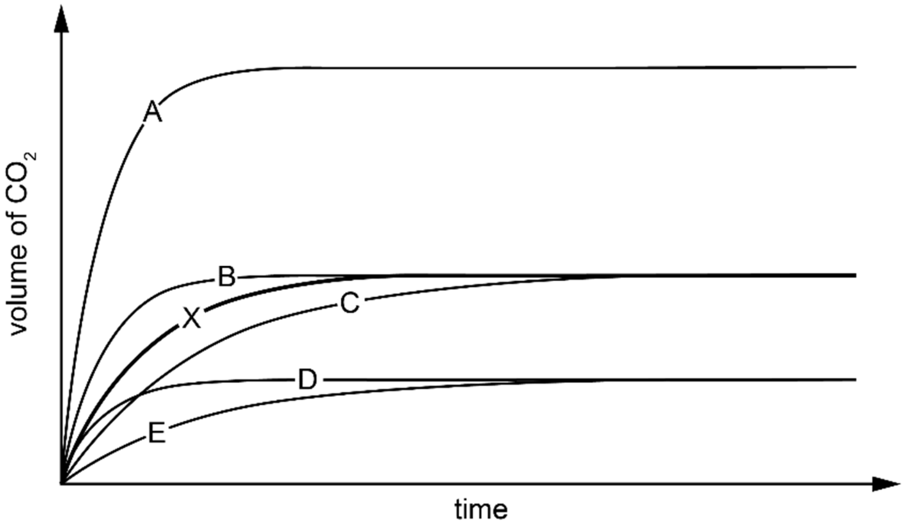


Exercise 91

Calcium carbonate reacts with hydrochloric acid. The reaction gives off carbon dioxide gas. Line X on the graph shows the volume of carbon dioxide formed against time when 100 cm^3 of 1.0 mol dm^{-3} of hydrochloric acid reacts with calcium carbonate chips at 20 °C. There was an excess of calcium carbonate chips.

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

Which line best represents the volume of carbon dioxide formed against time when the reaction is repeated with 50 cm^3 of 2.0 mol dm^{-3} of hydrochloric acid reacting with excess calcium carbonate chips at 20 °C?



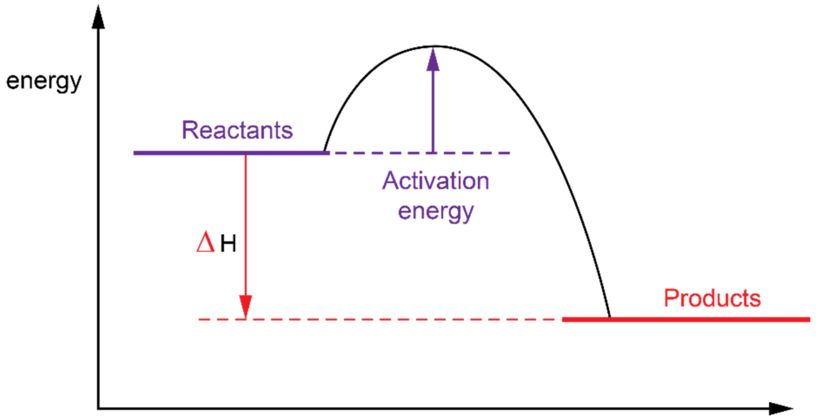
Exercise 92

Which row in the table correctly explains why an increase in temperature increases the rate of a reaction?

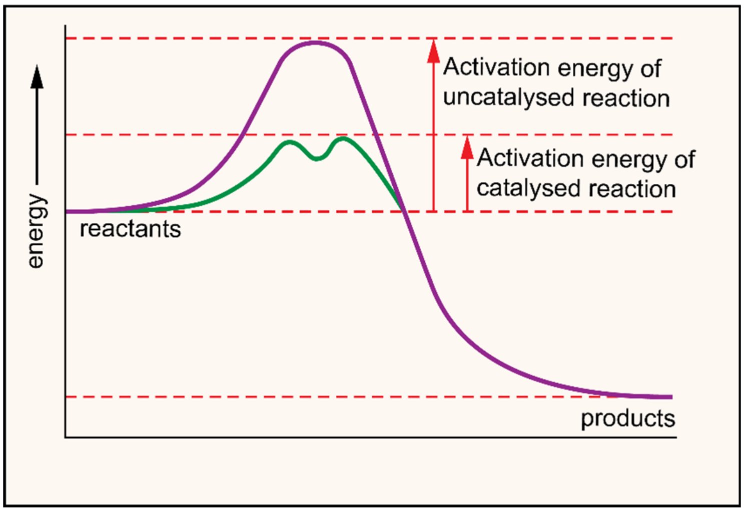
	effect on activation energy of reaction	effect on collision frequency between particles	effect on proportion of collisions which are successful
A	decreases	no effect	increases
B	increases	no effect	no effect
C	no effect	increases	no effect
D	increases	increases	no effect
E	decreases	no effect	no effect
F	no effect	no effect	increases
G	decreases	increases	increases
H	no effect	increases	increases

Using energy level diagrams to explain catalysis

An energy level diagram shows the concept of the activation energy. In the example below for an exothermic reaction, the reaction will not occur unless the activation energy barrier is overcome. Only then will the reactants form the products.

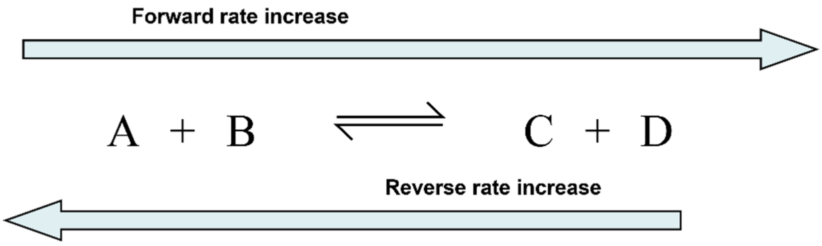


A catalyst is a substance that alters the rate of a chemical reaction. It is not used up in the reaction and is chemically unaltered at the end of reaction. A catalyst works by providing an alternative route (mechanism) for the reaction with a lower activation energy. This is explained in the energy diagram below.



In a reversible reaction, the use of a catalyst does not affect the position of equilibrium. This is because a catalyst will increase the rate of the forward reaction and the rate of the backward reaction by the same amount. This means that in a reversible reaction, equilibrium is reached at a faster rate, but the overall yield of the reaction is unaffected.

Catalysts



Exercise 93

A sample of hydrogen peroxide solution in an open beaker at room temperature started to decompose rapidly when aqueous potassium iodide (KI(aq)) was added. The decomposition is thought to proceed by a two-step mechanism:

Step 1: $H_2O_2 + I^- \rightarrow IO^- + H_2O$

Step 2: $IO^- + H_2O_2 \rightarrow H_2O + O_2 + I^-$

A student made three deductions from these equations:

1) The equation for the overall reaction is $2H_2O_2 \rightarrow 2H_2O + O_2$
2) The iodide ion is acting as a catalyst.
3) The rate of decomposition could be found by measuring the change in mass of the beaker and its contents at regular intervals.

Which selection of these deductions is correct?

A) none of them

B) 1 only

C) 2 only

D) 3 only

E) 1 and 2 only

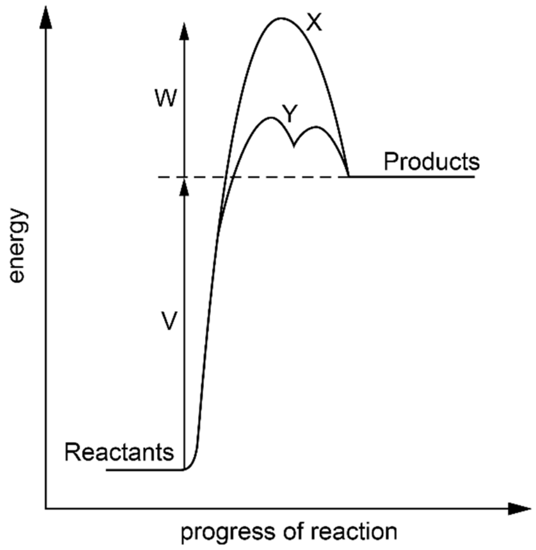
F) 1 and 3 only

G) 2 and 3 only

H) 1, 2 and 3

Exercise 94

The energy profile for a reaction is shown below.



Which of the following is a fully correct statement about this energy level profile?

A) The reaction is endothermic; V is the change in enthalpy of the reaction (positive sign) and X is the activation energy.

B) Products have more energy than the reactants; X shows the route taken when a catalyst is present and W is the activation energy.

C) Y is the route taken when a catalyst is present, V is the change in enthalpy of the reaction and the reaction is exothermic overall.

D) X shows the route taken without a catalyst, V + W is the activation energy and V (the change in enthalpy of the reaction) has a positive sign.

Photo: Science Photo Library

Solutions to Exercises 91 to 94

Exercise 91

We need to consider both the volume of carbon dioxide gas and the initial rate at which it is formed. Looking at the height and slope of the lines A to E, compared with X, line A produces twice the volume of gas, B and C produce the same volume of gas, B at a faster initial rate, C at a slower initial rate, and D and E produce half the volume of gas, D at the same initial rate and E at a slower initial rate.

Half the volume of acid at twice the concentration will contain the same number of acid particles and so will produce the same volume of carbon dioxide gas, however as the number of acid particles are in half the total volume of solution, 50 cm^3 rather than 100 cm^3, there will be more frequent collisions and hence more frequent successful collisions. The rate of reaction will therefore be faster with the line being steeper. The correct answer is therefore B.

Exercise 92

The value for the activation energy of any particular reaction is independent of temperature. Only a catalyst will lower this activation energy by providing an alternative route.

At a higher temperature, particles will have more kinetic energy on average and so they will move faster. There will therefore be more collisions within a given time, so collision frequency increases.

As the particles have more kinetic energy on average, more of the particles will have sufficient energy to react (the activation energy), so a greater number of the collisions that happen will be successful.

Therefore, though the activation remains fixed, both the frequency of collisions and proportion of successful collisions increase so the correct row is H).

Exercise 93

Taking the 3 statements in turn:

1) The equation for the overall reaction can be determined by combining the equations from the two steps and cancelling down the common species.

$H_2O_2 + I^- \rightarrow IO^- + H_2O$

$IO^- + H_2O_2 \rightarrow H_2O + O_2 + I^-$

$2H_2O_2 \rightarrow 2H_2O + O_2$

Statement 1 is therefore correct.

2) The iodide ion, I^-, is not used up in the reaction as it is regenerated at the end of the second step. It is therefore acting as a catalyst. Statement 2) is correct.

3) The reaction produces oxygen gas, O_2. As the reaction is being carried out in an open container, the gas will escape and so measuring this loss of mass at regular time intervals is an appropriate way of monitoring the rate of reaction.

The answer is therefore H) 1), 2) and 3).

Exercise 94

The energy of the products is higher than the energy of the reactants, the reaction is therefore endothermic and V is the energy change of the reaction. The arrow X, however, labels the route and not the activation energy of the uncatalysed reaction, and so statement A) is not fully correct.

In statement B), label X shows the route of the uncatalysed reaction, not the catalysed reaction. V + W shows the activation energy for the forward reaction, not simply W, which is the activation energy for the reverse reaction. The statement is therefore not correct.

In statement C), label Y does show the route for the catalysed reaction, the shape showing that the reaction occurs in two steps. V is the energy change for the reaction but the reaction is endothermic not exothermic and so the statement is not fully correct.

In statement D), label X does label the uncatalysed route with V + W as the activation energy. The sign of V will be positive, as the reaction is endothermic. All parts of the statement are correct.

The only fully correct statement is therefore D).

C11. Energetics

C11.1	Understand the concepts of an exothermic reaction, for which ΔH is negative (negative enthalpy change), and an endothermic reaction, for which ΔH is positive (positive enthalpy change).
C11.2	Know that if a reversible reaction is exothermic in one direction, it is endothermic in the other direction.
C11.3	Be able to interpret energy level diagrams.
C11.4	Be able to calculate energy changes from specific heat capacities and changes in temperature in calorimetry experiments.
C11.5	Know that bond breaking is endothermic, and bond formation is exothermic, and be able to use bond energy data to calculate energy changes.

Chemical and physical changes are driven by energy. It is therefore important to the chemist that the energy change during chemical or physical processes is monitored and measured. Although small quantities of sound or light may be released during a change, it is heat that is of most interest to the chemist.

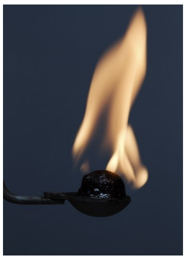
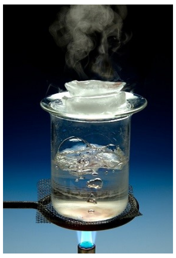
During a physical or chemical change, heat is either released to the surroundings or it is absorbed from the surroundings. These changes can be classified as exothermic and endothermic changes.

In an exothermic change, heat leaves or ‘exits’ the reaction. The reaction releases heat to the surroundings. As a result, the surroundings will get warmer, and the products will have less energy than the reactants.

In an endothermic reaction, heat is absorbed or ‘enters’ the reaction. In these changes the surroundings will get cooler, and the products will have more energy than the reactants.

The amount of heat given out or taken in during a reaction carried out at constant pressure is known as the enthalpy change. It is denoted by the symbol ΔH.

Enthalpy change values per mole of substance and are usually given in units of kJ mol^{-1}. For example, the enthalpy change of combustion of a substance is the heat released during the complete combustion of one mole of that substance.

	
The combustion of a fuel is an exothermic chemical change.	Both the melting of ice and the boiling of water are endothermic physical changes.

Some chemical and all physical changes can be reversed. The enthalpy change in each case will have the same magnitude but the movement of energy will be in opposite directions.

An example is the interconversion between anhydrous and hydrated copper(II) sulfate:

$$CuSO_4 + 5H_2O \rightarrow CuSO_4{\cdot}5H_2O$$

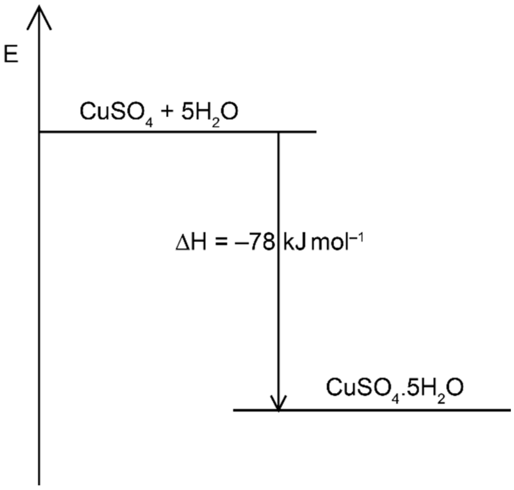
	
When water is added to anhydrous copper(II) sulfate, an exothermic change occurs (steam is visible in the picture).	When heated, hydrated copper sulfate releases water in an endothermic change.

In the exothermic reaction, the reaction releases heat. As a result, the product has less energy than the reactants. This is shown in the numerical values for the enthalpy change as a negative sign, for example:

$$CuSO_4 + 5H_2O \rightarrow CuSO_4{\cdot}5H_2O \quad \Delta H = -78\ \text{kJ mol}^{-1}$$

The endothermic process, $CuSO_4{\cdot}5H_2O \rightarrow CuSO_4 + 5H_2O$ is therefore $\Delta H = +78\text{kJ mol}^{-1}$.

This change can be shown in the following energy diagram.



In this diagram, the anhydrous $CuSO_4$ combines with the $5H_2O$ to make the hydrated $CuSO_4{\cdot}5H_2O$ and releases 78 kJ mol^{-1} as heat in an exothermic change.

Exercise 95

Calcium carbonate can be decomposed by heating.

The enthalpy change for this reaction is +178 kJ mol^{-1}.

State the enthalpy change for the reaction: $CaO + CO_2 \rightarrow CaCO_3$

State whether this is an endothermic or exothermic reaction and show this on an energy diagram.

Bond energies

Bond energies are a measure of the average bond strength for a particular covalent bond such as the O–H or the C–C bond.

Taking the O–H bond as an example: many different compounds contain an O–H bond, such as water, H–O–H (which contains two O–H bonds), ethanol, CH_3CH_2O–H, and ethanoic acid, CH_3COO–H. In each case, the O–H bond is slightly different in strength. The average of such specific bond energies gives the average (or mean) bond energy.

As an equation, the bond energy for the bond A–B would be written as:

$$\text{A–B(g)} \rightarrow \text{A(g)} + \text{B(g)}$$

The following table shows the bond energies for some common bonds.

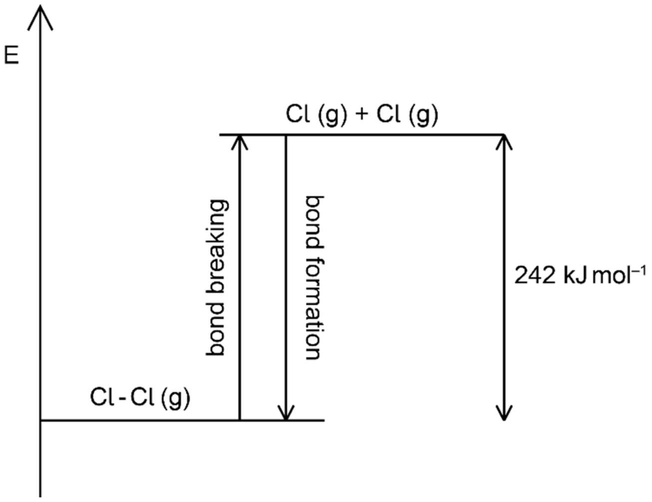
bond	bond energy / kJ mol^{-1}		bond	bond energy / kJ mol^{-1}
H–H	436		C–C	348
H–C	412		C–N	305
H–N	388		C–O	360
H–O	463		C–F	484
H–Cl	432		C–Cl	338
F–F	158		C–Br	276
Cl–Cl	242		C–I	238
Br–Br	193		C=C	612
I–I	151		C=O	743
O=O	496		N≡N	944

Note that bond energies are measured in compounds in the gaseous state and so these values only apply in calculations where all the reactants and all the products are in the gaseous state.

When a bond is broken, the electrostatic attraction between the atoms needs to be overcome - this requires energy. As a result, all bond energies signify endothermic processes and have positive numerical values.

In bond formation, the reverse process occurs and an equal quantity of energy to the bond energy is released in an exothermic change. The magnitude of the energy change must be exactly equal. If more energy was released on formation of a bond than was required to break it, or vice versa, then this would break the first law of thermodynamics.

This could also be represented on an energy diagram:



Calculating enthalpy changes using bond energies

Bond energies can be used to calculate an approximate value for the enthalpy change of a reaction.

To use bond energies, imagine breaking every bond so that a group of separate atoms is formed. The energy required to do this is given in the table. This will require energy and so this can be called ‘energy in’, which will be a positive value.

Using the combustion of methane as an example:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

4 × C–H bonds are broken in the methane and an O=O bond in each of the two oxygen molecules.

This will require: $[(4 \times 412) + (2 \times 496)] = +2640$ kJ mol^{-1}l. This is in the ‘energy in’.

If these bonds are broken, this leaves unbonded: a C atom, 4 H atoms and 2 O atoms.

These atoms combine to form the products forming 2 × C=O bonds (in the CO_2), and 4 × O–H bonds (in the H_2O).

This releases: $-[(2 \times 743) + (4 \times 463)] = -3338$ kJ mol^{-1}. This is the ‘energy out’.

The net change is the enthalpy change for the combustion of one mole of methane and is equal to:

$$\Delta H = +2640 - 3338 = -698 \text{ kJ mol}^{-1}$$

This is a negative number showing that the enthalpy change is exothermic which, for a combustion reaction, is not surprising.

In summary:

$$\Delta H = \text{[sum of energy in (all bonds broken)]} - \text{[sum of energy out (all bonds formed)]}$$

Exercise 96

Calculate the enthalpy change for the reaction:

$$CH_3CH_2Cl + NH_3 \rightarrow CH_3CH_2NH_2 + HCl$$

Limitations of bond energies

Bond energies are average values. This means that values calculated using them are not specific to the molecules used. It is not unusual for the actual (measured) value to have a difference from the calculated value of over 10%.

There is also the limitation that calculating the enthalpy change can only be done for reactions which take place entirely in the gaseous state.

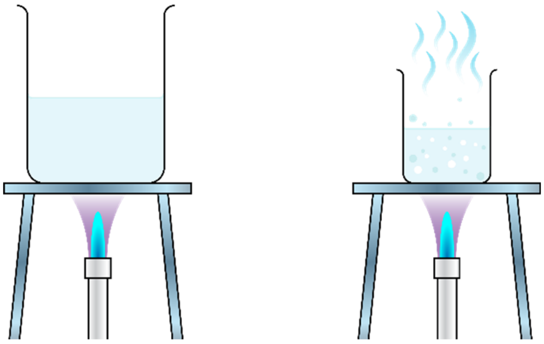
To obtain more accurate values for the enthalpy change of reactions, calorimetry experiments can be used.

Calorimetry

Calorimetry is the measurement of the enthalpy change of a reaction by experiment.

For ease, the rest of this explanation will assume that the reaction is exothermic and therefore the surroundings are warming up. The explanations can all be reversed for an endothermic reaction.

To measure the heat released or absorbed during a chemical change, three things need to be known.



First the mass, *m*, of the substance that's being heated needs to be known. Consider the above two beakers of water: the beaker containing the smaller mass of water heats up more quickly. Both beakers receive the same amount of heat, but their temperature rises will be different. If the chemical reaction is heating up water, then the more water used, the lower the temperature rise.

Second, what is being heated needs to be known. Raising the temperature of different substances by 1 °C requires different quantities of energy.

For example, it takes 4.2 J to heat up 1.0 g of water by 1 °C. To heat the same mass of lead by only 1 °C, only 0.13 J is needed. These values are called the specific heat capacities, *c*, and are specific to the individual materials.

Finally, the temperature change, ΔT, needs to be known. It will clearly take more energy to heat a substance up by 40 °C than by 20 °C.

These three factors combine into one equation to calculate the energy released during a reaction:

energy change, q (in joules) = mass of object heated × specific heat capacity × temperature change

$$q = mc\Delta T$$

where m is the mass of water, c is the specific heat capacity of water and ΔT is the temperature change.

Remember that enthalpy is usually measured per mole of substance in kJ mol^{-1}.

By dividing the energy change *q* by the number moles of a reactant or product, the enthalpy change ΔH per mole of a particular reactant or product can be calculated.

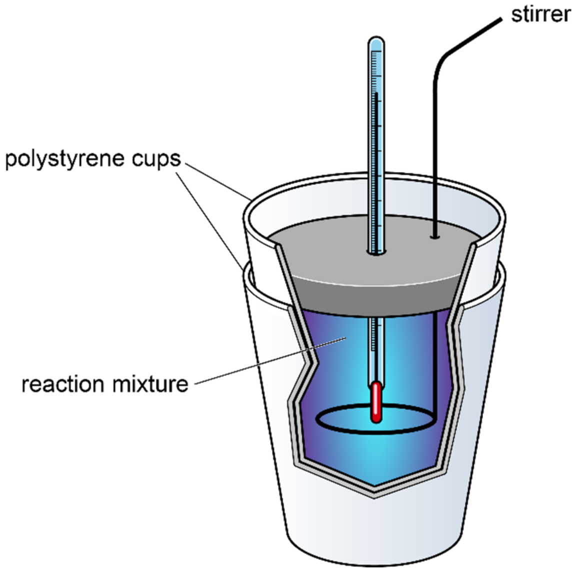
$$\text{enthalpy change } \Delta H = \frac{q}{\text{number of moles}}$$

Note: As exothermic reactions will have a negative value for the enthalpy change, the negative sign must be added at this stage. ΔH values for endothermic reactions should ideally have a positive sign explicitly shown, but omission of a sign is assumed to signify a positive value.

Calorimetry in aqueous reactions

Many reactions take place in aqueous solutions. An example is the neutralisation of aqueous sodium hydroxide using dilute hydrochloric acid.

In this experiment, a measured volume of a known concentration of the alkali is placed in the polystyrene/Styrofoam™ cup. These materials are chosen as the calorimeter because they are insulators. An insulator is used to prevent heat loss to (or heat gain from) the surroundings.



The temperature of the alkali is taken and then a measured volume of a known concentration of the acid is added.
The mixture is stirred, and the highest temperature rise is found. The temperature change, ΔT, can then be calculated.

Using the mass, the specific heat capacity and the temperature change, the energy change in joules and then the enthalpy change in kJ mol^{-1} can be calculated.

There are several assumptions made in these calculations:

- In most aqueous reactions, volumes rather than masses are measured. At room temperature and pressure, the density of water is 1.00 g cm^{-3}. Although the density of a solution will not be quite the same, dilute solutions will not deviate much from this and so it can be assumed that the density of the solution is also 1.00 g cm^{-3}. This means that 50 cm^3 of solution will be assumed to have a mass of 50 g.
- The specific heat capacity is particular to the substance being heated. In the reaction between sodium hydroxide and hydrochloric acid, the substance being heated is an aqueous solution. As most of the aqueous mixture is water, it can be assumed that the specific heat capacity of this solution is the same as that for pure water.

- As the water is the major component of the calorimeter and its contents, it can be assumed that only the water has absorbed any heat and that the calorimeter does not absorb any energy.

The number of moles of acid and alkali used are known because both the concentration and volume of each solution is known. When calculating Δ*H*, it needs to be clear which of the reactants or products is being used to define 'per mole'. In this case, for example, the number of moles of water produced could be chosen.

Exercise 97

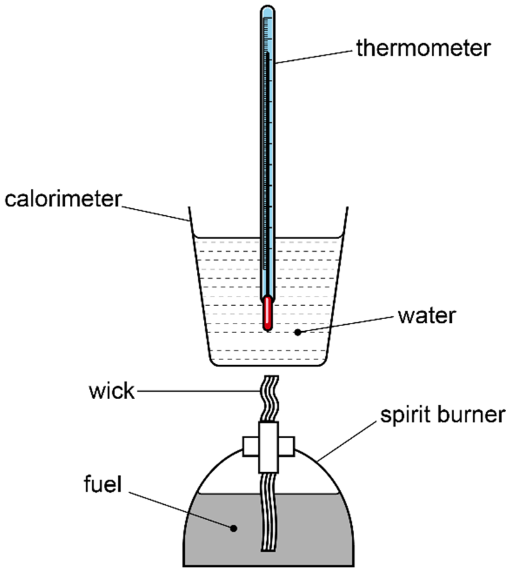
35.0 cm^3 of 1.00 mol dm^{-3} of aqueous sodium hydroxide is placed in a polystyrene calorimeter. 40.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid was added.

The initial temperature was 22.0 °C which rose to a maximum 27.6 °C.

Calculate the energy change of this reaction per mole of water produced.

Calorimetry in combustion experiments

When burning a fuel, the apparatus is set up differently. The fuel is placed in a burner and when lit, the energy is used to heat water contained in a copper calorimeter.



The energy released is then calculated by measuring the temperature change of the water. When measuring the enthalpy change in this way, there are additional sources of error:

- Incomplete combustion can be a problem

This is especially true when larger molecules are used as the fuel. The ratio of fuel:oxygen is higher for larger molecules and the air is only 21% oxygen. When a fuel does not burn completely, less energy is released.

- Heat loss to the surroundings is more likely in this open system

A closed polystyrene cup prevents, or at least slows, heat loss. In a combustion experiment, heat can be lost before it reaches the calorimeter, and it can also be lost from the calorimeter if not insulated. Heat loss and mass loss from the calorimeter is a more significant problem when the water is allowed to get very hot.

- Heat is lost to the calorimeter

The calorimeter in this experiment must be a conductor. Some heat will be absorbed by the calorimeter. This error could be removed by calculating the energy change of the calorimeter as well as the water and adding the values together.

Exercise 98

In a combustion experiment, the temperature of the water rose to 100 °C. The calculation of the enthalpy change gave a value much less exothermic than that in the data book.

Suggest why the value was less exothermic than expected.

Photos: Science Photo Library

Further uses of energy diagrams

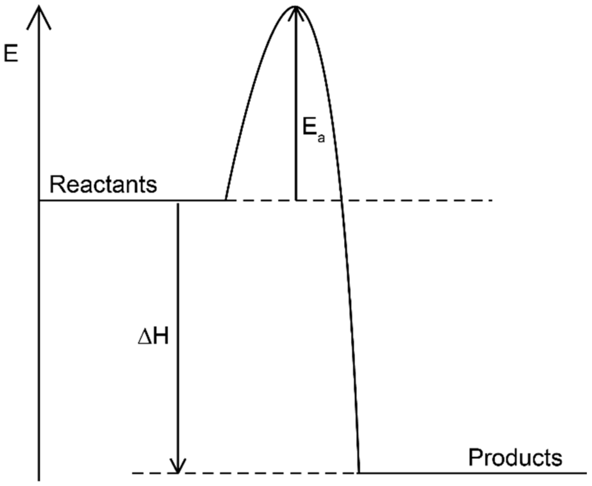
In all the enthalpy calculations, the energy of the chemicals before and after reaction is compared. The values of ΔH are therefore independent of the reaction route because the overall change will be the same.

What happens in between the initial and final states can also be represented on an energy diagram.

For a reaction to occur, particles must move and collide. They must have the right orientation and importantly they need at least a minimum energy. This minimum energy required for a reaction to occur is called the activation energy, E_a.

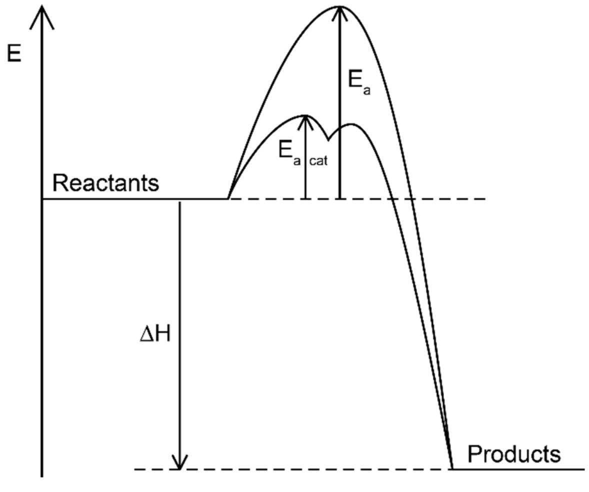
An example of this activation energy requirement is the combustion of a fuel, such as methane. If mixed, methane and oxygen do not react. If a small quantity of energy is then introduced, as a spark or lit match, then the particles gain enough energy and can react. The energy released in this reaction then gives more particles sufficient energy, and so on.

This activation energy, E_a, can be shown on an energy diagram:



In the diagram, the overall enthalpy change is still represented by the ΔH value but the diagram shows the energy, E_a, that the average particle needs to obtain before reaction can occur.

A catalysed reaction provides an alternative reaction route with a lower activation energy. This can also be shown on an energy diagram:



The catalysed reaction has a lower activation energy $E_{a,cat}$ which presents a lower 'barrier' to reaction than the uncatalysed reaction.

Note again that the overall enthalpy change is the same because the relative energies of the reactants and products are unaffected by the reaction route. Catalysts are chemically unchanged at the end of the reaction so they do not contribute anything to the overall enthalpy change.

Solutions to Exercises 95 to 98

Exercise 95

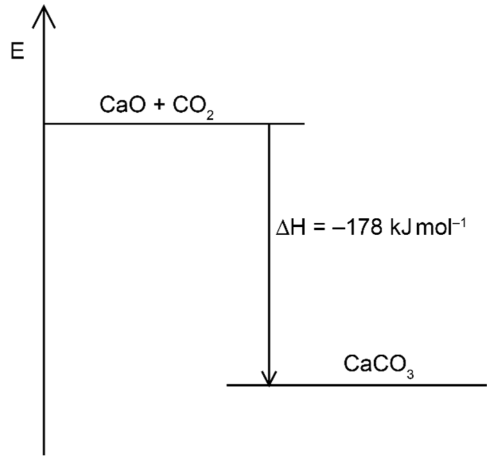
The decomposition of calcium carbonate is shown in an equation by:

$$CaCO_3 \rightarrow CaO + CO_2$$

The question asks for the exact reverse of this reaction and so the enthalpy change will have the same magnitude but the opposite sign.

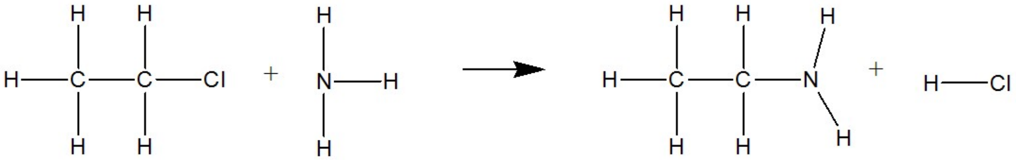
The enthalpy change is therefore –178 kJ mol^{-1}

The negative sign shows that this is an exothermic reaction.



Exercise 96

To start, draw out the structures to show every bond:



To break bonds, energy must be added to the system. To form bonds, energy is released.

Energy IN	**Energy OUT**
1 × C–C = (1 × 348) = +348 kJ mol^{-1} 5 × C–H = (5 × 412) = +2060 kJ mol^{-1} 1× C–Cl = (1 × 338) = +338 kJ mol^{-1} 3× N–H = (3 × 388) = +1164 kJ mol^{-1}	1 × C–C = –(1 × 348) = –348 kJ mol−1 5 × C–H = –(5 × 412) = –2060 kJ mol^{-1} 1 × C–N = –(1 × 305) = –305 kJ mol−1 2 × N–H = –(2 × 388) = –776 kJ mol^{-1} 1 × H–Cl = –(1 × 432) = –432 kJ mol−1
TOTAL IN = +3910 kJ mol^{-1}	TOTAL OUT = –3921 kJ mol^{-1}

Enthalpy change for reaction, ΔH = +3910 – 3921 = –11 kJ mol^{-1}

Exercise 97

The equation for the reaction is:

$$NaOH + HCl \rightarrow NaCl + H_2O$$

0.0350 mol of NaOH and 0.0400 mol of HCl were used. So 0.0350 mol of water will form because the HCl is in excess.

Assumptions:

- The density of the solution is the same as that of water: 1.00 g cm^{-3}.
- The specific heat capacity of the solution is the same as water, 4.2 J g^{-1} $°C^{-1}$.
- The calorimeter does not absorb any energy, and no heat is lost to the surroundings.

Total volume of the solution = 35.0 + 40.0 = 75.0 cm^3

Therefore, total mass of solution is = 75.0 g

Specific heat capacity of the solution = 4.2 J g^{-1} $°C^{-1}$

Temperature rise = 5.60 °C

Therefore, energy change = $75.0 \times 4.20 \times 5.60$ = 1764 J = 1.764 kJ

Number of moles of water formed = 0.0350 mol

enthalpy change $\Delta H = \frac{q}{\text{number of moles}} = -\frac{1.764}{0.0350} = -50.4 \text{ kJ mol}^{-1}$ [of water produced]

Exercise 98

If the temperature rises to 100°C, then the water will boil. At this point the temperature no longer rises as heat is added, which limits the value of ΔT that is measured and causes loss of water from the calorimeter. Therefore, the results will be unreliable and any calculation will be unreliable.

C12. Electrolysis

C12.1	Understand the terms *electrode*, *cathode* (*negative electrode*), *anode* (*positive electrode*) and *electrolyte*.
C12.2	Understand why direct current (dc), and not alternating current (ac), is used in electrolysis.
C12.3	Understand that in electrolysis at the cathode, the cations (positively charged ions) receive electrons (reduction) to change into atoms or molecules, and at the anode, the anions (negatively charged ions) lose electrons to form atoms or molecules (oxidation).
C12.4	Understand and be able to predict the products of the electrolysis of the following: a. aqueous solutions (including those of salts), including situations where more than one ion/molecule is attracted to a single electrode b. molten binary compounds
C12.5	Be able to write half-equations for the processes taking place at each electrode.
C12.6	Explain how electrolysis is used to electroplate objects.

Electrolysis

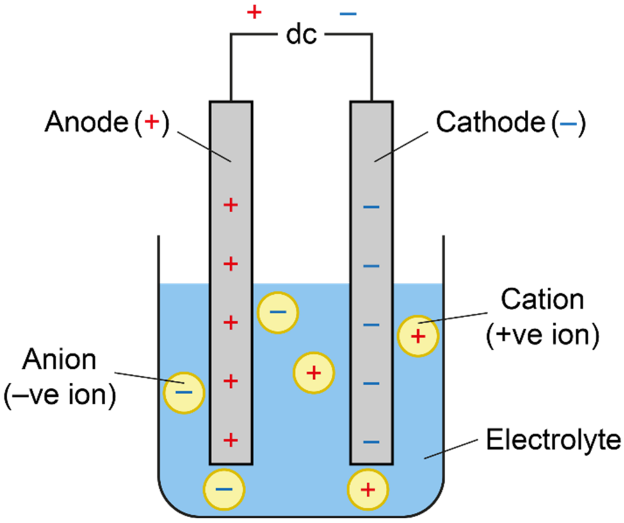
Electrolysis is the process by which a molten ionic substance or a solution containing ions (an electrolyte) is decomposed by an electric current.

The apparatus comprises an electrical cell that consists of two (usually) inert electrodes, which are conductors and often made of graphite, that are immersed into a beaker containing the electrolyte and allow electrons to enter or leave. The ions in the electrolyte are free to move and carry a charge thereby completing the electrical circuit.

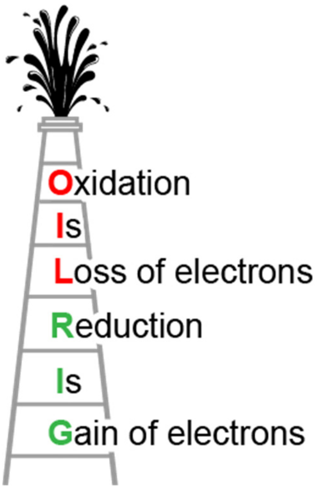
The power supply must be direct current (dc) so that the current passes in one direction only. The power supply is acting as an electron pump. The electrons flow through the external circuit and enter the electrolytic cell via the cathode, which gains a negative charge and so is the negative electrode. Electrons leave the electrolytic cell via the anode, which then has a positive charge and so is the positive electrode.

During the electrolysis, the positive ions (cations) are attracted to the cathode (negative electrode) where they gain electrons and are reduced to form neutral atoms/molecules. The negative ions (anions) are attracted to the anode (positive electrode) where they lose electrons and are oxidised to form neutral atoms/molecules.

Electrons flow in the external circuit from the positive electrode to the negative electrode. The oxidised/reduced ions produce pure elements.

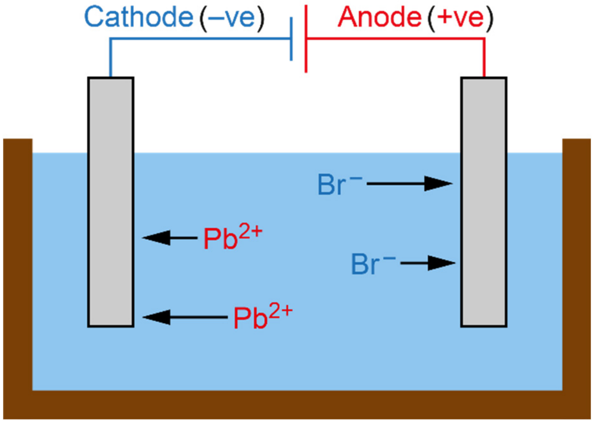


The types of process caused by electron loss or gain can be remembered using ‘OIL RIG’:



Electrolysis of molten lead bromide

In the electrolysis of molten lead bromide, the only ions present are Pb^{2+} and Br^-.



At the cathode (negative electrode), Pb^{2+} ions are attracted and are reduced to form atoms of lead. Lead metal will be seen forming at the electrode. The half-equation for this reaction is:

$$Pb^{2+}(l) + 2e^- \rightarrow Pb(s)$$

At the anode (positive electrode), Br^- ions are attracted and are attracted to form molecules of bromine gas. This gas will be seen as brown fumes at the electrode at the high temperature of the cell. The half-equation for this reaction is: $2Br^-(l) \rightarrow Br_2(g) + 2e^-$

The overall equation for the process is:

$$PbBr_2 \rightarrow Pb + Br_2$$

Exercise 99

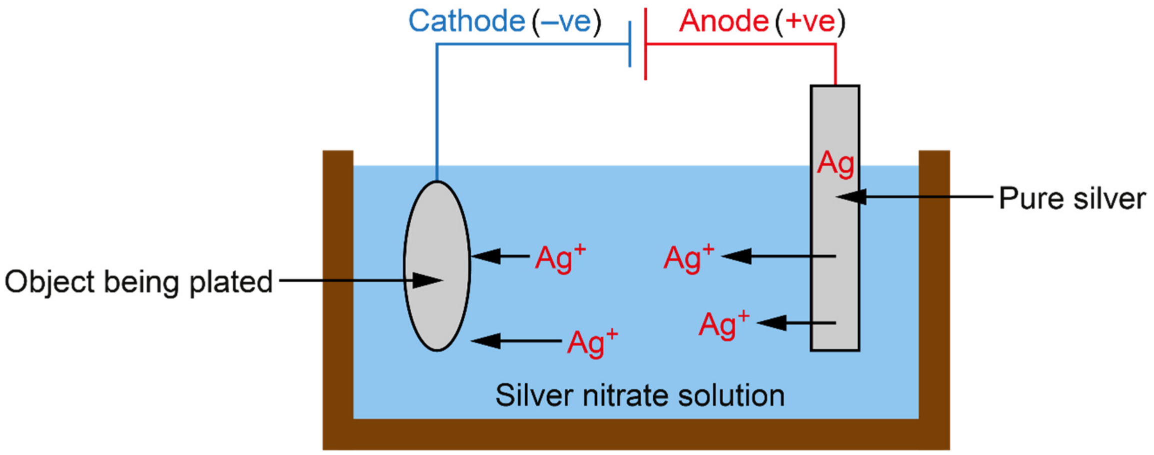
Which of the rows in the table correctly identifies the products of electrolysis of the electrolytes?

	electrolyte being electrolysed	**product at positive inert electrode (anode)**	**product at negative inert electrode (cathode)**
A	aqueous calcium bromide	bromine	calcium
B	aqueous copper nitrate	nitrogen	copper
C	aqueous potassium sulfate	oxygen	hydrogen
D	molten aluminium oxide	aluminium	oxygen
E	molten sodium chloride	chlorine	hydrogen

Electroplating

Electroplating uses electrolysis to coat a cheap metal with a more expensive one (for example, silver) or for protection (for example, chrome plating for car parts).

For example, in the following diagram the object to be silver-plated is made the cathode (negative electrode) in order to attract and reduce the positive metal ions. Both the anode and the electrolyte supply the silver ions for the electroplating. In this case, the anode is not inert.



At the anode, the silver atoms each lose an electron (are oxidised) to form silver ions. The half-equation for the anode reaction is:

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

At the cathode, the silver ions each gain an electron (are reduced) to form silver atoms, which are plated on to the object. This is the reverse of the anode reaction. The half-equation for the cathode reaction is:

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

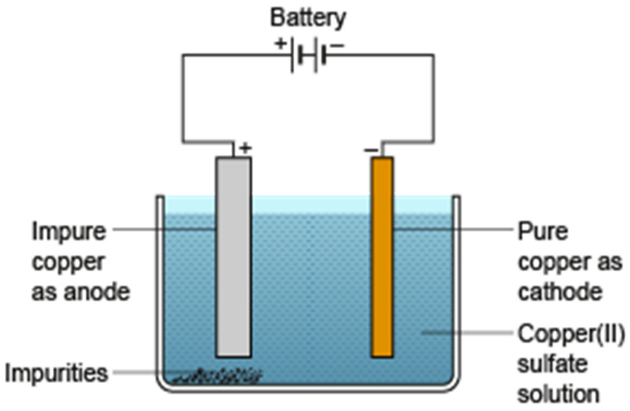
The concentration of silver ions in the electrolyte remains unchanged throughout the process.

Exercise 100

A nickel jug is to be electroplated with silver. Which combination of electrodes and electrolyte would be suitable?

	positive electrode	**negative electrode**	**electrolyte**
A	nickel jug	pure silver	nickel sulfate solution
B	pure silver	nickel jug	nickel sulfate solution
C	nickel jug	pure silver	silver nitrate solution
D	pure silver	nickel jug	silver nitrate solution
E	nickel jug	graphite	nickel sulfate solution
F	graphite	nickel jug	nickel sulfate solution
G	nickel jug	graphite	silver nitrate solution
H	graphite	nickel jug	silver nitrate solution

Purification of copper



Electrolytic refining is used to purify copper. A small piece of pure copper is chosen as the cathode. The anode and the electrolyte supply the copper ions for the electrolysis.

At the anode, copper atoms lose electrons (are oxidised) to form copper(II) ions. The half-equation for the anode reaction is:

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

At the cathode, copper(II) ions gain electrons (are reduced) to form copper atoms which are plated on to the pure copper electrode. The half-equation for the cathode reaction is:

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

Solutions to Exercises 99 to 100

Exercise 99

A) Incorrect – hydrogen gas would be formed at the negative electrode as hydrogen is less reactive than calcium.

B) Incorrect – oxygen would be formed at the positive electrode.

C) Correct – hydrogen gas would be formed at the negative electrode as hydrogen is less reactive than potassium and oxygen would be formed at the positive electrode.

D) Incorrect – the electrodes are given the wrong way round. Aluminium is formed at the negative electrode by reduction of Al^{3+} and oxygen is formed at the positive electrode by oxidation of O^{2-}.

E) Incorrect – these are the products from the electrolysis of aqueous sodium chloride. Sodium metal would be formed at the negative electrode in this electrolysis.

Exercise 100

The object to be electroplated is always made the negative electrode in order to attract the positive silver ions. The positive electrode should be made of the pure metal that is to be plated, in this case silver. The electrolyte should also contain the metal ions to be plated on to the jug.

The correct combination is therefore D).

C13. Carbon / Organic Chemistry

C13.1

General concepts:

a. Know that crude oil is the main source of hydrocarbons and that it is separated into fractions by fractional distillation (names and uses of specific fractions not expected).

b. Understand the link between carbon chain length and the following trends in physical properties of hydrocarbons: boiling points, viscosity, flammability.

c. Know the use of longer chain alkanes in cracking to form shorter chain alkanes and alkenes, and be able to write balanced chemical equations for these reactions.

d. Understand structural isomerism and be able to recognise examples.

e. Understand and be able to use the following terms: *molecular formula*, *full structural formula* (*displayed structure*) and *condensed structural formula*.

f. Understand and be able to use the terms *complete combustion* and *incomplete combustion*, and be able to write balanced chemical equations for such reactions.

g. Know the IUPAC guidelines for the systematic naming of carbon compounds, and apply the guidelines in order to be able to name all the compounds in this section of the specification.

h. Know and understand the terms *homologous series* and *functional group*.

Hydrocarbons

Hydrocarbons are compounds that consist of carbon and hydrogen only.

Examples of hydrocarbons are: methane, CH_4, butane, C_4H_{10}, octane, C_8H_{18}, and ethene, C_2H_4.

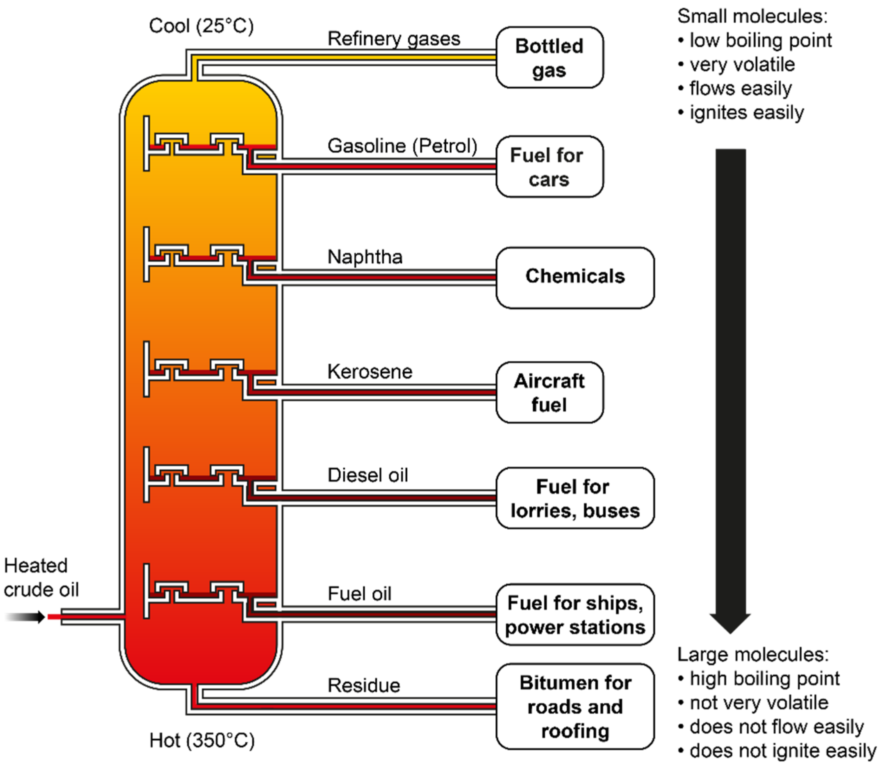
The principal source of hydrocarbons is crude oil: this is a dark, viscous liquid formed over millions of years from the remains of once living organisms.

Crude oil

Crude oil is a complicated mixture of many hydrocarbon molecules of different sizes and shapes. In its raw state crude oil is virtually useless; it needs to be refined to extract useful components from the mixture.

Refining crude oil starts with the process of fractional distillation.

The crude oil is vaporised and passed into the bottom of a long column (a fractionating column) which is hot at the bottom and cool at the top. The different component molecules of the vapour rise until they reach a point where the temperature is below their boiling point; here they condense, and the liquid is run off.



In this way the complex mixture of crude oil is separated into fractions. Each fraction is a smaller part of the starting mixture and consists of hydrocarbon molecules with a range of similar boiling points.

Note from the diagram that the fractions that contain the larger molecules have the higher boiling points, are more viscous (do not flow easily) and are less flammable.

Exercise 101

The table shows a trend in the boiling point of the straight-chain alkanes (a series of hydrocarbons). State and explain this trend.

hydrocarbon	formula	boiling point / °C
methane	CH_4	−164
ethane	C_2H_6	−88
propane	C_3H_8	−42
butane	C_4H_{10}	0
pentane	C_5H_{12}	36
octane	C_8H_{18}	126

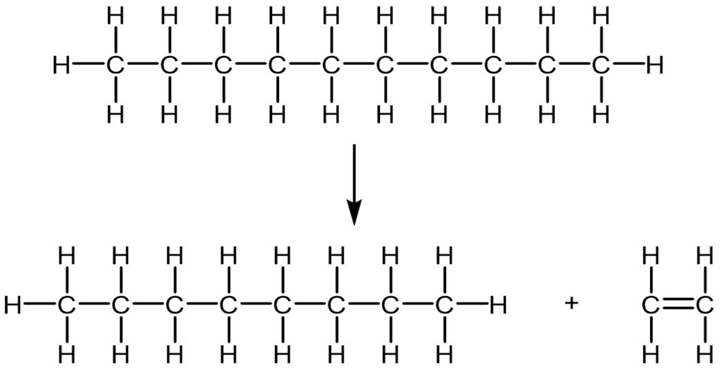
The fractions that contain the larger molecules are generally less useful than fractions containing the smaller molecules.

A second stage in the refining process allows for the production of more of the shorter chain molecules. This second stage is called catalytic cracking. The longer chain molecules are passed over a heated catalyst and are broken down into shorter chain molecules. There are no particular ways in which the larger molecules are broken down. They are random events producing smaller hydrocarbons, some of which contain carbon-to-carbon double bonds (alkenes).

An example of a reaction that might happen is:

decane → octane + ethene

$$C_{10}H_{22} \rightarrow C_8H_{18} + C_2H_4$$



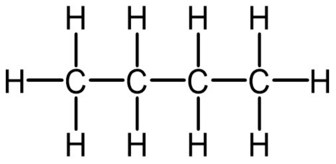
Exercise 102

When a molecule of dodecane ($C_{12}H_{26}$) is cracked, two molecules of ethene (C_2H_4) and one molecule of pentane (C_5H_{12}) are produced. One further molecule is also produced. What will the formula of this molecule be?

Molecular formula

The molecular formula of an organic compound is the formula that indicates the number of atoms of each element in one molecule of that compound. For example, the molecular formula of butane is C_4H_{10}.

However, as organic compounds usually have molecules that are made up of many atoms, it is necessary to specify how these atoms are arranged. This is done by means of a structural formula. For example, the full structural formula of butane is:



This is sometimes called the ‘displayed structure’.

Often the structural formula is shown in a more compact way as a ‘condensed’ structural formula. For example, the condensed structural formula of butane is:

$CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$

Exercise 103

Write out condensed structural formulae for the following compounds:

a. ethane, C_2H_6

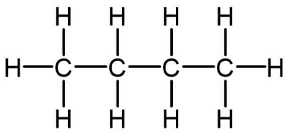
b. hexane, C_6H_{14}

c. ethene, C_2H_4

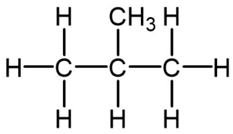
Structural isomerism

Structural isomerism arises when it is possible to sequence the atoms in a molecular formula in more than one way.
Structural isomers share the same molecular formula but have different structural formulas.

For example, butane and 2-methylpropane are structural isomers. They both share the same molecular formula, C_4H_{10} :



butane



2-methylpropane

Exercise 104

Give the structural formulae of the five structural isomers of molecular formula C_6H_{14}.

Combustion of hydrocarbons

The combustion of hydrocarbons is an important and useful reaction. Many hydrocarbons are easily ignited and release considerable amounts of energy when combusted.

The complete combustion of hydrocarbons relies on having a plentiful supply (an excess) of oxygen. The only products will then be carbon dioxide and water.

For example, the equation for the complete combustion of pentane, C_5H_{12}, is:

$$C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$$

The equation may look complicated, but it is surprisingly easy to write and to balance:

- The number of molecules of carbon dioxide formed will be given by the number of carbon atoms in the hydrocarbon.
- The number of molecules of water formed will be half of the number of hydrogen atoms in the hydrocarbon.
- All that remains is to balance the oxygen atoms.

Exercise 105

Write a balanced equation for the complete combustion of octane, C_8H_{18}.

Incomplete combustion of hydrocarbons results from an insufficient supply of oxygen being available to allow complete combustion. The usual outcomes are that instead of all the carbon atoms in the hydrocarbon forming carbon dioxide, some/all carbon atoms will form carbon monoxide (CO) or even be left as C atoms.

For example, an equation for the incomplete combustion of butane could be:

$$C_4H_{10} + 5.5O_2 \rightarrow 2CO + 2CO_2 + 5H_2O$$

Exercise 106

Write a balanced equation for the incomplete combustion of pentane, C_5H_{12}, where carbon monoxide is the only carbon-containing product.

Nomenclature

The naming system (nomenclature) for assigning names to organic compounds follows a set of guidelines set out by IUPAC (International Union of Pure and Applied Chemistry). The start of this naming system is outlined below.
Additional rules for particular families of compounds (homologous series) built from these.

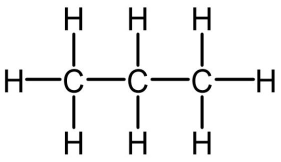
The longest straight chain in a molecule is given a prefix to its name to indicate the number of carbon atoms in that chain:

number of carbon atoms	**prefix**
one	meth-
two	eth-
three	prop-
four	but-
five	pent-
six	hex-
seven	hept-
eight	oct-

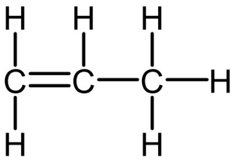
The suffix to the name indicates the homologous series of compounds to which the compound belongs:

- For the alkanes, the suffix is -ane.
- For the alkenes, the suffix is -ene.

For example:



is a straight-chain alkane with 3 carbon atoms. Hence it is propane.

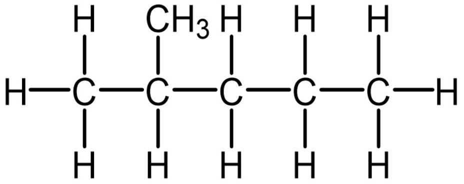


is a straight-chain alkene with 3 carbon atoms. Hence it is propene.

If the molecule has a branched chain, the following additional rules apply:

- The carbon atoms in the longest straight chain are numbered such that the position of the branches have the lowest possible numbers.
- The branches are named: methyl for a branch with one carbon atom, ethyl for a branch with two carbon atoms, and so on.
- The branches are named and numbered as a prefix to the main name.

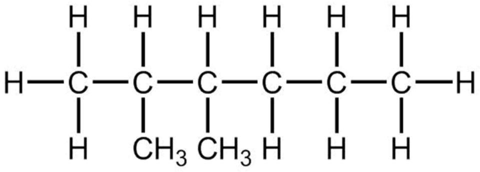
For example:



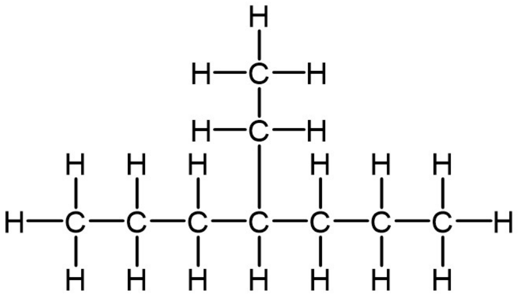
The longest straight chain has 5 carbon atoms, and is numbered from the left-hand end such that the branch is on the lowest possible numbered position – 2 in this case. (Note that if the chain were numbered from the right-hand end the branch would be on position 4).

The branch has one carbon atom, so it is a methyl branch.

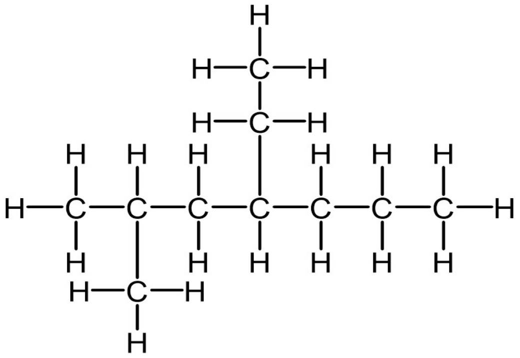
The name is 2-methylpentane.



This molecule is 2,3-dimethylhexane (Note the use of di- to indicate two methyl branches)



This molecule is 4-ethylheptane.

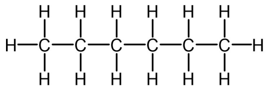


This molecule is 4-ethyl-2-methylheptane. (Note that the ethyl branch comes before the methyl branch as alphabetical order applies here).

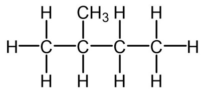
Exercise 107

Name the following alkanes:

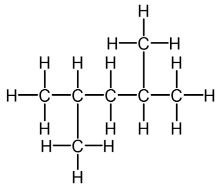
a)



b)



c)



d)

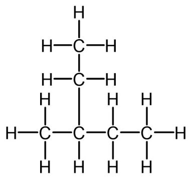


Photo: Pixabay

C13.2 Alkanes (saturated hydrocarbons):

a. Describe alkanes as a homologous series with the general formula of C_nH_{2n+2}.

b. Be able to name, or recognise from the name, the C1 to C6 straight-chain alkanes.

C13.3 Alkenes (unsaturated hydrocarbons):

a. Describe alkenes as a homologous series with a double bond and the general formula C_nH_{2n}.

b. Be able to name, or recognise from the name, C2 to C6 straight-chain alkenes, including the position of the double bond.

c. Recognise and be able to use the test for unsaturation with bromine water.

d. Know that addition reactions take place with the following substances: hydrogen, halogens, hydrogen halides and steam. Be able to write the balanced chemical equations for these reactions and recognise the formulae of the products formed. (Mechanisms and consideration of carbocation stability are not required.)

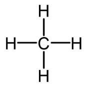
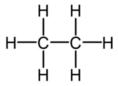
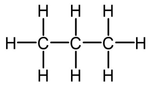
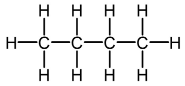
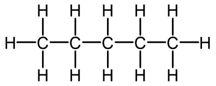
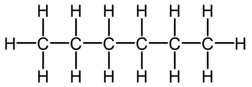
Homologous series

Homologous series are series of organic compounds that have similar chemical properties and the same general formula. The members of a homologous series have similar chemical properties because they share the same functional group (the reactive part of their molecules). The members of the same series differ only in the length of their carbon skeleton.

Alkanes

Alkanes are the simplest homologous series. This is a series of hydrocarbons that have no functional group. The members of the series are comprised of saturated chains of carbon atoms. Saturated means that all the carbon-to carbon bonds in the molecule are single bonds.

The first six members of the straight-chain alkanes are:

name	molecular formula	displayed structural formula
methane	CH_4	
ethane	C_2H_6	
propane	C_3H_8	
butane	C_4H_{10}	
pentane	C_5H_{12}	
hexane	C_6H_{14}	

From the molecular formulae it can be seen that each member of the series has one carbon atom and two hydrogens atoms more than the previous member. A general formula can be written for the alkanes:

C_nH_{2n+2} where n is the number of carbon atoms

Exercise 108

What is the molecular formula for the straight-chain alkanes that contain:

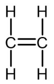
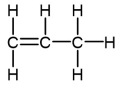
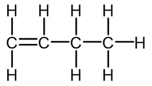
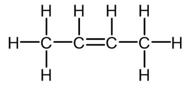
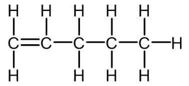
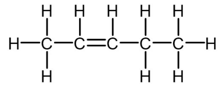
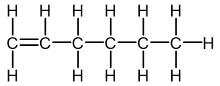
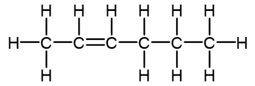
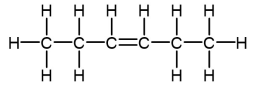
a. 10 carbon atoms?
b. a total of 26 atoms?
c. 60 hydrogen atoms?

Alkenes

Alkenes are a homologous series of unsaturated hydrocarbons.

Their molecules contain carbon and hydrogen atoms only, but there is at least one carbon-to-carbon bond in the molecule that is a double bond (C=C).

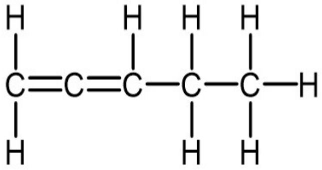
All of the straight-chain alkenes containing up to six carbon atoms and one double bond are shown below:

name	molecular formula	displayed structural formula
ethene	C_2H_4	
propene	C_3H_6	
but-1-ene	C_4H_8	
but-2-ene	C_4H_8	
pent-1-ene	C_5H_{10}	
pent-2-ene	C_5H_{10}	
hex-1-ene	C_6H_{12}	
hex-2-ene	C_6H_{12}	
hex-3-ene	C_6H_{12}	

Note the nomenclature rules that apply here:

- The number that indicates the position of the double bond is the lower of the two possible numbers. For example, in but-1-ene the double bond is between carbon atoms 1 and 2, but it is the lower number that is used.
- The number is inserted in the name after the prefix and before the suffix
- If there is more than one double bond, the suffix -diene, -triene, and so on, is used. Each double bond must have a number to indicate its position.

For example:



is pent-1,2-diene

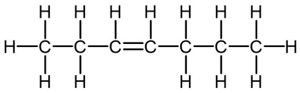
From the molecular formulae, it can be seen that the homologous series of alkenes (with one double C=C bond) has the general formula:

C_nH_{2n} where *n* is the number of carbon atoms

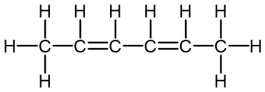
Exercise 109

Given that 7 carbon atom chain molecules have the prefix ‘hept-’, name the following alkenes:

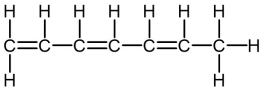
a)



b)



c)

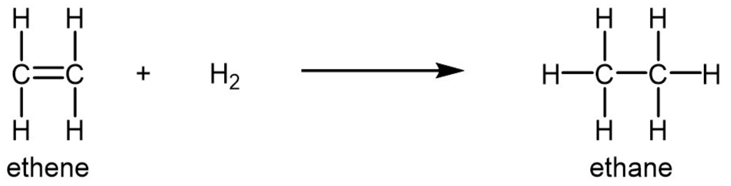


Reactions of the alkenes

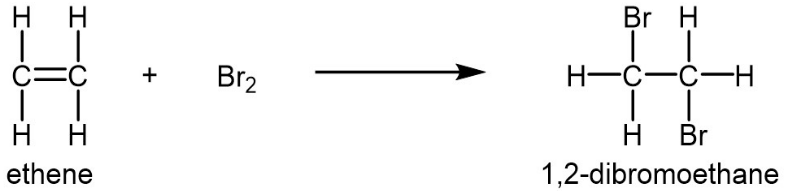
The reactive site (functional group) in alkene molecules is the C=C double bond. In addition reactions, the double bond opens up and allows two further atoms/groups to bond to the two carbon atoms of the double bond. In so doing, the ‘unsaturated’ reactant molecule (the alkene) becomes a ‘saturated’ product molecule.

Four addition reactions of alkenes are shown below. In each case, ethene is the alkene that is used as the example.

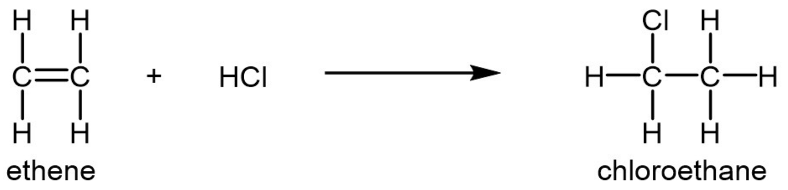
- Reaction with hydrogen



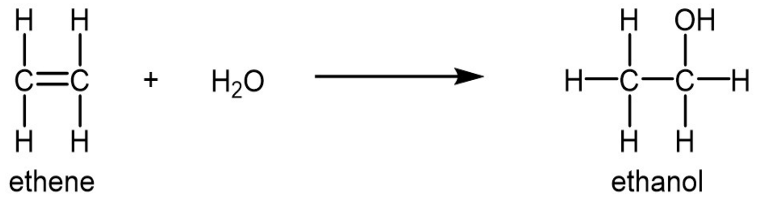
- Reaction with halogens (for example, bromine)



- Reaction with hydrogen halides (for example, hydrogen chloride)



- Reaction with steam



(Note that the water molecule has been added across the double bond. H goes to one carbon atom and OH goes to the other carbon atom.)

Exercise 110

Write balanced equations for, and name the products of, the following addition reactions of alkenes:

a) propene + hydrogen

b) pent-2-ene + chlorine

c) hex-3-ene + hydrogen bromide

d) but-2-ene + steam

A test for unsaturation

One of the four addition reactions is used as a test for unsaturation (the presence of C=C bonds) in a molecule.
When bromine is added across a double bond, the reaction is rapid, and the product molecule will be colourless. Hence an obvious colour change will be seen. The bromine used is usually in an aqueous solution called bromine water.

For example, if ethene gas is bubbled into a solution of bromine water, there will be a colour change in the solution from orange-brown (the colour of bromine in aqueous solution) to colourless (the colour of the 1,2-dibromoethene produced).

Pentene and hexene are liquids at room temperature and pressure. In these cases, the test is carried out by adding a few drops of bromine water to a sample of the liquid alkene. The result is the same: the bromine water is decolourised.

No such addition reactions can happen when bromine water is added to samples of alkanes. Hence this reaction is used to distinguish between alkanes and alkenes.

C13.4

Polymers:

a. Addition polymerisation, polyalkenes:

  i. Know that alkenes or other molecules with a C=C bond may react with each other to form long-chain saturated molecules called polymers by addition reactions called polymerisation, and that the unsaturated molecules are called monomers.

  ii. If given an unsaturated monomer molecule, be able to recognise the structure of the polymer and vice versa.

  iii. Be able to recognise the repeating unit of these polymers.

b. Condensation polymerisation, polyesters and polyamides (to include amino acids forming proteins):

  i. If given the monomer molecules, be able to recognise the structure of the polymer and *vice versa*.

  ii. Be able to recognise the repeating unit of these polymers.

c. Understand the terms *biodegradable* and *non-biodegradable* when applied to polymers.

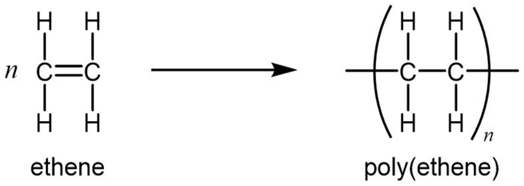
Addition polymerisation

This is an important and useful reaction of alkenes. During polymerisation, the reactant alkene molecules react with each other to form very long-chain product molecules.

The following are key features of addition polymerisation:

- The small reactant alkene molecules are unsaturated and are called monomers.
- During polymerisation, one of the bonds in the C=C of the monomer molecules is broken, and C-C bonds are formed end to end between neighbouring monomer molecules.
- The reaction described is an addition reaction.
- The long-chain molecule incorporates variable numbers of monomer molecules, but it is usually in the region of single thousands to tens of thousands.
- The large product molecule is saturated and is called a polymer.

The process can be summarised by means of an equation. For example, the equation for the addition polymerisation of ethene is:



In this instance, *n* represents a large number and -[-CH_2-CH_2-]- is called the repeating unit of the polymer. Note also that the name of the polymer is derived from the name of the monomer with the addition of the prefix ‘poly-’.

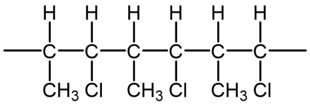
The conditions used for addition polymerisation reactions vary, but they normally involve high pressures and the use of catalysts.

Exercise 111

Write an equation for the polymerisation of the alkene propene.

Exercise 112

The following is a section of a polyalkene:



a) Draw the repeat unit of the polymer.

b) Draw the structure and give the name of the monomer involved in the formation of the polymer.

Condensation polymerisation

Like addition polymerisation, condensation polymerisation is a reaction in which small molecules called monomers join to produce a long-chain molecule called a polymer.

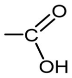
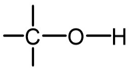
In addition polymerisation the addition reaction that links the monomer molecules does not produce any other product. However, in condensation polymerisation a small molecule, typically H_2O or HCl, is eliminated every time a linkage is made, and so there is a by-product to the reaction. The joining of two molecules with the elimination of a small molecule as a by-product is called a condensation reaction.

A further difference between the two types of polymerisation is that in an addition polymerisation there is only one type of monomer molecule. However, condensation polymerisation often involves two different types of monomer molecules. Each monomer must have at least two (similar or different) functional groups. This allows it to form linkages at two different positions in the molecule.

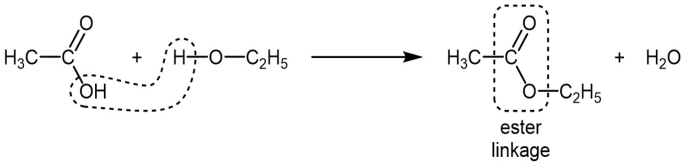
The two main types of condensation polymers are polyesters and polyamides.

Polyesters

Polyesters are condensation polymers in which the monomers are joined by ester linkages.

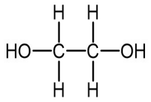
To form an ester linkage the carboxyl group of a carboxylic acid,  ,combines with a hydroxyl group of an alcohol, 

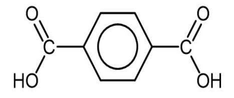
When these two functional groups react a molecule of water is eliminated and the two carbon atoms are linked by an oxygen atom. For example:



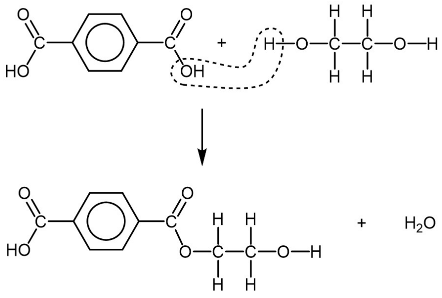
An example of a polyester is terylene which can be made as a fibre to make clothing.

Terylene is made by a condensation polymerisation reaction involving two monomers: ethane-1,2-diol and benzene1,4-dicarboxylic acid.


ethane-1,2-diol

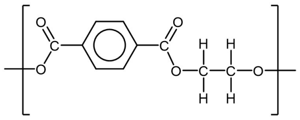

benzene-1,4-dicarboxylic acid

An ester linkage is formed as follows:



Further ester linkages can now happen at both ends of the above molecule, giving a larger molecule that can also form ester linkages at both its ends. This continues and a very large molecule, the polymer, is built.

The simplest repeat unit of this polymer (terylene) is:



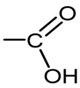
Exercise 113

Hexanedioic acid, $HOOC(CH_2)_4COOH$, and butane-2,3-diol, $HOCH(CH_3)CH(CH_3)OH$, can act as monomers to produce a condensation polymer.

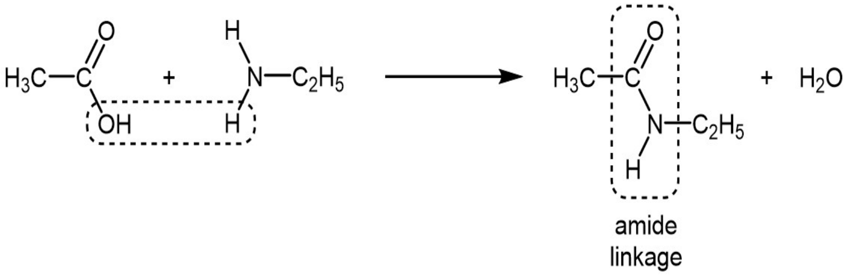
Draw the repeat unit of this polymer, and then draw a section of the polymer that contains 3 repeat units.

Polyamides

Polyamides are condensation polymers in which the monomers are joined by amide linkages.

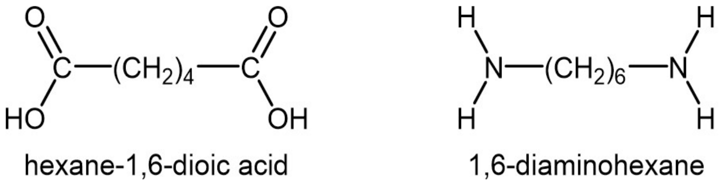
To form an amide linkage the carboxyl group of a carboxylic acid,  $-COOH$ combines with an amine group, $-NH_2$.

When these two functional groups react a molecule of water is eliminated. For example:

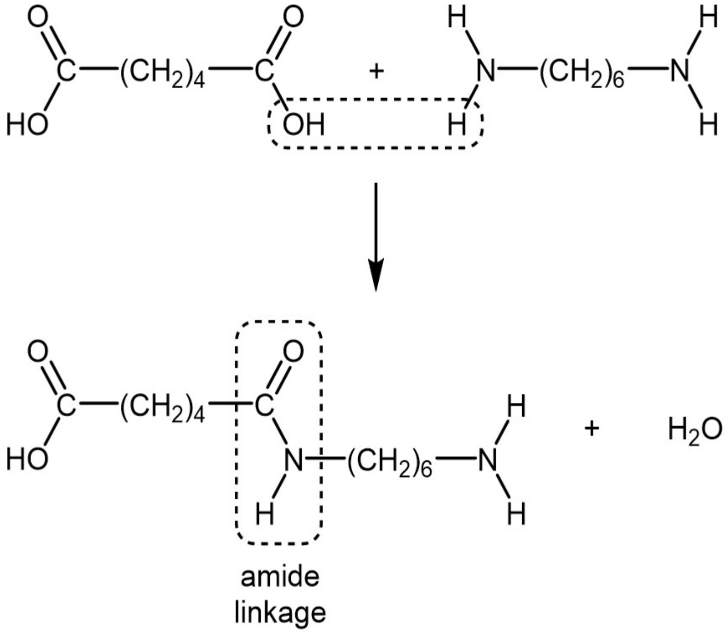


An example of a polyamide is nylon-6,6 which can also be made as a fibre with which to make clothing.

Nylon-6,6 is made by a condensation polymerisation reaction involving two monomers: hexane-1,6-dioic acid and 1,6diaminohexane.

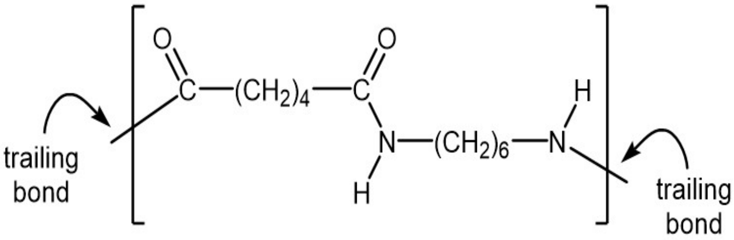


An amide linkage is formed as follows:



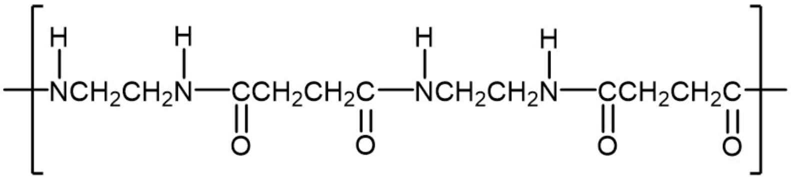
Further amide linkages can now happen at both ends of the above molecule, giving a larger molecule that can also form amide linkages at both its ends. This continues and a very large molecule, the polymer, is built.

The simplest repeat unit of this polymer (nylon-6,6) is:



Exercise 114

The following is a section of a polyamide:



$$\left[-\overset{H}{N}CH_2CH_2\overset{H}{N}-\underset{O}{C}CH_2CH_2\underset{O}{C}-\overset{H}{N}CH_2CH_2\overset{H}{N}-\underset{O}{C}CH_2CH_2\underset{O}{C}-\right]$$

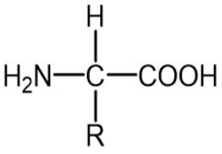
Draw the structures of the two different types of monomer used to make this polymer.

Proteins

Proteins are formed from long chains of amino acids joined by amide linkages (although in this context these linkages are normally called peptide bonds). These long chains are then folded into particular shapes to make the protein.

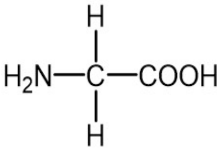
Amino acids, are a group of organic molecules that consist of an amino group (−NH_2), a carboxyl group (−COOH), and an organic ‘R-group’ (or ‘side-chain’) that is unique to each amino acid. These three groups are bonded to the same (central) carbon atom. The fourth bond to this carbon atom is a C−H bond.

The simplest amino acid is glycine, where the organic R-group is another hydrogen atom.



$$H_2N-\overset{H}{\underset{R}{C}}-COOH$$

general formula of an amino acid

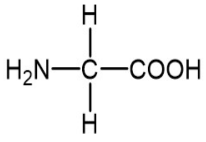


$$H_2N-\overset{H}{\underset{H}{C}}-COOH$$

glycine, the simplest amino acid

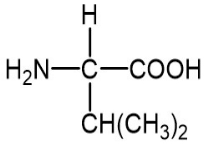
Exercise 115

Three different amino acids are shown below:



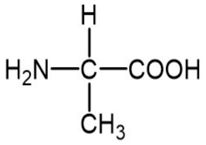
$$H_2N-\underset{H}{\overset{H}{C}}-COOH$$

glycine (Gly)



$$H_2N-\underset{CH(CH_3)_2}{\overset{H}{C}}-COOH$$

valine (Val)



$$H_2N-\underset{CH_3}{\overset{H}{C}}-COOH$$

alanine (Ala)

A ‘tripeptide’ molecule is formed when three amino acid molecules link together.
Draw the structure of the tripeptide formed when the three amino acids link in the sequence alanine-glycine-valine (Ala-Gly-Val).

Biodegradable and non-biodegradable polymers

Biodegradable polymers break down (degrade) after their intended use to produce such natural products as: CO_2, N_2, H_2O, and so on. This natural breakdown is usually brought about by the action of microorganisms or enzymes.

Biodegradable polymers often contain ester or amide linkages.

An example of a biodegradable polymer is PLA, poly(lactic acid), used to make eco-friendly plastic cups.

Non-biodegradable polymers are not broken down after their intended use. Most polymers are of this type and they tend to consist of long chains of carbon and hydrogen atoms. The strong bonding between these atoms makes them resistant to breakdown by microorganisms or enzymes.

C13.5
Alcohols:

- *a.* Describe alcohols as a homologous series with the general formula $C_nH_{2n+1}OH$.
- *b.* Be able to name, or recognise from the name, C1 to C6 straight-chain alcohols, including the position of the -OH group.
- *c.* Describe the reaction of alcohols with sodium metal.

C13.6
Carboxylic acids:

- a. Describe carboxylic acids as a homologous series with the general formula $C_nH_{2n+1}COOH$.
- b. Be able to name, or recognise from the name, C1 to C6 straight-chain carboxylic acids.
- c. Describe the chemical properties of carboxylic acids as those of weak acids, and so be able to predict their reactions and determine the formulae of their salts.
- d. Know that carboxylic acids react with alcohols in the presence of an acid catalyst to produce esters.

Alcohols

Alcohols are a homologous series of organic compounds that contain the hydroxyl functional group, -OH.

The formula3 of the first four members of the series are:

CH_3OH C_2H_5OH C_3H_7OH C_4H_9OH

From this it can be seen that the members of the series share the general formula $C_nH_{2n+1}OH$.

Exercise 116

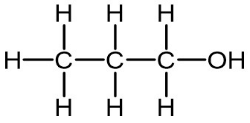
a) What is the formula of an alcohol with six carbon atoms?

b) What is the formula of an alcohol with a total of 20 hydrogen atoms?

The naming system (nomenclature) of the alcohols involves all previous rules, and the following additional rules apply:

- The suffix (ending) to the name is '-ol'.
- The prefix to the name indicates the number of carbon atoms in the molecule. '-an-' (for saturated carbon chains) is added to the usual prefix. For example: 'methan-', 'ethan-' .
- A number is used, where necessary, to indicate the position of the -OH group. This number is placed between the prefix and the suffix.

For example:



$$\begin{array}{c} \quad H \quad H \quad H \\ \quad | \quad\; | \quad\; | \\ H-C-C-C-OH \\ \quad | \quad\; | \quad\; | \\ \quad H \quad H \quad H \end{array}$$

is propan-1-ol

Note that methanol (CH_3OH) and ethanol (C_2H_5OH) do not need a number because the -OH group can only be in one position in the molecule.

Exercise 117

Name the following alcohols:

a) $CH_3CH(OH)CH_3$

b) $CH_3CH_2CH_2CH(OH)CH_2CH_3$

c) $CH_3CH_2CH_2CH_2OH$

Exercise 118

What are the structural formulae for and names of all the straight-chain alcohols with five carbon atoms?

Alcohols react with sodium metal in a similar way to the way in which water reacts with sodium metal. The structures of water and alcohols have a similarity:

$H-OH$	CH_3-OH	C_2H_5-OH
water	methanol	ethanol

When sodium is added to water, the reaction is fast and vigorous. The products are hydrogen gas and a colourless solution of sodium hydroxide.

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

When sodium is added to ethanol the reaction is much slower and more moderate. The products are hydrogen gas and a colourless solution of sodium ethoxide.

$$2Na + 2C_2H_5OH \rightarrow 2C_2H_5ONa + H_2$$

Sodium ethoxide, C_2H_5ONa, like sodium hydroxide, is a strong alkali when in aqueous solution. The formula of sodium ethoxide may not look like that of sodium hydroxide because of the way in which sodium hydroxide is usually written.

However, if sodium hydroxide is written as HONa the similarity to sodium ethoxide is more obvious.

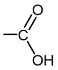
The reaction can be used as a test for the -OH group in alcohols. Tt can also be used as a means for more safe disposal of sodium.

Exercise 119

Write a balanced equation for the reaction of sodium with methanol. Name the organic product of the reaction.

Carboxylic acids

Carboxylic acids are a homologous series of organic compounds that contain the carboxyl functional group:



The formulae of three consecutive members of the series are:

CH_3COOH C_2H_5COOH C_3H_7COOH

From this it can be seen that the members of this homologous series share the general formula: $C_nH_{2n+1}COOH$.

Exercise 120

a) What would be the formula of a carboxylic acid with 6 carbon atoms?

b) CH_3COOH is not the first member of the series. What is the molecular formula of the first member of the series?

The naming system (nomenclature) of the carboxylic acids involves all previous rules, and the following additional rules apply:

- The suffix (ending) to the name is '-oic acid'.
- The prefix to the name indicates the number of carbon atoms in the molecule (including the carbon atom of the carboxyl group). '-an-' (for saturated carbon chains) is added to the usual prefix. For example: 'methan-', 'ethan-'.
- No number is needed to indicate the position of the carboxyl group. This is because the carbon atom of the carboxyl group must be the first carbon atom in the chain (it has already got three bonds, and can therefore only link once into the chain of carbon atoms).

For example: CH_3COOH is ethanoic acid.

Exercise 121

a) What will be the name of the carboxylic acid for which $n = 4$ in $C_nH_{2n+1}COOH$?

b) Draw the structural formula for hexanoic acid.

Carboxylic acids are weak acids.

They are only partially dissociated into ions when in aqueous solution:

$$RCOOH(aq) \rightleftharpoons RCOO^-(aq) + H^+(aq)$$

The reactions of the carboxylic acids include all the reactions generally associated with acids. They react with:

- metals – to form a salt and hydrogen
- bases – to form a salt and water
- carbonates – to form a salt, water and carbon dioxide

For example, ethanoic acid reacts with magnesium:

$$\underset{\text{ethanoic acid}}{2CH_3COOH} + Mg \rightarrow \underset{\text{magnesium ethanoate}}{(CH_3COO)_2Mg} + H_2$$

Note:

- the acids are monoprotic
- the names of the salts end with '-oate'
- the formula of the salt is often written in an unusual way with the anion first

Exercise 122

Write equations for the following reactions and name the salt produced

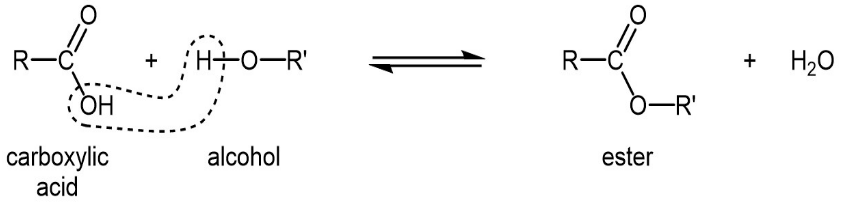
a) propanoic acid + sodium hydroxide

b) butanoic acid + zinc

c) propanoic acid + magnesium oxide

d) ethanoic acid + potassium carbonate

Carboxylic acids react with alcohols to produce esters. In this reaction a carboxylic acid molecule and an alcohol molecule join together, and a molecule of water is eliminated. Note that the reaction is reversible.



The reaction requires the use of an acid catalyst. Concentrated sulfuric acid is often used.

For example, the reaction between ethanoic acid and methanol:

$$\underset{\text{ethanoic acid}}{CH_3COOH} + \underset{\text{methanol}}{CH_3OH} \xrightleftharpoons{\text{conc. } H_2SO_4} \underset{\text{methyl ethanoate}}{CH_3COOCH_3} + \underset{\text{water}}{H_2O}$$

Note that, in naming the ester, the first part of the name comes from the alcohol and the second part of the name is the salt of the carboxylic acid.

Exercise 123

What are the formulae and names of the esters produced from the following pairs of carboxylic acids and alcohols?

a) ethanoic acid + ethanol

b) methanoic acid + ethanol

c) propanoic acid + methanol

Solutions to Exercises 101 to 123

Exercise 101

The larger the molecule (the longer the chain) the higher is the boiling point of the alkane. The process of boiling involves overcoming the attractive forces between molecules in the liquid state.

The larger the molecule, the larger these intermolecular forces are. Hence, more energy is needed to overcome them and the higher the boiling point will be.

Exercise 102

$C_{12}H_{26} \rightarrow 2C_2H_4 + C_5H_{12} + X$

X must contain 12 − 9 = 3 carbon atoms, and 26 − 20 = 6 hydrogen atoms.

Hence, X must be C_3H_6 (propene).

Exercise 103

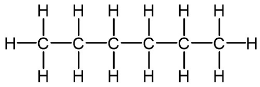
a. CH_3CH_3

b. $CH_3(CH_2)_4CH_3$

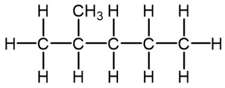
c. $CH_2{=}CH_2$

Note: Whilst single carbon-to-carbon bonds are not shown in condensed structural formulae, it is usual to show carbon-to-carbon double bonds (C=C).

Exercise 104



1



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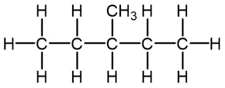

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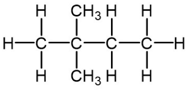

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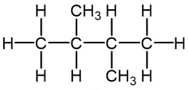
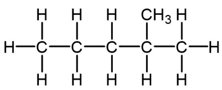
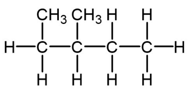


5

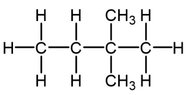
Note:



is the same as structure **2**



is the same as structure **3**



is the same as structure **5**

Exercise 105

The unbalanced equation is: $C_8H_{18} + O_2 \rightarrow CO_2 + H_2O$

The 8 carbon atoms in C_8H_{18} will lead to the production of $8CO_2$

The 18 hydrogen atoms in C_8H_{18} will lead to the production of $9H_2O$

The equation now becomes: $C_8H_{18} + O_2 \rightarrow 8CO_2 + 9H_2O$

There are 16 + 9 = 25 oxygen atoms on the right-hand side of the equation, and so to balance this there needs to be $\frac{25}{2}$ = 12.5 molecules of O_2 on the left-hand side.

The final equation is: $C_8H_{18} + 12.5O_2 \rightarrow 8CO_2 + 9H_2O$

The equation can be left like this but it can also be doubled to give whole numbers:

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$$

Exercise 106

The unbalanced equation is: $C_5H_{12} + O_2 \rightarrow CO + H_2O$

The 5 carbon atoms in C_5H_{12} will lead to the production of 5CO.

The 12 hydrogen atoms in C_5H_{12} will lead to the production of $6H_2O$.

The equation now becomes: $C_5H_{12} + O_2 \rightarrow 5CO + 6H_2O$

There are 5 + 6 = 11 oxygen atoms on the right-hand side of the equation, and so to balance this there needs to be $\frac{11}{2}$ = 5.5 molecules of O_2 on the left-hand side.

The final equation is: $C_5H_{12} + 5.5\ O_2 \rightarrow 5CO + 6H_2O$

The equation can be left like this but it can also be doubled to give whole numbers:

$$2C_5H_{12} + 11O_2 \rightarrow 10CO + 12H_2O$$

Exercise 107

a) hexane

b) 2-methylbutane

c) 2,4-dimethylpentane

d) 3-methylpentane (note that this could be mistakenly named 2-ethylbutane, but the longest straight chain has 5carbon atoms and so it is named as a branched pentane)

Exercise 108

a) Applying C_nH_{2n+2} with n = 10, the number of hydrogen atoms is 22.

The molecular formula is $C_{10}H_{22}$

b) From the general formula: $n + (2n + 2) = 26$

So, $3n = 24$ and $n=8$

The molecular formula is C_8H_{18}

c) If the number of hydrogens is 60, the number of carbons is $\frac{60-2}{2}$ = 29 The molecular formula is $C_{29}H_{60}$

Exercise 109

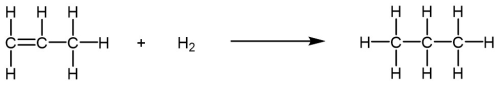
a) Seven carbon atoms. One double bond between carbon atoms 3 and 4. Hence, it is hept-3-ene.

b) Six carbon atoms. Two double bonds between carbon atoms 2 and 3, and between carbon atoms 4 and 5. Hence, it is hex-2,4-diene.

c) Seven carbon atoms. Three double bonds between carbon atoms 1 and 2, 3 and 4, and 5 and 6. Hence, it is hept-1,3,5-triene.

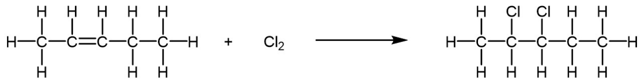
Exercise 110

a)



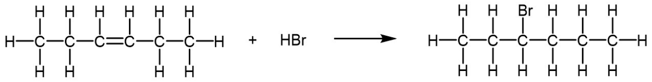
propane

b)



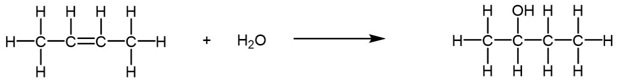
2,3-dichloropentane

c)



3-bromohexane

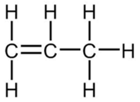
d)



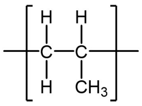
butan-2-ol

Exercise 111

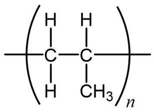
Propene is the monomer and has the structure:



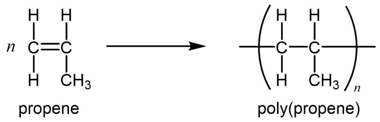
The repeating unit of the polymer is derived by changing the double bond to a single bond, and then adding trailing single bonds to the two carbon atoms of the double bond.



The polymer is then shown as the repeating unit, complete with its ‘trailing’ bonds, inside square brackets with a small subscript ‘n’ outside the closing bracket.
Thus:



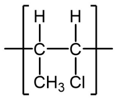
The equation for the polymerisation of propene is therefore:



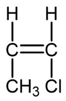
Note that to balance the equation there must be *n* monomer molecules on the reactant side.

Exercise 112

To find the repeat unit of a polyalkene simply take the first two carbon atoms in the chain and add a trailing bond to the second carbon atom. Hence for a) the repeat unit is:



To derive the monomer from the repeat unit, remove the trailing bonds and re-instate the C=C bond.
Hence for b) the structure of the monomer is:

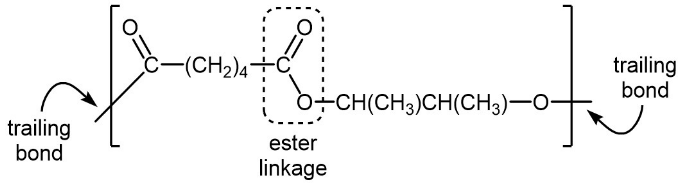


The name of this monomer is 1-chloroprop-1-ene. Note that it is necessary to indicate the position of the double bond (…-1-ene) to show that both the chlorine and the double bond are on the first carbon atom.

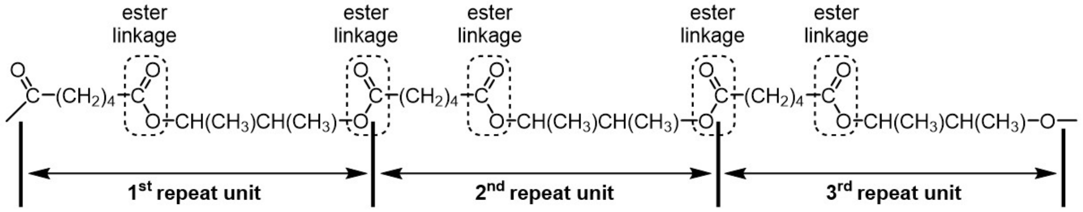
Exercise 113

The repeat unit can be arrived at by first linking the two monomers by an ester linkage. Attention should then turn to the two functional groups at the ends of this molecule: the atoms that would be eliminated to form the next ester linkages should be removed leaving trailing bonds in their place. This can be checked by imagining the molecule wrapped around so that the two ends meet. If the two trailing bonds are joined there should now be another ester linkage.

In this case the repeat unit is:

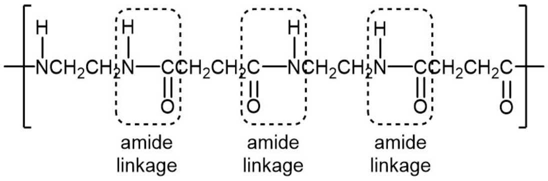


To draw a section of the polymer containing three repeat units 6 monomer molecules are needed, 3 of each type. Alternate these monomers in a chain and join them with five ester linkages. Finally remove the atoms that would be eliminated at each end of the molecule in forming the next ester linkages (as when drawing the repeat unit).



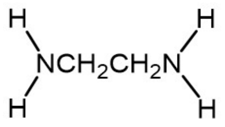
Exercise 114

First identify the amide linkages:

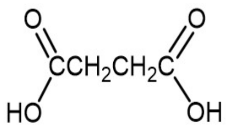


There are 3 amide linkages joining 4 monomer molecules.

Working from the left-hand side and the first amide linkage it is possible to see that the first monomer unit is:

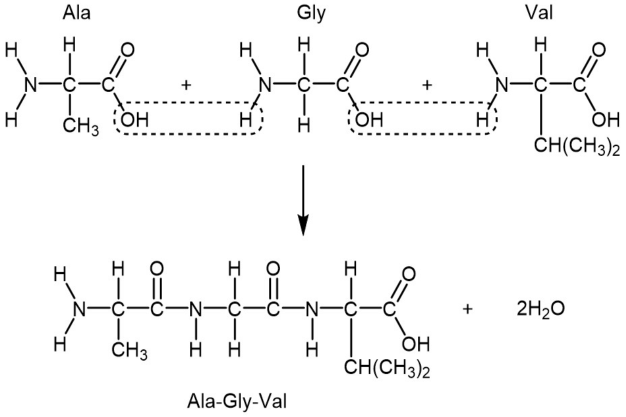


Working from the first and second linkages it is possible to see that the second monomer unit is:



Exercise 115

To draw this structure, arrange the three amino acids in the correct sequence and then form the two amide linkages (peptide bonds) necessary to join the three amino acids.



Exercise 116

a) $n = 6$ and hence the formula is $C_6H_{13}OH$

b) There are 20 hydrogen atoms in total. One of these is in the OH group, leaving 19 hydrogens.

Hence $2n + 1 = 19$, and therefore $n = 9$. The formula is $C_9H_{19}OH$.

Exercise 117

a) This structure has a chain of three carbon atoms, and the -OH group is on the second carbon atom.

Hence it is propan-2-ol.

b) This structure has a chain of six carbon atoms, and the -OH group is on the third carbon atom.

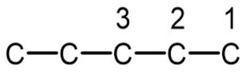
Hence it is hexan-3-ol.

c) This structure has a chain of four carbon atoms, and the -OH group is on the first carbon atom.

Hence it is butan-1-ol.

Exercise 118

With a chain of five carbon atoms, the -OH group can be in any of the following positions:



$$\overset{}{C}-C-\overset{3}{C}-\overset{2}{C}-\overset{1}{C}$$

Hence there are three possible structural formulae:

$CH_3CH_2CH_2CH_2CHOH$ pentan-1-ol

$CH_3CH_2CH_2CH(OH)CH_3$ pentan-2-ol

$CH_3CH_2CH(OH)CH_2CH_3$ pentan-3-ol

Exercise 119

Following the example for ethanol, the equation is:

$$2Na + 2CH_3OH \rightarrow 2CH_3ONa + H_2$$

CH_3ONa is sodium methoxide.

Exercise 120

a) The 6 carbon atoms include the carbon atom of the carboxyl group. Hence there are 5 carbon atoms in the stem, so $n = 5$. The formula is therefore $C_5H_{11}COOH$.

b) The first member of the series will be when $n = 0$. The formula of the first member is therefore HCOOH.

Exercise 121

a) If $n = 4$, the formula will be C_4H_9COOH.

This carboxylic acid has 5 carbon atoms, and is therefore pentanoic acid.

b) Hexanoic acid will have a total of 6 carbon atoms. Hence its structural formula is:

$$CH_3CH_2CH_2CH_2CH_2COOH$$

Exercise 122

a) $C_2H_5COOH + NaOH \rightarrow C_2H_5COONa + H_2O$

The salt is sodium propanoate

b) $2C_3H_7COOH + Zn \rightarrow (C_3H_7COO)_2Zn + H_2$

The salt is zinc butanoate

c) $2C_2H_5COOH + MgO \rightarrow (C_2H_5COO)_2Mg + H_2O$

The salt is magnesium propanoate

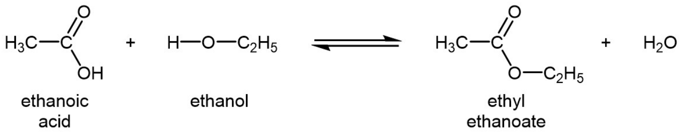
d) $2CH_3COOH + K_2CO_3 \rightarrow 2CH_3COOK + CO_2 + H_2O$

The salt is potassium ethanoate

Exercise 123

Draw the structures of the acid first followed by the alcohol (drawn in the manner HO-R). Join the molecules together by eliminating a molecule of water, as shown above, and the result will be the formula of the ester.

For a):



the first part of the name comes from the alcohol, ‘ethyl’ from ethanol. The second part of the name is from the salt of the carboxylic acid, ‘ethanoate’.

Similarly, for b) and c):

b) The ester is $HCOOC_2H_5$ – ethyl methanoate

c) The ester is $C_2H_5COOCH_3$ – methyl propanoate

C14. Metals

C14.1 Understand that the reactivity of a metal is linked to its tendency to form positive ions and the ease of extraction of the metal.

C14.2 Be able to use displacement reactions to establish the order of reactivity of metals and vice versa.

C14.3 Describe how the uses of metals are related to their physical and chemical properties, e.g. Al, Fe, Cu, Ag, Au, Ti, and understand that alloys can be formed to produce materials with specific properties.

C14.4 Know that most metal ores are the oxides of the metal, and that the extraction of metals always involves reduction processes.

C14.5 Know that common properties of transition metals include:

  a. they are able to form stable ions in different oxidation states
  b. they often form coloured compounds
  c. they are often used as catalysts (as ions or atoms).

A collection of metals (from bottom left: copper, aluminium, zinc, iron and lead)

The reactivity series of metals

The reactivity series of metals is a measure of how easily metals lose electrons to form positive ions.

When forming compounds, a Group 1 metal atom loses its outer shell electron to form an ion with a single positive charge, for example Na^+.

A Group 2 metal atom has two outer shell electrons that can be lost to form doubly charged ions, for example Mg^{2+}. the process of losing 2 electrons requires more energy so Group 2 metals are less reactive than Group 1 metals (in the same Period).

Aluminium in Group 13 is even less reactive as the loss of three outer shell electrons to form the Al^{3+} ion requires an even greater amount of energy.

Within Groups 1 or 2, reactivity increases down the group because the outer shell electrons are further away from the positively charged nucleus. This results in less attraction between the nucleus and outer shell electrons, so these electrons require less energy to be removed. For example, this explains why potassium is more reactive than sodium.

Transition metals are the least reactive metals and are able to lose a differing number of electrons. For example, iron can lose two or three electrons to form the stable ions Fe^{2+} and Fe^{3+}. Silver can lose one electron to form Ag^+. Most transition metals typically lose two electrons to form the M^{2+} ion as their most common ion.

The following list shows a typical reactivity series of metals (which does not need to be learnt), with carbon and hydrogen included to indicate their relative positions:

potassium	most reactive	K
sodium	↑	Na
calcium		Ca
magnesium		Mg
aluminium		Al
carbon		C
zinc		Zn
iron		Fe
tin		Sn
lead		Pb
hydrogen		H
copper		Cu
silver		Ag
gold	↓	Au
platinum	least reactive	Pt

Extraction of metals

The ease of extraction of a metal from its ore depends on the position of the metal in the reactivity series.

Most metals are found in the Earth's crust as ores that are rocks containing the metal in the form of ionic compounds, the metal often being combined with oxygen. After the ore has been mined and concentrated, the metal ions in the compound need to be reduced (by gaining electrons) to obtain the metal.

The most reactive metals form the most stable compounds and will require more energy to extract, making the process more expensive.

The metals at the bottom of the reactivity series, such as Ag, Au and Pt. are found as the uncombined metal in nature, but will still need to be purified before use.

The inclusion of the non-metal carbon in the reactivity series is significant. Metals below carbon can be extracted from their ores by reduction using carbon or carbon monoxide, such as iron from iron ore (haematite) in a blast furnace. The ore contains iron(III) oxide, Fe_2O_3, which is then reacted with carbon monoxide. The equation for the reaction is:

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

Carbon is higher in the reactivity series than iron and is therefore able to remove the oxygen from iron(III) oxide to form iron metal. In this reaction, the Fe^{3+} ions gain three electrons to form Fe and are therefore reduced. In turn the carbon monoxide is oxidised to carbon dioxide.

Metals above carbon in the reactivity series cannot be extracted using carbon and therefore must be extracted using electrolysis. In this process, electricity is used to break down the molten ionic compound into its constituent ions. The positive metal ions are then attracted to the negative electrode (cathode) where they are discharged by gaining electrons.

Aluminium is extracted from aluminium ore (bauxite) by electrolysis. When purified, the ore is aluminium oxide, Al_2O_3, which is dissolved in molten cryolite and then electrolysed.

At the cathode (negative electrode), the aluminium ions each gain three electrons in a reduction reaction:

$Al^{3+} +$

$3e^- \rightarrow Al$

The overall reaction is: $2Al_2O_3 \rightarrow 4Al + 3O_2$

Extraction by electrolysis use a considerable amount of electrical energy, making the process very expensive.

With all metals, the cheapest method of metal extraction is chosen so as to be economically viable. New methods with lower energy requirements are constantly being developed by the chemical industry. Copper ores in particular are becoming scarce and new ways of extracting copper from low-grade ores such as phytomining (using plants) and bioleaching (using bacteria) have been devised to avoid traditional mining methods involving digging, moving and disposing of large amounts of rock.

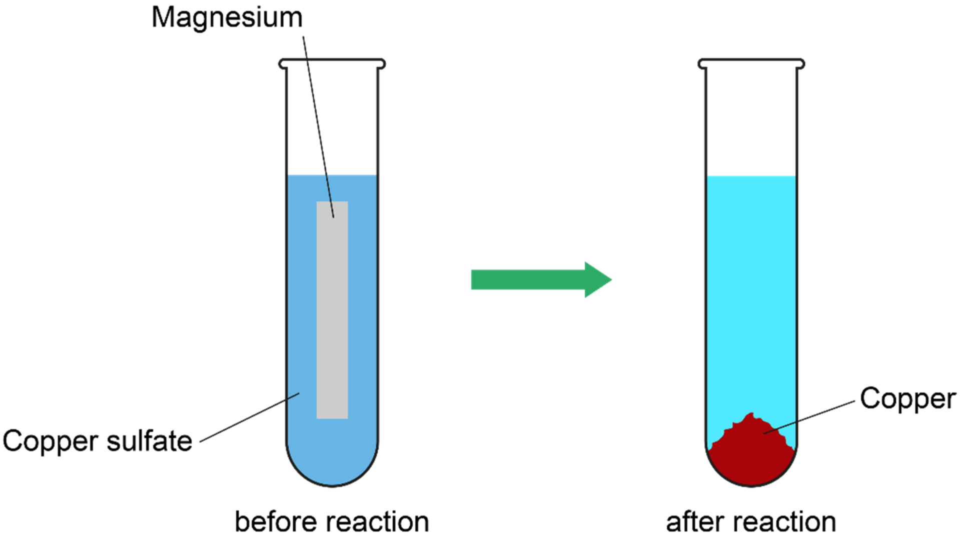
Displacement reactions

Displacement reactions of metals occur when a more reactive metal is added to a dissolved compound of a less reactive metal.

For example, if magnesium is added to copper(II) sulfate solution, the following reaction occurs:

$Mg(s) + CuSO_4(aq) \rightarrow Cu(s) + MgSO_4(aq)$

The formation of a brown solid (copper) and the blue solution fading in colour are evidence of the reaction occurring. If copper is added to magnesium sulfate solution, there will be no reaction as copper cannot displace magnesium because copper is less reactive than magnesium. The presence or absence of a displacement reaction can be used to place metals in order of reactivity.



Displacement reactions of metals may also occur in the solid phase. A good example of this is in the thermite reaction in which aluminium is added to iron(III) oxide. The powdered mixture of solids is ignited and the energy produced from the reaction is used to weld railway tracks together. The following reaction occurs:

$Al(s) + Fe_2O_3(s) \rightarrow Fe(s) + Al_2O_3(s)$

The reaction between metals and acids may also be considered as a displacement reaction. The position of hydrogen in the reactivity series can be used to explain why magnesium will react with dilute sulfuric acid but copper will not.

$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$

(magnesium is above hydrogen in the reactivity series)

$Cu + H_2SO_4 \rightarrow$ no reaction

(copper is below hydrogen in the reactivity series)

Exercise 124

Metal A can only be extracted from its purified ore using electrolysis.

Metal B is found uncombined in the Earth's crust.

Metal C forms ions more readily than metal B.

Metal C will react with metal A sulfate solution.

Using this information, place the three metals in order of reactivity, with the most reactive first.

Exercise 125

Titanium is a metal that lies just above zinc but below aluminium in the reactivity series.

Which one of the following could not be used to obtain the metal from its ore?

a electrolysis of the molten metal chloride

b heating of the chloride with metallic sodium

c heating of the oxide with metallic aluminium

d treating titanium(IV) sulfate with metallic iron

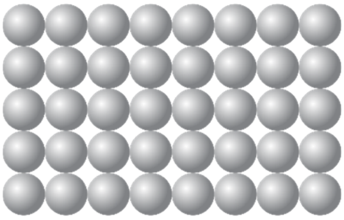
e treating titanium(IV) chloride with metallic magnesium.

Uses of metals

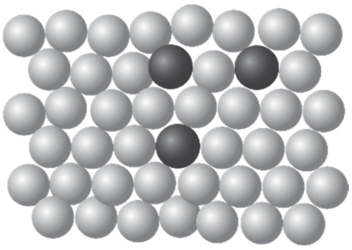
Uses of metals depends on their physical and chemical properties.

Most metals in everyday use are alloys. An alloy is two or more metals mixed together to combine properties. In a pure metal, the particles are arranged in layers that can slide over each other. In an alloy, the different sized particles disrupt the structure and prevent the layers from sliding over each other, thereby greatly increasing the strength of the material.

Particles in a pure metal



Particles in an alloy



Aluminium is a silvery-white, lightweight metal. It is soft and malleable. It is corrosion resistant and non-toxic, and it is used in a huge variety of products including cans, kitchen foil and utensils, and building facades. Its low density and good electrical conductivity make it useful in conductor cables. When alloyed, aluminium provides high strength and low density and is used in aeroplane parts.

Pure iron is soft. Impure iron (from a blast furnace) is abundant and cheap to produce though it is brittle and of little commercial use. Impure iron is purified and then mixed with controlled amounts of carbon to produce steel which is strong, malleable (can be shaped) and ductile (can be drawn into wires). Different steels contain different proportions of carbon. High carbon steel is strong but brittle and is used in cutting tools and drill bits. Low carbon steel is softer and more easily shaped, and is used in car bodies. Steel (and iron) corrode (rust) in the presence of air and water and other metals may also be added, for example chromium and nickel to make stainless steel.

Copper is a good conductor of electricity and is ductile so is used for electrical wiring. It is a good conductor of heat and is unreactive, so it is used for cooking utensils. Copper is malleable and strong, which together with its unreactivity, makes it suitable for use in water pipes and heating systems.

Silver is the best thermal and electrical conductor of all the metals; it is ideal for electrical applications but is used sparingly due to its high cost. Silver is antimicrobial and non-toxic which make it useful in medicine and as silver nanoparticles to inhibit odour in socks and sportswear. Its high lustre and reflectivity make it perfect for jewellery, silverware and mirrors.

Gold is a soft heavy metal (density: 19.3 g cm^{-3}) and is both extremely ductile and malleable so is used extensively in jewellery. One gram of gold can be hammered out into a thin sheet of gold leaf about 230 atoms thick and a square metre in area. Gold is an excellent electrical conductor with resistance to corrosion and is used in electronic circuits.

Titanium is as strong as steel but much less dense. It is therefore important as an alloying agent with many metals including aluminium, molybdenum and iron. These alloys are mainly used in aircraft, spacecraft and missiles because of their low density and ability to withstand extremes of temperature.

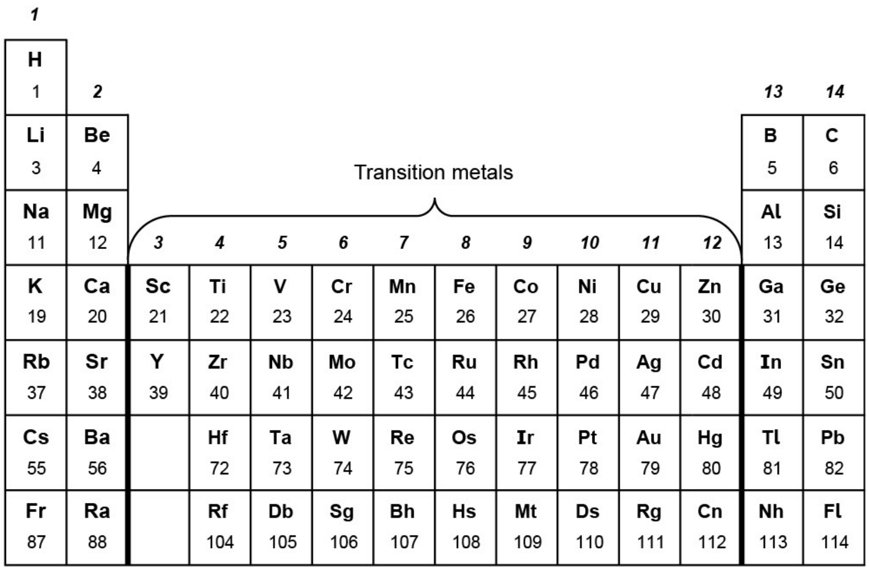
Exercise 126

Describe the desired properties for a hip replacement joint and explain why a titanium nickel alloy would be a better material to use than pure titanium.

Transition metals

Transition metals are conveniently referred to as the elements in the centre of the Periodic table in Groups 3 to 12, though the Group 12 elements often do not behave like typical transition metals. For example, mercury is a liquid at room temperature and pressure, which makes it suitable for use in thermometers.

They are usually strong with high density, high melting points and are generally unreactive. Many transition metal particles are similar in size to each other, which makes them particularly suitable for alloying



1	2	3	4	5	6	7	8	9	10	11	12	13	14
H 1													
Li 3	Be 4											B 5	C 6
Na 11	Mg 12											Al 13	Si 14
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50
Cs 55	Ba 56		Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82
Fr 87	Ra 88		Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	Nh 113	Fl 114

Transition metals form stable ions in different oxidation states.

This property makes transition metal compounds useful as catalysts, for example in the Contact Process for making sulfuric acid. The reaction between sulfur dioxide and oxygen to form sulfur trioxide can be catalysed by using vanadium(V) oxide. The equations representing the process are as follows:

$$SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$$

$$V_2O_4 + \frac{1}{2}O_2 \rightarrow SO_3 + V_2O_5$$

Overall: $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$

Vanadium has an oxidation state of +5 in V_2O_5, which is then reduced to +4 in V_2O_4 in the first step of the reaction and then is oxidised back to +5 in the second step. As a catalyst, it remains chemically unchanged at the end of the reaction and is not used up.

Transition metals themselves are also useful catalysts. For example, iron is used as a catalyst in the Haber process for making ammonia and nickel is used as the catalyst in the hydrogenation of unsaturated vegetable oils in margarine manufacture.

Transition metal compounds are often coloured because they are able to absorb visible light of a particular wavelength and reflect the complementary colour. For example, copper compounds often absorb red light and therefore reflect blue light, giving them a characteristic turquoise colour.

Copper(II) sulfate solutions of different concentrations

Exercise 127

How do the properties of transition metals differ from Group 1 elements?

Photos: Science Photo Library

Solutions to Exercises 124 to 127

Exercise 124

The first two statements show that metal A is more reactive than metal B as metal A requires considerable energy to extract from its ore whilst metal B must be very unreactive as it is found uncombined in the Earth's crust.

The third statement shows that metal C is more reactive than metal B as a more reactive metal will more easily lose electrons and form ions.

The final statement refers to a displacement reaction and will only occur if metal C is more reactive than metal A.

The order of reactivity of the three metals (most reactive first) is therefore: C, A, B

Exercise 125

Knowledge of the reactivity series is essential in identifying which method will NOT work for titanium.

a Correct – electrolysis can be used to extract all metals from their ores.

b Correct – sodium is more reactive than titanium (displacement).

c Correct – aluminium is more reactive than titanium (displacement).

d Incorrect – iron is less reactive than titanium (and zinc).

e Correct – magnesium is more reactive than titanium (displacement).

The answer is therefore d.

Exercise 126

The key properties for an artificial hip joint would be high strength, low density, corrosion resistance and biocompatibility.

A titanium-nickel alloy has different sized particles in the structure. This gives the structure higher strength than pure titanium. In pure titanium, the particles are located in layers, which slide over each other, but in a titanium nickel alloy the particles are different sizes. This disrupts the metal structure preventing the particles sliding over each other and so enhancing the strength of the structure.

Exercise 127

Compared to Group 1 metals, transition metals have high melting points and boiling points. They are also strong, hard and unreactive. Transition metals often form coloured compounds and form ions of different charges that enable them to be used as catalysts.

C15. Kinetic Particle Theory

C15.1 Be able to describe the packing and movement of particles in the three states of matter: solid, liquid and gas.

C15.2 Understand the changes to the packing and movement of particles in the following changes of state: freezing, melting, boiling/evaporating, and condensing. Understand that the energy required for these processes is related to the bonding and structure of the substance, including a consideration of intermolecular forces.

The three states of matter

We classify objects and materials around us as solids, liquids and gases based on their properties.

Some of the characteristic properties of the three states of matter are shown in the table.

property	solid	liquid	gas
shape	fixed shape (unless acted on by a force)	takes the shape of a container and can be poured	fills the container, will 'escape' from an open container and can be poured
compressibility	cannot be compressed	cannot be compressed	easily compressed
rate of diffusion	does not diffuse	diffuses slowly	diffuses quickly
density	relatively high	relatively high	very low

These properties are explained by the kinetic theory, which is based on the following ideas:

- All substances are made up of particles (atoms, ions and molecules).
- The particles are attracted to each other, some strongly and others weakly.
- The particles move around (have kinetic energy).
- The kinetic energy of the particles increases with temperature.

Solid state

Particles that make up a solid substance:

- are very close together (and in a regular arrangement in crystalline solids)
- can only vibrate about fixed positions

Liquid state

Particles that make up a liquid substance:

- are very close together (the arrangement is not regular)
- can slide past one another

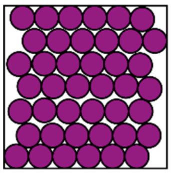
(One way of thinking about the packing of particles in a liquid is to imagine a lift filled with as many people as possible – so that they cannot move at all. Then open the lift doors, pull one person out and shut the doors again – now the people in the lift can slide past one another but they are still close together.)

Gas state

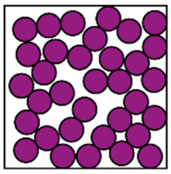
Particles that make up a gas substance:

- are far apart and there are very large spaces between them
- move very quickly and in straight lines between collisions

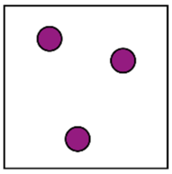
The diagrams below illustrate the packing of (spherical) particles in the three states.



solid



liquid



gas

Change of state

Particles in a solid substance are held in their fixed positions by the attractive forces between them.

If the solid substance is heated, the particles vibrate more and more vigorously. Energy is passed from particle to particle by the collisions between neighbouring particles. The more vigorous vibrations cause the particles to separate a little and the substance expands.

With continued heating, the particles eventually have sufficient energy to overcome some of the attractive forces holding them in their fixed positions, and they slide past one another. The substance is melting. The temperature at which this occurs is the melting point of the substance (at a given pressure).

During melting, the temperature does not rise (even with continued heating) as the energy supplied is being used to overcome attractive forces. Once all the substance has melted (become a liquid), the temperature of the liquid will rise.

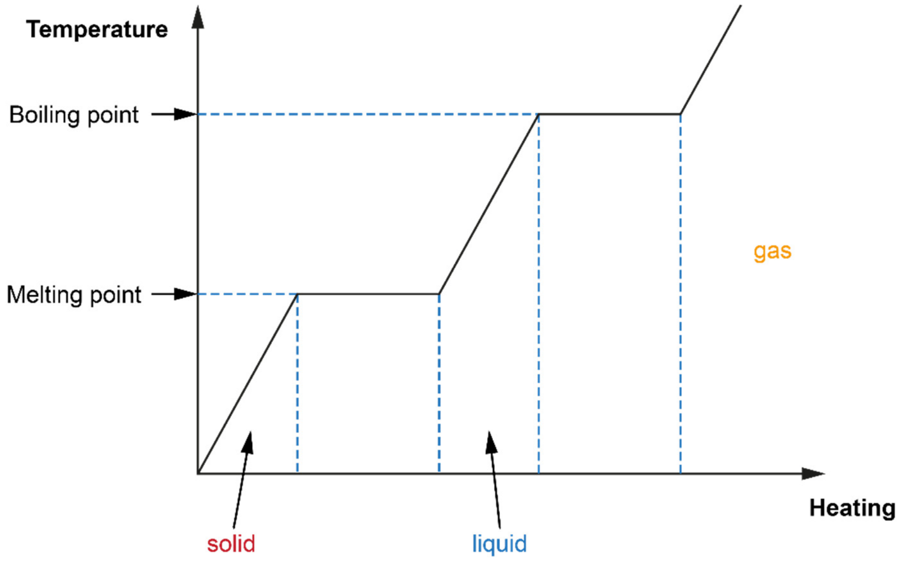
Although the particles in a liquid can move past one another, they are closely packed and they cannot escape into the gas (vapour) state as there are still attractive forces holding them together (forces are broken as the particles move and are re-formed with new neighbouring particles).

Some particles on the surface of the liquid can, through collisions, have enough energy to completely overcome the attractive forces holding them in the liquid and they escape into the gas (vapour) state. This is evaporation, and it occurs at temperatures below the boiling point of the substance.

If sufficient energy is supplied, many particles gain enough energy to completely overcome the forces of attraction holding them in the liquid and they escape into the gas (vapour) state forming bubbles in the liquid. The substance is boiling. The temperature at which this occurs is the boiling point of the substance (at a given pressure).

During boiling, the temperature does not rise (even with continued heating) as the energy supplied is being used to overcome the attractive forces. Once all the substance has boiled (become a gas), the temperature of the gas will rise.

The changes in temperature during the heating of a solid substance is shown in the graph below.



If a substance in the gas state is cooled, the reverse of the processes described above occurs.

The particles of the gas substance move slower and eventually do not have the energy to overcome the forces of attraction between them and they ‘stick’ together, forming droplets of liquid. The substance is condensing. While the gas is condensing, the temperature does not drop (even with continued cooling) because energy is released as the new attractive interactions form. The temperature at which this occurs is the boiling point of the substance (at a given pressure).

If the liquid substance is cooled, the particles move slower and eventually do not have the energy to move past one another as more and more attractive interactions develop between them. The substance is freezing. While the liquid is freezing, the temperature does not drop (even with continued cooling) because energy is released as the forces of attraction form. The temperature at which this occurs is the melting point (sometimes called the freezing point) of the substance (at a given pressure).

Forces of attraction between particles

The strength of the forces of attraction between the particles of a substance depends on the type of bonding in the substance and its structure.

Simple molecular substances

These substances are made of relatively small molecules and the forces of attraction between the molecules are known as intermolecular forces. These forces are weak, and so substances with this type of bonding and structure have low melting and boiling points. For example: hydrogen, methane, water.

The stronger the intermolecular force, the higher the melting and boiling point of the simple molecular substance.

For a homologous series, for example the straight-chain alkanes, as the molecules increase in length, the intermolecular forces become stronger causing the melting and boiling points to become higher.

Branching in alkanes weakens intermolecular forces, this causes branched molecules to have lower melting and boiling points than straight chain molecules with the same M_r.

Giant covalent structures

In order to melt, or boil, covalent substances that have giant structures, a great many strong covalent bonds must be broken in order for the atoms to be able to move. Therefore, these substances have very high melting and boiling points. For example: graphite and silicon dioxide.

Metals

Metals have giant structures and many (usually) strong attractions between the atoms and delocalised electrons have to be broken for the metal to melt, and so metals usually have high melting and boiling points.

Ionic compounds

Ionic compounds have giant structures held together by very strong electrostatic forces acting in all directions around the ions, and so these substances have high melting and boiling points. For example: sodium chloride.

Summary

Substances which are solids at room temperature and pressure have strong forces of attraction between the particles, because a lot of energy is required to overcome the forces and so they have high melting and boiling points.

Substances which are liquids at room temperature and pressure have weak forces of attraction between the particles, and therefore have relatively low melting and boiling points.

Substances which are gases at room temperature and pressure have very weak forces of attraction between the particles, which are very easily overcome with very little energy and so they have very low melting and boiling points.

Exercise 128

The melting point of Br_2 is −7 °C and the boiling point of Br_2 is 59 °C

At atmospheric pressure, what state is bromine in at:

a) −10 °C

b) 30 °C

c) 60 °C

Solution to Exercise 128

Exercise 128

At temperatures below its melting point, bromine will be a solid.

At temperatures between its melting and boiling points, bromine will be a liquid.

At temperatures above its boiling point, bromine will be a gas.

a) −10 °C is below −7 °C, so bromine is a solid.

b) 30 °C is between −7 °C and 59 °C, so bromine is a liquid.

c) 60 °C is above 59 °C, so bromine is a gas.

C16. Chemical Tests

C16.1 Know and recognise the following tests for gases:

a. hydrogen – explodes with a ‘squeaky pop’ when a burning splint is held at the open end of a test tube
b. oxygen – relights a glowing splint
c. carbon dioxide – limewater turns cloudy when shaken with the gas
d. chlorine – damp blue litmus paper turns red and then is bleached (paper turns white)

C16.2 Know, recognise and describe the following tests for the anions:

a. carbonates – using a dilute acid
b. halides – using an aqueous solution of silver nitrate in the presence of dilute nitric acid (chlorides form a white precipitate; bromides form a cream precipitate; iodides form a yellow precipitate)
c. sulfates – using an aqueous solution of barium chloride in the presence of dilute hydrochloric acid

C16.3 Know and recognise the test for the following metal cations using aqueous sodium hydroxide:

a. Al^{3+}, Ca^{2+} and Mg^{2+} each form a white precipitate.
b. Cu^{2+} forms a blue precipitate.
c. Fe^{2+} forms a green precipitate.
d. Fe^{3+} forms a brown precipitate.

C16.4 Recall and recognise the flame test for the cations of the following metals:
Li (crimson red), Na (yellow-orange), K (lilac), Ca (red-orange), Cu (green).

C16.5 Know and recognise the test for the presence of water using anhydrous copper(II) sulfate (colour change from white to blue).

A chemical test is a chemical reaction that is used to identify a substance. Chemical tests, which are often completed in a test tube, can be described as qualitative or quantitative.

Each test exploits a reaction of the substance that leads to a specific observation such as precipitation (production of an insoluble substance), effervescence (bubbling/fizzing), a temperature change, a colour change, and so on.

Some tests are specific and can identify a single substance, but some are more generic and identify the general type of substance such as an acid or an alkali. By combining tests, many simple compounds can be identified.

Gas tests

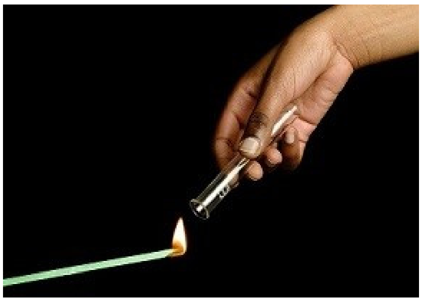
Reactions that show effervescence are releasing a gaseous product. By identifying the gas, some information about the substance being tested can be inferred.

Hydrogen

Hydrogen is usually produced when a reactive metal such as an alkali metal reacts with water or an alcohol.

If a burning splint is placed in a test tube containing hydrogen, the hydrogen burns to produce water. The reaction occurs as a small explosion which is heard as a ‘squeaky pop’ noise.

Testing for hydrogen

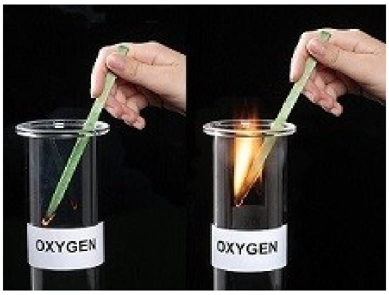


Oxygen

Some reactions release oxygen as a gas. One that does is the decomposition of hydrogen peroxide, H_2O_2, to water and oxygen. This reaction is very slow at room temperature and can be speeded up using a catalyst such as MnO_2.

Testing for oxygen requires a glowing splint. In this test, a burning splint is blown out to leave red glowing embers. If this splint is added to a test tube containing oxygen, the splint relights.

Testing for oxygen



Carbon dioxide

Carbon dioxide is produced in the combustion of organic compounds or the thermal decomposition of a carbonate salt.

Limewater is a solution of calcium hydroxide, $Ca(OH)_2$. When carbon dioxide is bubbled through limewater, it reacts to form insoluble calcium carbonate. The white calcium carbonate precipitates and the limewater is said to have gone cloudy.

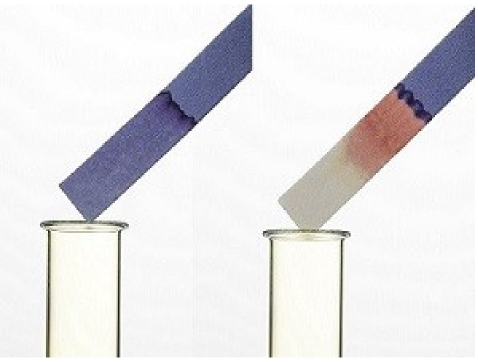
Note that the extinguishing of a fire/burning splint is not a test for carbon dioxide. Many other gases can extinguish a fire.

Testing for carbon dioxide

Chlorine

Although chlorine is a green gas, the colour is rarely seen in the lab because it is so pale and little is made in a test tube reaction. It does have a distinctive smell but smells are not considered enough to identify a substance. To test for chlorine, a piece of damp blue litmus or indicator paper is held in the gas. Chlorine forms an acidic solution in water which turns the litmus red. Chlorine is also a bleach so the red and blue colours will then both fade to leave a white colour.

Testing for chlorine



Testing for anions (negatively charged ions)

Carbonate ions, CO_3^{2-}

Carbonate ions react with an acid to release carbon dioxide gas. Effervescence is observed and the production of carbon dioxide can be confirmed using limewater. A solution of a carbonate will also be alkaline, which can be shown using universal indicator or a pH probe.

This test can be used the other way round and so a carbonate can also be used to demonstrate the existence of an acid.

The ionic equation is: $2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2O(l) + CO_2(g)$

Halide ions, Cl^-, Br^-, I^-

Except for silver nitrate, silver compounds are nearly all insoluble. This means that any anion in solution which is not a nitrate ion will bond with $Ag^+(aq)$ to form a precipitate.

Common ions found in solution include halide ions, sulfate ions, carbonate/hydrogencarbonate ions and hydroxide ions. All of these would precipitate with aqueous silver ions.

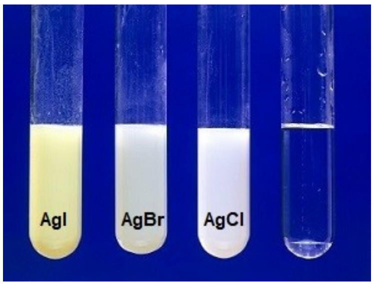
When testing for the presence of a halide ion, any other anions must be excluded. Hydroxide or carbonate ions can be removed from a solution by adding an excess of dilute nitric acid.

The test for halide ions in aqueous solution is therefore to add dilute nitric acid and then to add a few drops of silver nitrate solution to the unknown solution. Halide ions will then precipitate as silver halides. Each silver halide precipitate has a distinctive colour.

- silver iodide is yellow
- silver bromide is cream coloured
- silver chloride is white

The ionic equation, using X^- to represent the halide ion, is: $Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$

Silver halide precipitates



Sulfate ions, SO_4^{2-}

Barium nitrate and barium chloride are both soluble in water. Most other barium compounds are only sparingly soluble. If anions other than halide or nitrate ions are present, a precipitate will therefore form.

By adding a small quantity of dilute nitric or hydrochloric acid, any hydroxide or carbonate ions are removed. Any precipitate then formed by the addition of $BaCl_2(aq)$ or $Ba(NO_3)_2(aq)$ will be barium sulfate, which is white.

Therefore, the test is addition of dilute nitric or hydrochloric acid to the unknown solution, followed by a solution of barium nitrate or chloride. A white precipitate indicates the presence of sulfate ions.

The ionic equation for the precipitation is: $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

Precipitation of barium sulfate

Order of tests

If it is not known which anions are present in a sample, it is important to test for the ions in a specific order.

1. Test for the presence of carbonate ions using a dilute acid
2. Test for the presence of sulfate ions using $HCl/BaCl_2(aq)$
3. Test for halide ions using $HNO_3/AgNO_3(aq)$

Exercise 129

An unknown sample was dissolved in water to make a colourless solution. Aqueous silver nitrate was added and a cream precipitate was observed.
Why cannot it be certain that bromide ions are present?

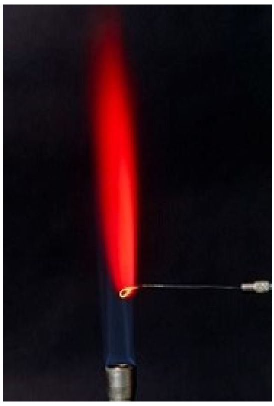
Testing for cations (positive ions)

Flame tests

In a flame test a thin wire is washed in a little acid. This clean wire is then dipped into the unknown substance. A small quantity of the substance sticks to the wire which is then placed in a hot (blue) flame of a Bunsen burner. Metal cations change the colour of the Bunsen flame. The colour observed indicates the cation present.

Nichrome or platinum is used for the wire because they are both relatively inert and have high melting points. They therefore do not melt or give a visible colour of their own in a flame test.

The flame test is particularly useful for identifying metal ions from Groups 1 or 2 which have few other identifying chemical tests.



lithium
crimson red

sodium
yellow-orange

potassium
lilac

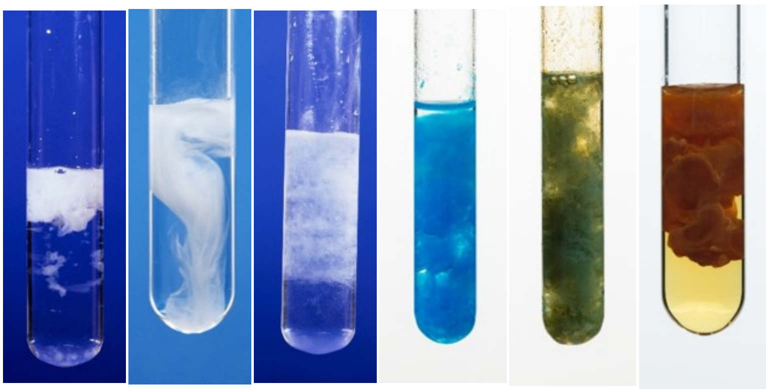
calcium
red-orange

copper
green

Testing using sodium hydroxide

Group 1 metal hydroxide compounds are soluble in water. Group 2 metal hydroxides are slightly soluble with a trend of becoming more soluble down the group. Even the most soluble hydroxide, $Ba(OH)_2$ is only soluble up to around 0.1 mol dm^{-3}.

This means that if sodium hydroxide solution is added to a solution containing a metal ion with a concentration more than 0.1 mol dm^{-3} that is not from Group 1, precipitation will occur. Coloured precipitates are formed from transition metal ions and white precipitates from other metal ions.



Mg^{2+}	Ca^{2+}	Al^{3+}	Cu^{2+}	Fe^{2+}	Fe^{3+}
white	white	white	blue	green	brown

Both the Group 2 metal hydroxide are the same colour (white) and the precipitates are insoluble on the addition of excess sodium hydroxide.

The aluminium hydroxide is also a white precipitate but this precipitate will dissolve in an excess of sodium hydroxide to leave a colourless solution.

When testing for Fe^{2+}, note that the green precipitate of $Fe(OH)_2$ that initially forms will turn brown on standing as it oxidises in the air to form $Fe(OH)_3$.

The general ionic equation, using M^{n+} to represent the metal ion, is: $M^{n+}(aq) + nOH^-(aq) \rightarrow M(OH)_n(s)$

Testing for water

Water can be identified using solid copper(II) sulfate, $CuSO_4(s)$.

This solid is white when anhydrous but blue when hydrated. As a result, a few drops of water on anhydrous copper(II) sulfate will produce a colour change from white to blue.

Copper(II) sulfate

The equation for this process is: $CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4 \cdot 5H_2O(s)$

If excess water is added, the copper(II) sulfate will dissolve to form a blue solution, $CuSO_4(aq)$.

Combining tests

To identify an ionic substance, both the anion and the cation will need to be identified. A combination of tests could therefore be used.

Exercise 130

An aqueous solution contains an ionic compound. A series of tests were performed to identify the substance.

Test 1:

Dilute nitric acid was added. No visible change occurred.

Test 2:

Dilute hydrochloric acid and aqueous barium nitrate was added to a fresh sample. No visible change occurred.

Test 3:

Dilute nitric acid and aqueous silver nitrate was added to a fresh sample. A yellow precipitate was observed.

Test 4:

A small quantity of the unknown solid was held in a blue Bunsen flame. A red flame was observed.

What is the ionic compound?

Quantitative analysis

Each of the tests described are providing qualitative data for identifying a substance. Some of these tests can also be used to provide quantitative data. For example, if a solution is known to contain sodium sulfate, the concentration of the sulfate ions can be found by adding an excess of barium chloride solution. The precipitate can be filtered, dried and weighed. The number of moles of barium sulfate can be determined from the mass of dry solid. From the volume of solution tested, the concentration of sulfate ions can be found.

Exercise 131

A solution contains only sodium and chloride ions. The solution was tested to determine the concentration of sodium chloride present.

10.0 cm^3 of the solution was added to a test tube.

Nitric acid was added and an excess of silver nitrate added.

The resulting precipitate was filter and dried. The mass of the precipitate was 0.932g.

Calculate the concentration of the sodium chloride solution.

Photos: Science Photo Library

Solutions to Exercises 129 to 131

Exercise 129

Silver compounds are nearly all insoluble. If almost any ion other than a nitrate ion is present, a silver compound will precipitate.

If no acid was added, the precipitate could be silver hydroxide which decomposed to silver oxide, or it could be silver carbonate or silver sulfate.

A preliminary test for carbonate ions and to remove hydroxide ions must be done. It should then be established that sulfate ions are not present using barium chloride solution.

Only then can it be concluded that the silver compound precipitated is AgBr.

Exercise 130

No change is observed with an acid. The anion is not carbonate.

No change with acidified barium ions. The anion is not sulfate.

Yellow precipitate with acidified silver nitrate indicates that the anion is the iodide ion.

A red flame in a flame test suggests the lithium ion.

Therefore, the compound is lithium iodide.

Exercise 131

The ionic equation for the reaction is: $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

M_r (AgCl) = 143.4

Number of moles of AgCl = $\frac{0.932}{143.4} = 6.50 \times 10^{-3}$ mol

From the equation, this is also the number of moles of Cl^-.

Therefore, number of moles of NaCl = 6.50×10^{-3} mol

Concentration = $\frac{number\ of\ moles}{volume} = \frac{6.50\times10^{-3}}{\frac{10.0}{1000}} = 0.650\ \text{mol dm}^{-3}$

C17. Air and Water

C17.1	Know and be able to use the composition of dry air, and understand that fractional distillation can be used to separate the components of air.
C17.2	Know the origins and describe the effects of greenhouse gases such as CO_2 and CH_4.
C17.3	Know the origins and effects of gaseous pollutants such as CO, CO_2, SO_2 and NO_x.
C17.4	Know the purpose of chlorine and fluoride ions in the treatment of drinking water.

The composition of air

Air is the mixture of gases that surround the Earth in its atmosphere.

The main components of dry air are:

constituent	chemical symbol	percentage in dry air
nitrogen	N_2	78.1
oxygen	O_2	20.95
argon	Ar	0.9
carbon dioxide	CO_2	0.04

Note that water vapour is also present in the atmosphere (up to about 5%) depending on levels of humidity and other conditions. Smaller proportions of other gases are also present.

Exercise 132

150 cm^3 of dry air (measured at room temperature and pressure) is passed over an excess of heated copper turnings. If the reaction is allowed to go to completion, what volume of gases (measured at room temperature and pressure) will remain?

Fractional distillation of air

In industry, the gases in air are separated by a fractional distillation process.

Fractional distillation is a process by which liquids with different boiling points are separated. So first the air has to be cold enough for all of it to condense into a liquid. It has to be cooled to a temperature below −200 °C.

This cooling is done by first compressing the air to 150 times atmospheric pressure. This actually warms the air up, so the pressurised air is cooled back down by passing the air over pipes carrying cold water.

The main cooling takes place when the pressure is released and as this happens the air expands rapidly – similar to what happens when an aerosol is sprayed from a deodorant can. The temperature drops enough for the gases in the air to condense as liquids. The carbon dioxide and water are removed from the mixture (usually before the final cooling) as they are solids at this low temperature, otherwise they would block the fine jets used in the expansion phase.

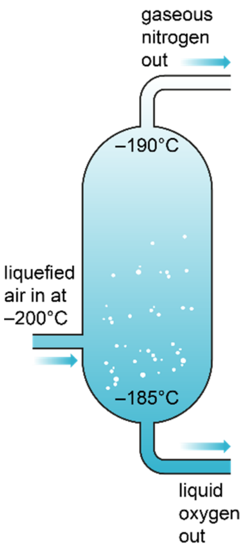
The main substances left in the mixture are:

substance	boiling point / °C
nitrogen	−196
argon	−186
oxygen	−183

The liquid is then warmed up. At −196 °C, the nitrogen boils off first and is collected at the top of a tall fractioning column.

Liquid nitrogen is used to cool things down to very low temperatures, for instance in the storage of sperm in hospitals to help with fertility treatment. Nitrogen gas is very unreactive and is used in the food industry in sealed packaging to stop food going off. In the chemical industry, nitrogen is used to make ammonia, which is then converted in fertilisers such as ammonium nitrate.

The separated oxygen is used to increase the supply of oxygen to people with impaired lung function or wounds that are difficult to heal in hospitals or to provide an artificial atmosphere for fighter jet pilots or deep-sea divers to breathe. It can also be used to remove impurities from iron in the steel making process.



Exercise 133

How can water and carbon dioxide be removed from the air before the mixture enters the fractioning column?

Exercise 134

Consider the boiling points of nitrogen, argon and oxygen.

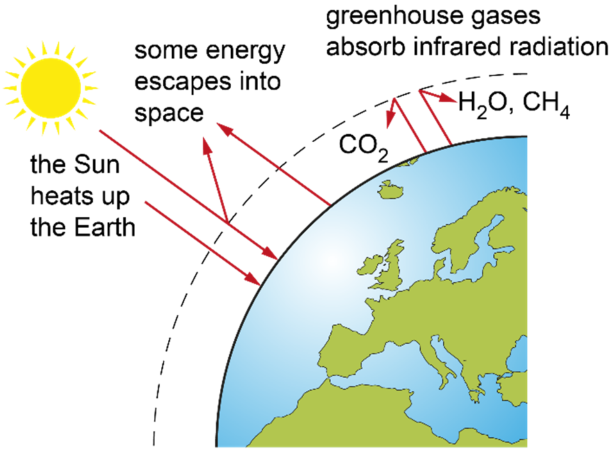
a. Which gas boils off after nitrogen?

b. Why is it difficult to obtain 100% pure oxygen?

Greenhouse gases

Greenhouse gases in the atmosphere maintain temperatures on Earth high enough to support life.

Carbon dioxide, methane and water vapour are greenhouse gases.



carbon dioxide, methane and water vapour are the main greenhouse gases

As the energy from the Sun reaches the Earth, greenhouse gases allow short wavelength radiation, such as ultraviolet and visible light, to pass through, heating the surface of the Earth. As the Earth then cools, it emits longer wavelength radiation, such as infrared radiation.

Greenhouse gases, such as CO_2 and CH_4, are able to absorb infrared radiation, so some of the energy radiated from the Earth is trapped in the atmosphere and the temperature rises. The higher the proportion of greenhouse gases in the atmosphere, the more energy is absorbed.

Human activities have caused increases in the levels of:

- carbon dioxide
    - burning of fossil fuels
    - deforestation

- methane
    - cattle farming
    - rice fields
    - landfill sites

Gaseous pollutants

Pollution arising from the combustion of fossil fuels

As the Earth's population has increased, using more industrial technology, so have the levels of air pollution.

Air pollution is caused by the release of poisonous/harmful chemicals into the air. These chemicals either directly or indirectly harm living things, damage the environment or damage buildings. Most of the pollutants released into the air come from the burning of fossil fuels. Details of these pollutants are given below.

Carbon monoxide

This gas has the formula CO. It is formed by the incomplete combustion of fossil fuels.

Common sources of carbon monoxide as a pollutant are:

- gas fires used in heating
- gas boilers used for heating (water/central heating)
- engines in cars and other vehicles

Carbon monoxide is a colourless, odourless, poisonous gas.

It binds more strongly to the haemoglobin in the blood than oxygen and greatly reduces the amount of oxygen that the blood can carry around the body.

Even brief exposure to tiny amounts can lead to headaches and drowsiness. Exposure to slightly larger amounts for a relatively short time can lead to death.

Exercise 135

Balance these equations:

$\_\_CH_4 + \_\_O_2 \rightarrow \_\_CO + \_\_H_2O$

$\_\_C_3H_8 + \_\_O_2 \rightarrow \_\_CO + \_\_H_2O$

Carbon dioxide

The small percentage of carbon dioxide naturally present in the air was until recently not regarded as a pollutant.

In the absence of human activity, the amount of carbon dioxide in the air has been regulated by opposing factors involved in the carbon cycle. .

- Carbon dioxide enters the air:
    - respiration (by plants and animals)
    - decay of dead plants or animals dissolved
    - carbon dioxide escaping from water (mainly sea water)
- Carbon dioxide removed from the air:
    - photosynthesis
    - carbon dioxide dissolving in water (especially rain water and sea water and forming carbonate rocks)

However, when fossil fuels are burned, vast amounts of carbon dioxide are released into the air, far more than can be regulated by the natural carbon cycle.

Carbon dioxide is formed from the complete combustion of fossil fuels.

The result of this increase is that there has been a slow increase in the proportion of carbon dioxide in the air over the last century or so.

Carbon dioxide is now considered a pollutant and its increase in the atmosphere is contributing further to the greenhouse effect, leading to global warming and climate change.

Exercise 136

Balance these equations:

$\_\_CH_2 + \_\_O_2 \rightarrow \_\_CO_2 + \_\_H_2O$

$\_\_C_3H_8 + \_\_O_2 \rightarrow \_\_CO_2 + \_\_H_2O$

Exercise 137

A diesel van produces 88 g of carbon dioxide per kilometre. Calculate the number of moles of carbon dioxide produced over a 20 km journey.

[A_r values: C = 12.0, O = 16.0]

Sulfur dioxide

Most fuels contain small amounts of sulfur containing compounds as impurity. The sulfur present in them is oxidised to give sulfur dioxide (SO_2).

For simplicity, the reaction is often written as:

$$S + O_2 \rightarrow SO_2$$

Sulfur dioxide is a poisonous, colourless, acidic gas with a choking smell.

It reacts with water and oxygen in the atmosphere to produce sulfuric acid, one of the components of ‘acid rain’.

The sulfuric acid in acid rain erodes stonework, increases metal corrosion, increases the leaching of soil (removal of important minerals) and is also harmful to animal and plant life (especially all forms of marine life).

Sulfur dioxide also causes breathing difficulties and can trigger asthma attacks.

Oxides of nitrogen (NOx gases)

Fossil fuels do not usually contain any nitrogen-containing compounds. When combustion occurs, the fuel is reacting with oxygen from the air and not with the nitrogen. Nitrogen is not a very reactive gas.

However, at the high temperatures and pressures generated within burner units (for example in car engines), it is possible for the nitrogen in the air to react with the oxygen to give a number of different oxides of nitrogen.

As it is possible to produce a mixture of oxides of nitrogen, these oxides are sometimes given the generalised formula NO_x.

They react with oxygen and water in the atmosphere to generate nitric acid, another component of ‘acid rain’.

They are also toxic gases and can trigger asthma attacks.

Chlorine and fluoride ions in drinking water

To ensure that water is fit to drink, it undergoes a treatment process. Chemicals added to water in this process include:

- chlorine (Cl_2)
- fluoride ions (F^-)

Chlorine gas is added to water in controlled quantities to sterilise the water as it kills harmful bacteria.

Fluoride ions (for example, in sodium fluoride) may be added to drinking water as fluoride helps protect against tooth decay.

Solutions to Exercises 132 to 137

Exercise 132

The only gas in dry air that will react with the heated copper is oxygen, which makes up approximately 21% of dry air.

21% of 150 cm^3 is $\frac{21}{100}$ × 150 = 31.5 cm^3

The volume of gases that will remain = 150 – 31.5 = 118.5 cm^3

Be aware that gases expand on heating and contract on cooling, but all volume measurements here have been made at room temperature and pressure.

Exercise 133

As the liquefied air enters the fractioning column at −200 °C, water and carbon dioxide will be in the solid state and so they can be filtered off before the liquefied air enters the column.

Exercise 134

a. Argon

b. Oxygen and argon have very similar boiling points, making complete separation difficult to achieve.

Exercise 135

$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$

$2C_3H_8 + 7O_2 \rightarrow 6CO + 8H_2O$

Exercise 136

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

Exercise 137

Total mass of CO_2 produced = 88 × 20 = 1760 g

Number of moles = $\frac{\text{mass}}{M_r} = \frac{1760}{44}$ = 40 mol