Edexcel

AS - Level

Chemistry

CODE: (WCH11)

Topic 7 and Topic 8

Intermolecular forces

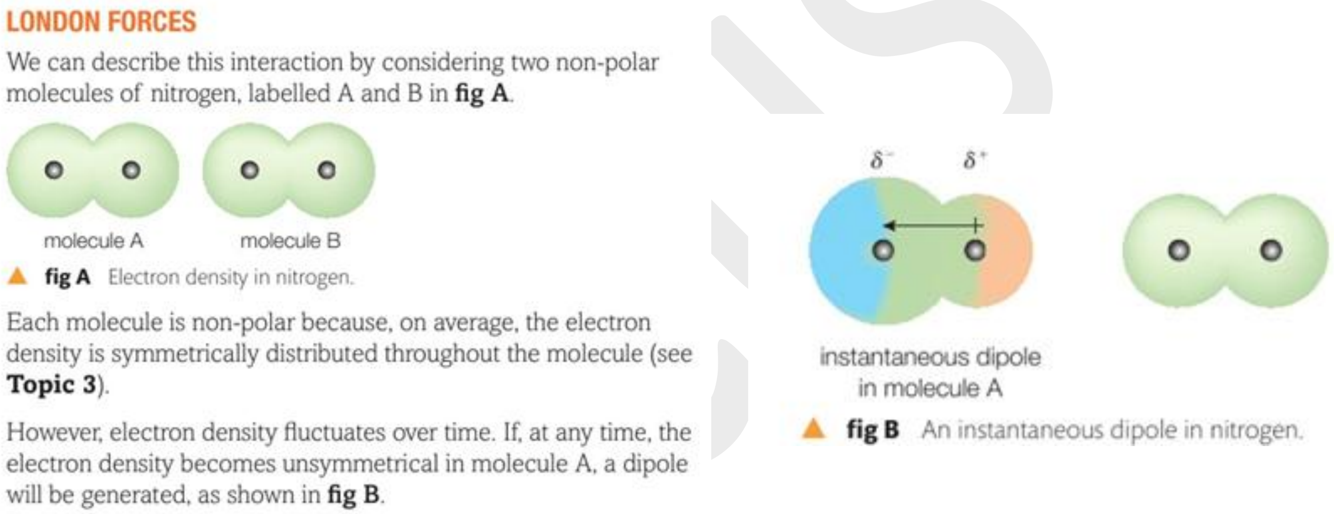
BACKGROUND TO NON-BONDED INTERMOLECULAR INTERACTIONS

A number of interactions between molecules are considerably weaker than typical covalent and polar covalent bonds. These interactions are usually described as:

- 'non-bonded interactions' or

- 'intermolecular' because they occur between molecules. The most important non-bonded interactions are 'London forces'. They have this name because their existence was first suggested in 1930 by Fritz London, a German physicist. London forces are also sometimes referred to as 'dispersion forces'.

Although they are weaker than covalent and polar covalent bonds, London forces play an important part in determining the physical and chemical properties of many molecules.
Other intermolecular interactions arise from the permanent dipoles that exist in some molecules.



LONDON FORCES

We can describe this interaction by considering two non-polar molecules of nitrogen, labelled A and B in **fig A**.

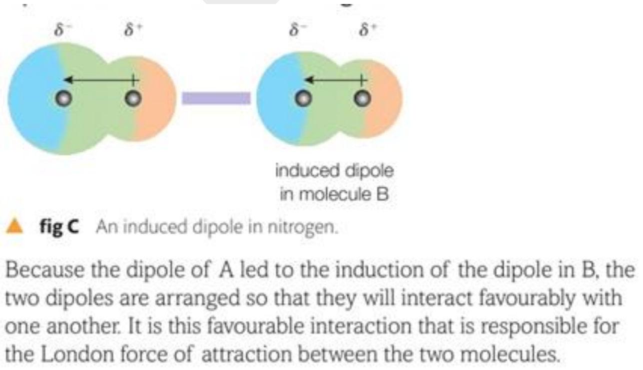
▲ **fig A** Electron density in nitrogen.

Each molecule is non-polar because, on average, the electron density is symmetrically distributed throughout the molecule (see **Topic 3**).

However, electron density fluctuates over time. If, at any time, the electron density becomes unsymmetrical in molecule A, a dipole will be generated, as shown in **fig B**.

▲ **fig B** An instantaneous dipole in nitrogen.

The electron density on the left of a molecule increases, resulting in a partial negative charge (8-), while the right has a partial positive charge (8+). This creates an instantaneous dipole in molecule A, while the electron density of molecule B pulls to the left.



▲ **fig C** An induced dipole in nitrogen.

Because the dipole of A led to the induction of the dipole in B, the two dipoles are arranged so that they will interact favourably with one another. It is this favourable interaction that is responsible for the London force of attraction between the two molecules.

GAS	HELIUM	NEON	ARGON	KRYPTON	XENON	RADON
Boiling temperature / K	4.3	27.1	87.4	121	165	211

table A Boiling temperatures of the noble gases.

London forces in molecules are influenced by electron density, shape, size, and contact points. The more electrons in a molecule, the greater the fluctuation in electron density and the larger instantaneous and induced dipoles. These forces are always present between molecules, regardless of their permanent dipole or hydrogen bond formation.

PERMANENT DIPOLES

If the molecules possess permanent dipoles, they will also interact with one another. If the dipoles are aligned correctly, then there will be a favourable interaction and the two molecules will attract one another (fig D).

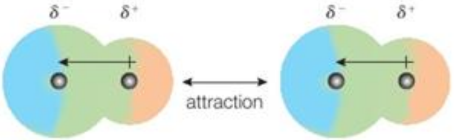


fig D Attraction between permanent dipoles.

The problem here is that, for example, in a liquid, the random movement of the molecules is such that the dipoles are not always aligned to produce a favourable interaction.

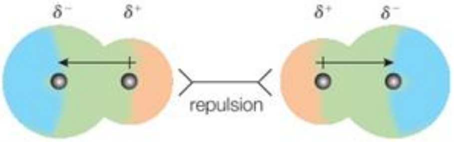


fig E Repulsion between permanent dipoles.

It is possible for a molecule with a permanent dipole to induce a dipole in a nearby molecule. The two types of interaction, permanent dipole–permanent dipole and permanent dipole–induced dipole, are sometimes put together under the heading permanent dipole–dipole forces.

SUMMARY

Table B is a useful reminder of the origins of non-bonded intermolecular interactions.

NAME OF INTERACTION	ORIGIN
London forces	instantaneous dipole-induced dipole interaction
Permanent dipoles	permanent dipole-permanent dipole interaction

table B Summary of non-bonded intermolecular interactions.

THE HYDROGEN BOND

There is one other intermolecular interaction that is, in some cases, very important. It is called a **hydrogen bond**.

The key to understanding the nature of the hydrogen bond is appreciating that the atom bonded to hydrogen has to be more electronegative than hydrogen, and that there must be some evidence of bond formation between the hydrogen and another atom, either within the same molecule ('intramolecular hydrogen bonding') or in a different molecule ('intermolecular hydrogen bonding').

HYDROGEN BONDING THROUGH OXYGEN

All compounds containing an -O-H group form intermolecular hydrogen bonds.
The most important example is water.
The hydrogen bond forms between the oxygen atom of one water molecule and the hydrogen atom of a second water molecule (fig F).

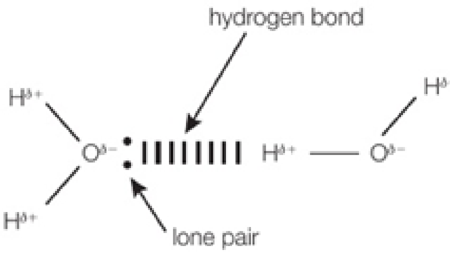


fig F Hydrogen bonding between water molecules.

Alcohols (see **Topic 10**) also form intermolecular hydrogen bonds.

Fig G shows the formation of a hydrogen bond between two ethanol molecules.

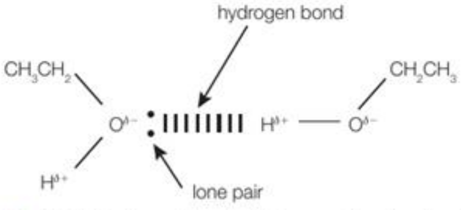


fig G Hydrogen bonding between ethanol molecules.

HYDROGEN BONDING THROUGH NITROGEN

All compounds containing an –N—H group can form intermolecular hydrogen bonds. An example is the organic group of compounds known as primary amines, which have the general formula RNH_2. **Fig H** shows the hydrogen bonding in ammonia, NH_3.

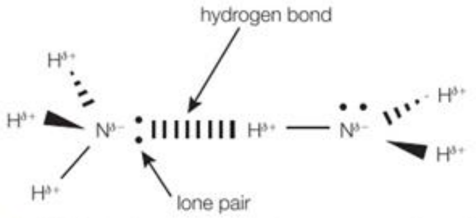


fig H Hydrogen bonding between ammonia molecules.

HYDROGEN BONDING THROUGH FLUORINE

The only fluorine compound with intermolecular hydrogen bonding is hydrogen fluoride.

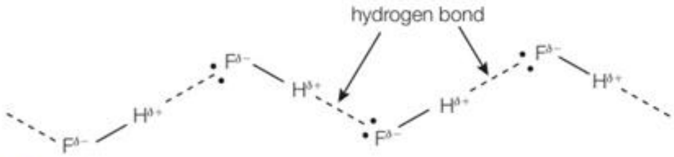


fig I Hydrogen bonding between hydrogen fluoride molecules.

SUBJECT VOCABULARY

hydrogen bond an intermolecular interaction (in which there is some evidence of bond formation) between a hydrogen atom of a molecule (or molecular fragment) bonded to an atom which is more electronegative than hydrogen and another atom in the same or a different molecule

7B Intermolecular interactions and physical properties

BOILING TEMPERATURES OF ALKANES AND ALCOHOLS

UNBRANCHED ALKANES

The alkanes are a homologous series of hydrocarbons with the general formula C_nH_{2n+2} (see **Topic 4**).

The graph in **fig A** shows the relationship between the boiling temperature and the relative molecular mass for the first 10 unbranched alkanes (i.e. CH_4 to $C_{10}H_{22}$ inclusive).

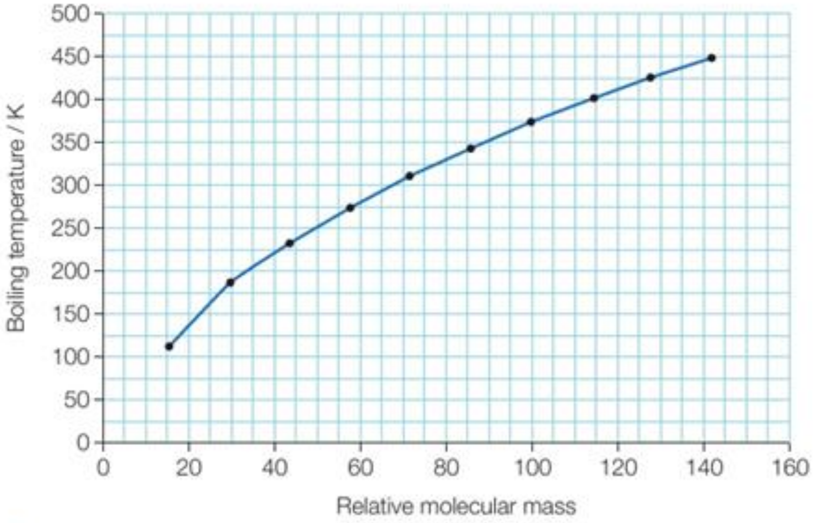


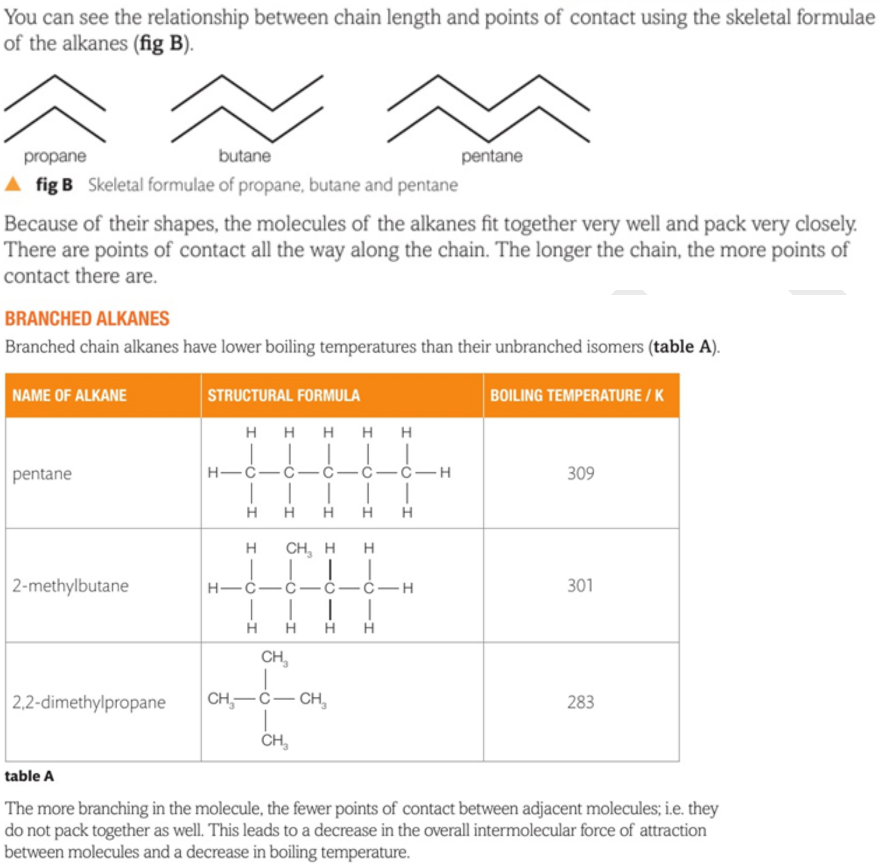
fig A The relationship between boiling temperature and relative molecular mass for the first ten alkanes.

The only significant intermolecular interaction between alkane molecules is the London force.

There are two reasons for the increase in boiling temperature with increasing molecular mass:

1 As molecular mass increases, the number of electrons per molecule increases and so the instantaneous and induced dipoles also increase (see Topic 7A.1).

2 As the length of the carbon chain increases, the number of points of contact between adjacent molecules increases. Instantaneous dipole-induced dipole forces exist at each point of contact between the molecules, so the more points of contact there are, the greater the overall intermolecular (London) force of attraction.



You can see the relationship between chain length and points of contact using the skeletal formulae of the alkanes (**fig B**).

fig B Skeletal formulae of propane, butane and pentane

Because of their shapes, the molecules of the alkanes fit together very well and pack very closely. There are points of contact all the way along the chain. The longer the chain, the more points of contact there are.

BRANCHED ALKANES

Branched chain alkanes have lower boiling temperatures than their unbranched isomers (**table A**).

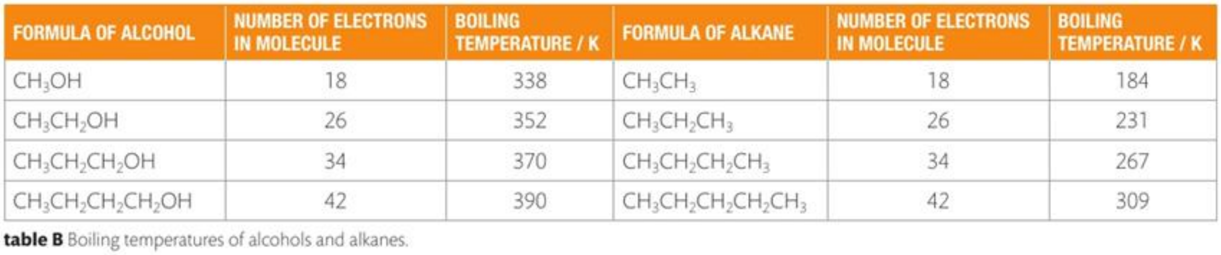
NAME OF ALKANE	STRUCTURAL FORMULA	BOILING TEMPERATURE / K
pentane	$\begin{array}{ccccccccccc} & H & & H & & H & & H & & H & \\ & \vert & & \vert & & \vert & & \vert & & \vert & \\ H- & C & - & C & - & C & - & C & - & C & -H \\ & \vert & & \vert & & \vert & & \vert & & \vert & \\ & H & & H & & H & & H & & H & \end{array}$	309
2-methylbutane	$\begin{array}{ccccccccc} & H & & CH_3 & & H & & H & \\ & \vert & & \vert & & \vert & & \vert & \\ H- & C & - & C & - & C & - & C & -H \\ & \vert & & \vert & & \vert & & \vert & \\ & H & & H & & H & & H & \end{array}$	301
2,2-dimethylpropane	$\begin{array}{ccc} & CH_3 & \\ & \vert & \\ CH_3- & C & -CH_3 \\ & \vert & \\ & CH_3 & \end{array}$	283

table A

The more branching in the molecule, the fewer points of contact between adjacent molecules; i.e. they do not pack together as well. This leads to a decrease in the overall intermolecular force of attraction between molecules and a decrease in boiling temperature.

ALCOHOLS

Alcohols are a homologous series of compounds with the general formula C,H2n+1OH (see Topic 10). They contain an-O-H group and can therefore form intermolecular hydrogen bonds in addition to London forces. This additional bonding affects the boiling temperature of alcohols when compared with the equivalent alkane. This is shown in table B.



FORMULA OF ALCOHOL	NUMBER OF ELECTRONS IN MOLECULE	BOILING TEMPERATURE / K	FORMULA OF ALKANE	NUMBER OF ELECTRONS IN MOLECULE	BOILING TEMPERATURE / K
CH_3OH	18	338	CH_3CH_3	18	184
CH_3CH_2OH	26	352	$CH_3CH_2CH_3$	26	231
$CH_3CH_2CH_2OH$	34	370	$CH_3CH_2CH_2CH_3$	34	267
$CH_3CH_2CH_2CH_2OH$	42	390	$CH_3CH_2CH_2CH_2CH_3$	42	309

table B Boiling temperatures of alcohols and alkanes.

You will notice the same trend in the other compounds in table B. It is sometimes stated that the predominant, or main, bonding in alcohols is hydrogen bonding. We have already mentioned that this is not always the case (Topic 7A.1). Table C provides evidence that for the first few members of the alcohol series hydrogen bonding is predominant. However, London forces eventually predominate as the chain length increases.

ALCOHOL	ENTHALPY CHANGE OF VAPORISATION / $kJ\,mol^{-1}$
CH_3CH_2OH	38.6
$CH_3CH_2CH_2OH$	47.5
$CH_3CH_2CH_2CH_2OH$	52.4
$CH_3CH_2CH_2CH_2CH_2OH$	57.0
$CH_3CH_2CH_2CH_2CH_2CH_2OH$	61.6

ALKANE	ENTHALPY CHANGE OF VAPORISATION / $kJ\,mol^{-1}$
$CH_3CH_2CH_3$	15.7
$CH_3CH_2CH_2CH_3$	21.0
$CH_3CH_2CH_2CH_2CH_3$	26.4
$CH_3CH_2CH_2CH_2CH_2CH_3$	31.6
$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	36.6

table C Enthalpy changes of vaporisation of alcohols and alkanes.

The enthalpy change of vaporisation is a measure of the amount of energy that is required to *completely* separate the molecules of a liquid and convert it into a gas at the same temperature. It is, therefore, a direct measure of the strength of the intermolecular interactions. The greater the enthalpy change of vaporisation, the greater the forces of attraction between the molecules.

In the case of ethanol, the total energy required to separate one mole of molecules is 38.6 kJ.

Of this, approximately 15.7 $kJ\,mol^{-1}$ can be attributed to London forces. For this reason, the hydrogen bonding is the predominant bonding, providing approximately 59% of the total.

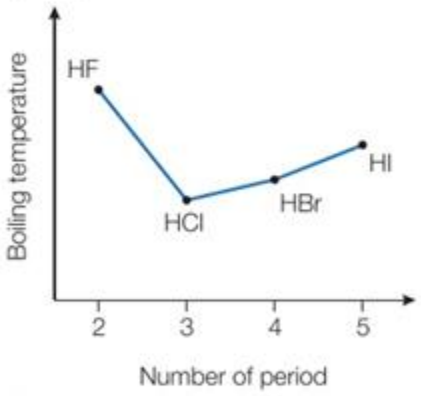
[(38.6 – 15.7) = 22.9; 22.9 is 59% of 38.6]

ALCOHOL	APPROXIMATE PERCENTAGE CONTRIBUTION OF HYDROGEN BONDING
$CH_3CH_2CH_2OH$	56
$CH_3CH_2CH_2CH_2OH$	50
$CH_3CH_2CH_2CH_2CH_2OH$	45
$CH_3CH_2CH_2CH_2CH_2CH_2OH$	41

table D Percentage contribution of hydrogen bonding in alcohols.

BOILING TEMPERATURES OF THE HYDROGEN HALIDES

The graph in **fig C** shows the boiling temperatures of the hydrogen halides HF to HI.



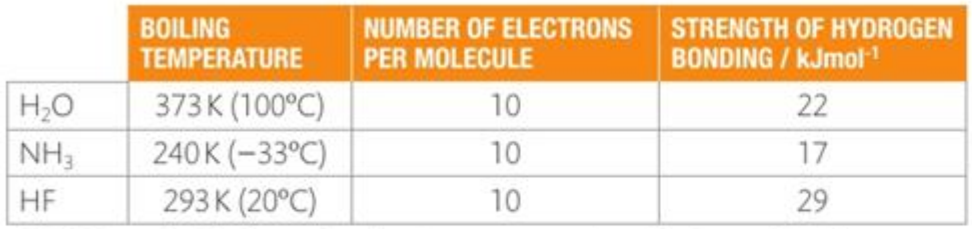
▲ **fig C** Boiling temperatures of the hydrogen halides.

ANOMALOUS PROPERTIES OF WATER

Water has some anomalous properties. The following two are particularly important:
1 It has a relatively high melting and boiling temperature for a molecule with so few electrons.
2 The density of ice at 0°C is less than that of water at 0°C.

MELTING AND BOILING TEMPERATURES

The hydrogen bonds between water molecules are relatively strong (see Topic 3E.2). As a result, the overall intermolecular forces of attraction in water are greater than would be expected from the number of electrons (10) in the molecule.



	BOILING TEMPERATURE	NUMBER OF ELECTRONS PER MOLECULE	STRENGTH OF HYDROGEN BONDING / $kJmol^{-1}$
H_2O	373 K (100°C)	10	22
NH_3	240 K (−33°C)	10	17
HF	293 K (20°C)	10	29

table E Strength of hydrogen bonding in water, ammonia and hydrogen fluoride.

The number of electrons per molecule is identical, so we would expect the London forces to be similar between each set of molecules. The differences are a result of different extents of hydrogen bonding.
The hydrogen bond strength for HF is greater than the hydrogen bond strength for H2O, but surprisingly, its boiling temperature is lower. This is because of two factors.

1 HF forms two hydrogen bonds per molecule, whereas water molecules can form up to four hydrogen bonds per molecule. This means that the hydrogen bonding is much more extensive in water.

2 Not all of the hydrogen bonds in HF are broken on vaporisation, since HF is substantially polymerised, even in the gas phase.

Ammonia has the lowest boiling temperature of the three compounds. The amount of hydrogen bonding in ammonia is limited by the fact that each nitrogen atom only has one lone pair. In a group of ammonia molecules, there are not enough lone pairs to go around to satisfy all the hydrogen atoms.

DENSITY OF ICE

As we mentioned above, water has another unusual property: the density of the solid (ice) is less than the density of the liquid at 0°C.

The molecules in ice are arranged in rings of six, held together by hydrogen bonds (fig D).

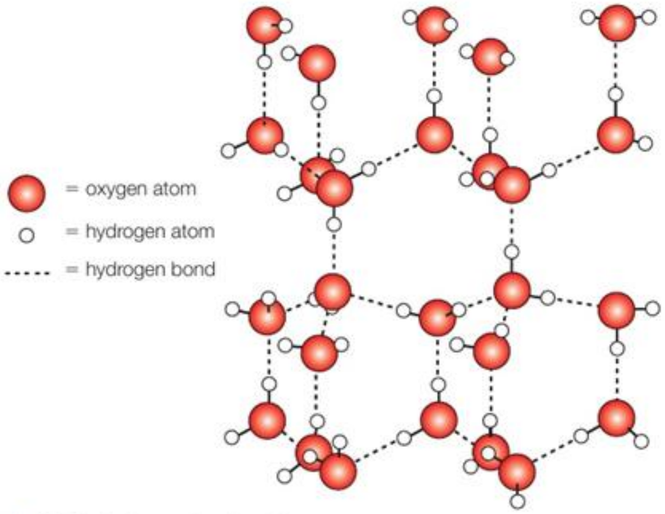


fig D Hydrogen bonding in ice.

CHOOSING SUITABLE SOLVENTS

For a substance to dissolve, the following two conditions must be met.

1. The solute particles must be separated from each other and then become surrounded by solvent particles.
2. The forces of attraction between the solute and solvent particles must be strong enough to overcome the solvent-solvent forces and the solute-solute forces.

DISSOLVING IONIC SOLIDS

Many ionic solids dissolve in water. The energy required to separate the ions in the solid is either completely, or partially, supplied by the hydration of the ions.
Fig E shows the process of dissolving for sodium chloride.

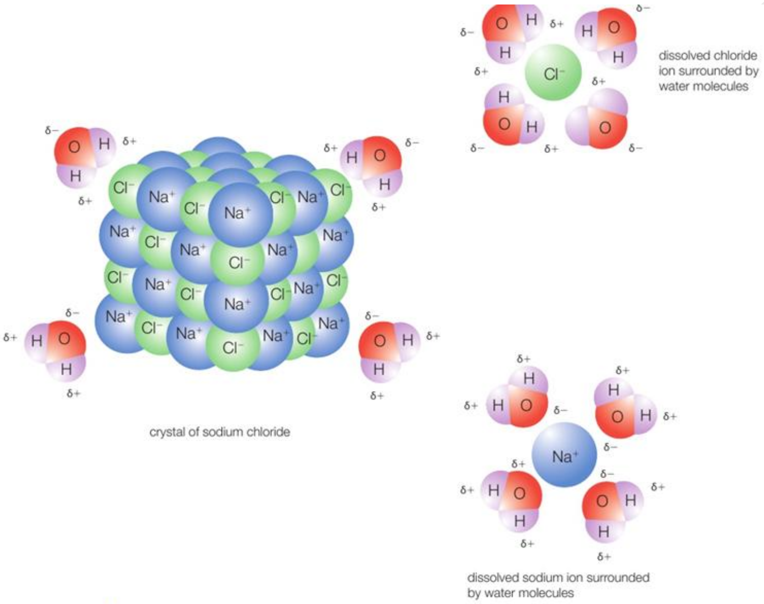
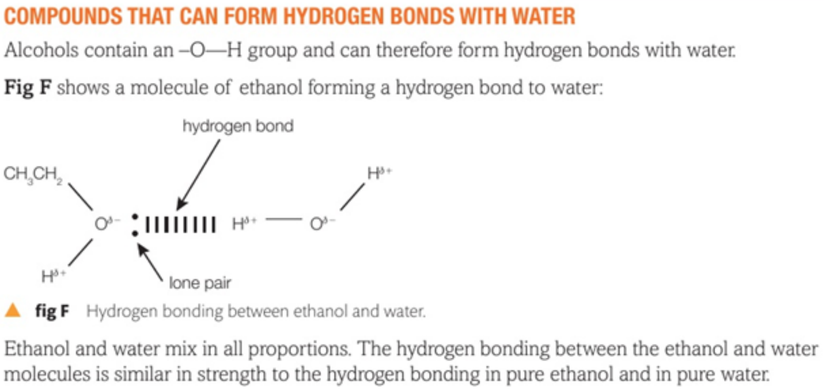


fig E Dissolving of sodium chloride.



COMPOUNDS THAT CAN FORM HYDROGEN BONDS WITH WATER

Alcohols contain an –O—H group and can therefore form hydrogen bonds with water.

Fig F shows a molecule of ethanol forming a hydrogen bond to water:

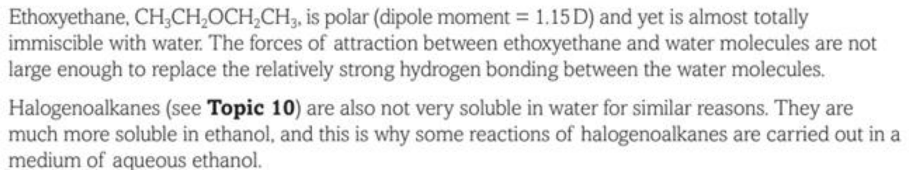
fig F Hydrogen bonding between ethanol and water.

Ethanol and water mix in all proportions. The hydrogen bonding between the ethanol and water molecules is similar in strength to the hydrogen bonding in pure ethanol and in pure water.

COMPOUNDS THAT CANNOT FORM HYDROGEN BONDS WITH WATER

Non-polar molecules such as the alkanes do not dissolve in water. The attraction between the alkane molecules and water molecules is not sufficiently strong to disrupt the hydrogen bonded system between the water molecules.

Many polar molecules also have limited solubility in water. This is because they either do not form hydrogen bonds with water, or the hydrogen bonds they do form are weak compared with the hydrogen bonds in water.



Ethoxyethane, $CH_3CH_2OCH_2CH_3$, is polar (dipole moment = 1.15 D) and yet is almost totally immiscible with water. The forces of attraction between ethoxyethane and water molecules are not large enough to replace the relatively strong hydrogen bonding between the water molecules.

Halogenoalkanes (see **Topic 10**) are also not very soluble in water for similar reasons. They are much more soluble in ethanol, and this is why some reactions of halogenoalkanes are carried out in a medium of aqueous ethanol.

NON-AQUEOUS SOLVENTS

A general rule is that 'like dissolves like'. In other words, substances that are very similar dissolve each other. If you are searching for a solvent for a non-polar substance, or for a substance that has a substantial non-polar part to its molecule, then liquids that contain similar molecules are often the answer.

For example, alkanes are soluble in one another. Crude oil is a complex mixture of alkanes dissolved in each other. Non-polar bromine dissolves readily in non-polar hexane (C6H14), and this solution is sometimes used to test for unsaturation in molecules. It is more convenient to use than bromine water, since the molecules being tested will also be soluble in hexane, whereas they are likely to be insoluble in water.

Edexcel

AS - Level

Chemistry

CODE: (WCH11)

Topic 8

Redox chemistry and groups 1,2 and 7

8A 1 Electron loss and gain

BACKGROUND TO OXIDATION AND REDUCTION

You originally knew 'oxidation' as the addition of oxygen and 'reduction' as the removal of oxygen.
The reaction between iron(III) oxide and carbon monoxide that takes place in the blast furnace provides an example of each (fig A).

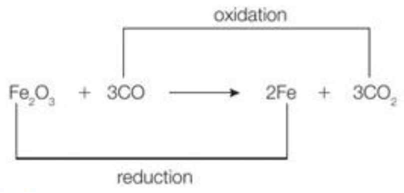


fig A Example of oxidation and reduction during the reaction between iron(III) oxide and carbon monoxide.

We then expanded these definitions so that oxidation is described as the removal of hydrogen and reduction is described as the addition of hydrogen. The reaction between chlorine and hydrogen sulfide provides an example (**fig B**).

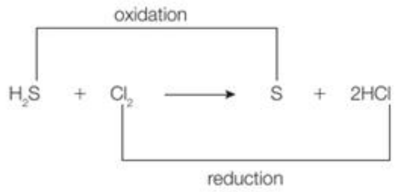


fig B Example of oxidation and reduction during the reaction between chlorine and hydrogen sulfide.

A reaction that involves both reduction and oxidation is called a redox reaction.

OXIDATION AND REDUCTION IN TERMS OF ELECTRON LOSS AND GAIN

ELECTRON TRANSFER IN REDOX REACTIONS

The approach preferred by chemists today to describe oxidation and reduction involves the transfer of electrons.
When magnesium burns in oxygen it forms magnesium oxide:

$$2Mg + O_2 \rightarrow 2MgO$$

The magnesium has been oxidised because it has gained oxygen. The oxygen must have been reduced, but by what definition?

The reaction results in the formation of Mg^{2+} and O^{2-} ions. Each of the two magnesium atoms has lost two electrons:

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

The oxygen molecule has gained four electrons to become oxide ions:

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

The magnesium has been *oxidised* because it has lost electrons.

Oxygen has been *reduced* because it has gained electrons.

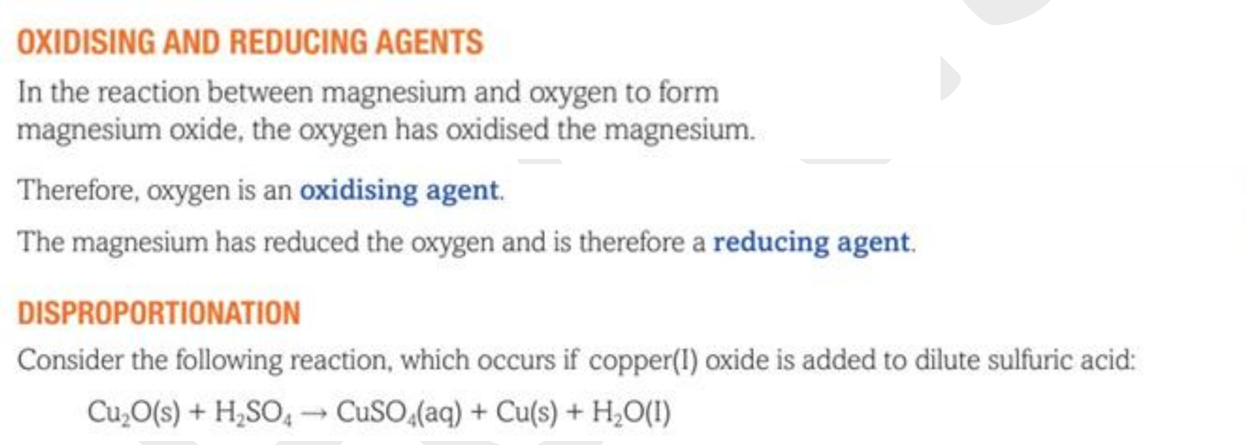
DEFINITIONS OF OXIDATION AND REDUCTION

We now have new definitions of oxidation and reduction:
Oxidation is the loss of electrons.
Reduction is the gain of electrons.
These new definitions are easily remembered using the mnemonic OIL RIG.

Oxidation
Is
Loss (of electrons)
Reduction
Is
Gain (of electrons)

We can now describe the reduction of iron(III) oxide in the blast furnace as the gain of three electrons by the iron(III) ion in the oxide:

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



OXIDISING AND REDUCING AGENTS

In the reaction between magnesium and oxygen to form magnesium oxide, the oxygen has oxidised the magnesium.

Therefore, oxygen is an **oxidising agent**.

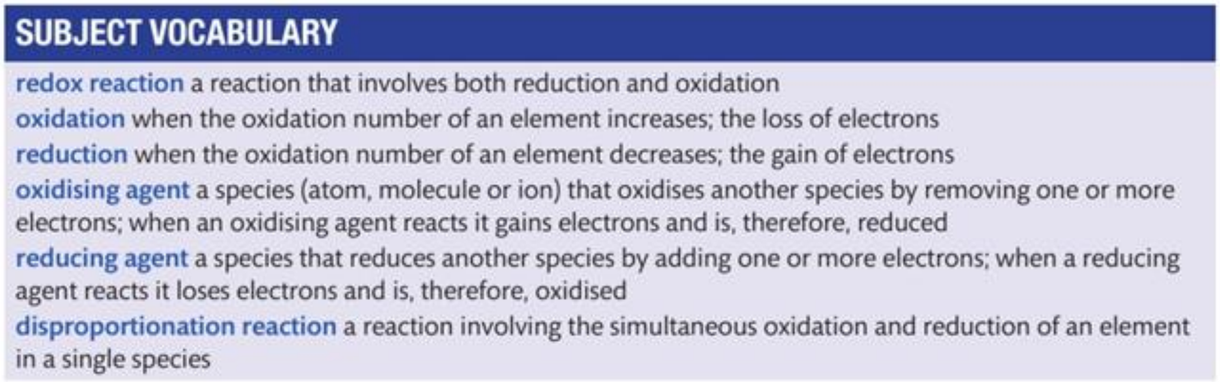
The magnesium has reduced the oxygen and is therefore a **reducing agent**.

DISPROPORTIONATION

Consider the following reaction, which occurs if copper(I) oxide is added to dilute sulfuric acid:

$$Cu_2O(s) + H_2SO_4 \rightarrow CuSO_4(aq) + Cu(s) + H_2O(l)$$

One of the Cu+ ions in copper(I) oxide has lost an electron to become Cu^{2+}. At the same time, the other Cut ion has gained an electron to become Cu. Both oxidation and reduction have occurred but the same element, copper, is involved in both changes.
This is an example of a **disproportionation reaction**.



SUBJECT VOCABULARY

redox reaction a reaction that involves both reduction and oxidation
oxidation when the oxidation number of an element increases; the loss of electrons
reduction when the oxidation number of an element decreases; the gain of electrons
oxidising agent a species (atom, molecule or ion) that oxidises another species by removing one or more electrons; when an oxidising agent reacts it gains electrons and is, therefore, reduced
reducing agent a species that reduces another species by adding one or more electrons; when a reducing agent reacts it loses electrons and is, therefore, oxidised
disproportionation reaction a reaction involving the simultaneous oxidation and reduction of an element in a single species

8A 2 Assigning oxidation numbers

OXIDATION NUMBER

So far we have restricted our discussion of oxidation and reduction to atoms and ions. For redox reactions involving these species it is easy to see which species are losing and which are gaining electrons. However, many compounds are covalent and for them a simple treatment involving ions is not appropriate.

To get around this difficulty, the concept of **oxidation number** has been developed.

RULES FOR DETERMINING THE OXIDATION NUMBER

Here are some rules to help you calculate the oxidation number.

- The oxidation number of an uncombined element is zero.

- The sum of the oxidation numbers of all the elements in a neutral compound is zero.

- The sum of the oxidation numbers of all the elements in an ion is equal to the charge on the ion.

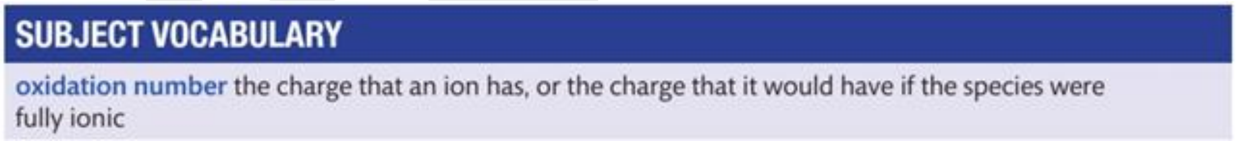
- The more electronegative element in a substance is given a negative oxidation number.

- The oxidation number of fluorine is always -1.

- The oxidation number of hydrogen is +1, except when combined with a less electronegative element. Then it becomes -1.

- The oxidation number of oxygen is -2, except in peroxides where it is -1 and when combined with fluorine when it is +2.

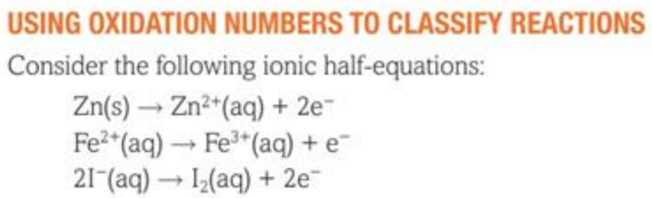
The best way to get used to these rules is to put them into practice, which is what we shall now do.



SUBJECT VOCABULARY

oxidation number the charge that an ion has, or the charge that it would have if the species were fully ionic

8A 3 Recognizing reactions using oxidation numbers



USING OXIDATION NUMBERS TO CLASSIFY REACTIONS

Consider the following ionic half-equations:

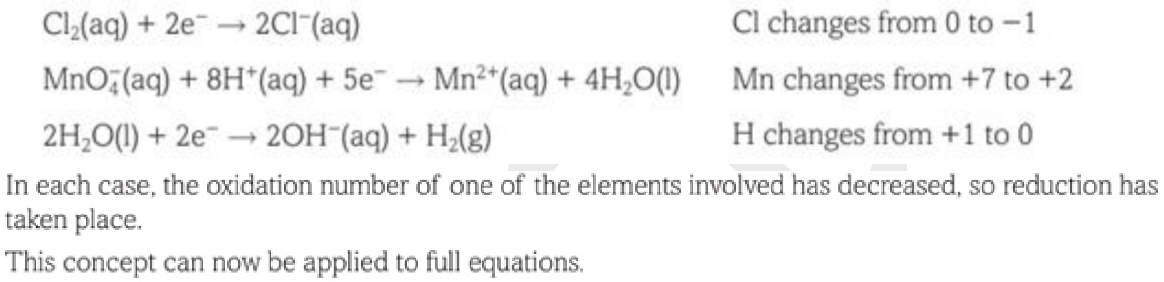
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$
$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$
$$2I^-(aq) \rightarrow I_2(aq) + 2e^-$$

In all three cases, electrons have been lost so the reactions are oxidations. But also notice that the oxidation number of the element has increased in each case.

- Zn has increased from 0 to +2.
- Fe has increased from +2 to +3.
- I has increased from -1 to 0.

This leads to another definition of **oxidation and reduction.**

Consider the following ionic half-equations:



$Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$ Cl changes from 0 to −1

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ Mn changes from +7 to +2

$2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$ H changes from +1 to 0

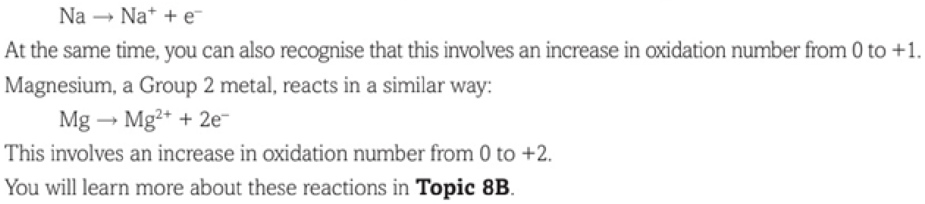
In each case, the oxidation number of one of the elements involved has decreased, so reduction has taken place.

This concept can now be applied to full equations.

REACTIONS OF S-BLOCK ELEMENTS

We can make some predictions about the reactions of s-block elements in terms of redox.

Reactive metals in Groups 1 and 2 lose electrons when they react. For example, the Group 1 element sodium loses one electron, which can be represented in this ionic half-equation:



$$Na \rightarrow Na^+ + e^-$$

At the same time, you can also recognise that this involves an increase in oxidation number from 0 to +1.

Magnesium, a Group 2 metal, reacts in a similar way:

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

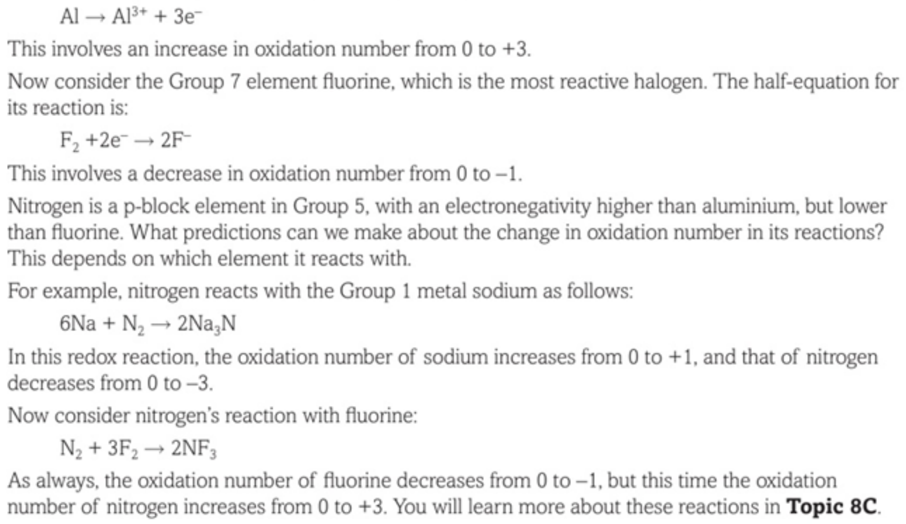
This involves an increase in oxidation number from 0 to +2.

You will learn more about these reactions in **Topic 8B**.

REACTIONS OF P-BLOCK ELEMENTS

We can also make some predictions about the reactions of p-block elements in terms of redox. Unfortunately, it is not as straightforward as with s-block elements. This is because the p-block contains elements with different characteristics.

For example, the Group 3 element aluminium is a metal with a reactivity nearly as high as magnesium, so it reacts in a similar way:



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

This involves an increase in oxidation number from 0 to +3.

Now consider the Group 7 element fluorine, which is the most reactive halogen. The half-equation for its reaction is:

$F_2 + 2e^- \rightarrow 2F^-$

This involves a decrease in oxidation number from 0 to −1.

Nitrogen is a p-block element in Group 5, with an electronegativity higher than aluminium, but lower than fluorine. What predictions can we make about the change in oxidation number in its reactions? This depends on which element it reacts with.

For example, nitrogen reacts with the Group 1 metal sodium as follows:

$6Na + N_2 \rightarrow 2Na_3N$

In this redox reaction, the oxidation number of sodium increases from 0 to +1, and that of nitrogen decreases from 0 to −3.

Now consider nitrogen's reaction with fluorine:

$N_2 + 3F_2 \rightarrow 2NF_3$

As always, the oxidation number of fluorine decreases from 0 to −1, but this time the oxidation number of nitrogen increases from 0 to +3. You will learn more about these reactions in **Topic 8C**.

8A 4 Oxidation numbers and nomenclature

SYSTEMATIC NAMES

When an element can have more than one oxidation state, the names of its compounds and its ions often include the oxidation number of the element, written as a Roman numeral in brackets. This name is often referred to as the 'systematic name'.

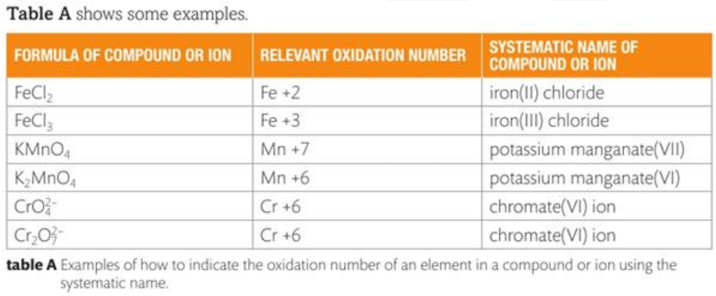


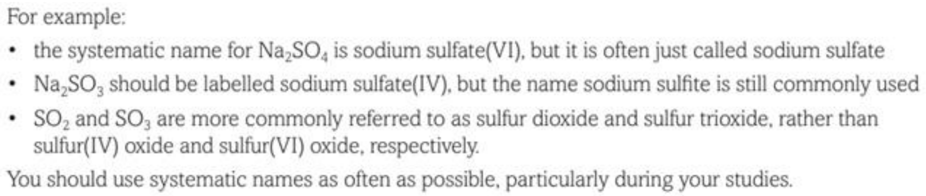
Table A shows some examples.

FORMULA OF COMPOUND OR ION	RELEVANT OXIDATION NUMBER	SYSTEMATIC NAME OF COMPOUND OR ION
$FeCl_2$	Fe +2	iron(II) chloride
$FeCl_3$	Fe +3	iron(III) chloride
$KMnO_4$	Mn +7	potassium manganate(VII)
K_2MnO_4	Mn +6	potassium manganate(VI)
CrO_4^{2-}	Cr +6	chromate(VI) ion
$Cr_2O_7^{2-}$	Cr +6	chromate(VI) ion

table A Examples of how to indicate the oxidation number of an element in a compound or ion using the systematic name.

WHEN TO USE SYSTEMATIC NAMES

We often use systematic names in chemistry so that we can be specific about the compounds and ions we are referring to. However, in the wider world the numbers are often left out.
For example:



For example:

- the systematic name for Na_2SO_4 is sodium sulfate(VI), but it is often just called sodium sulfate
- Na_2SO_3 should be labelled sodium sulfate(IV), but the name sodium sulfite is still commonly used
- SO_2 and SO_3 are more commonly referred to as sulfur dioxide and sulfur trioxide, rather than sulfur(IV) oxide and sulfur(VI) oxide, respectively.

You should use systematic names as often as possible, particularly during your studies.

WRITING FORMULAE WHEN YOU HAVE THE OXIDATION NUMBER

The other skill you need to develop is to work backwards from the oxidation number to deduce the formula of the compound or ion concerned.

8A 5 Constructing full ionic equations

BALANCING BY COUNTING ELECTRONS

STRAIGHTFORWARD EXAMPLES

When solid zinc is added to an aqueous solution of copper(II) sulfate, the following two changes take place:

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

Both ionic half-equations involve two electrons, so to construct the full ionic equation for this reaction you simply add together the two half-equations so that the electrons cancel out:

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

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

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

Now let's try an example where the electrons are not the same in the two ionic half-equations.

When chlorine gas is bubbled into an aqueous solution of iron(II) chloride, the iron(II) ions are oxidised to iron(III) ions and the chlorine molecules are reduced to chloride ions.

The two ionic half-equations are:

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$ and $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

This time, one of the half-equations contains one electron, while the other contains two electrons. Before these can be added together to produce a full equation, the equation containing Fe^{2+} must be multiplied by 2.

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

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

$$2Fe^{2+}(aq) + Cl_2(g) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$$

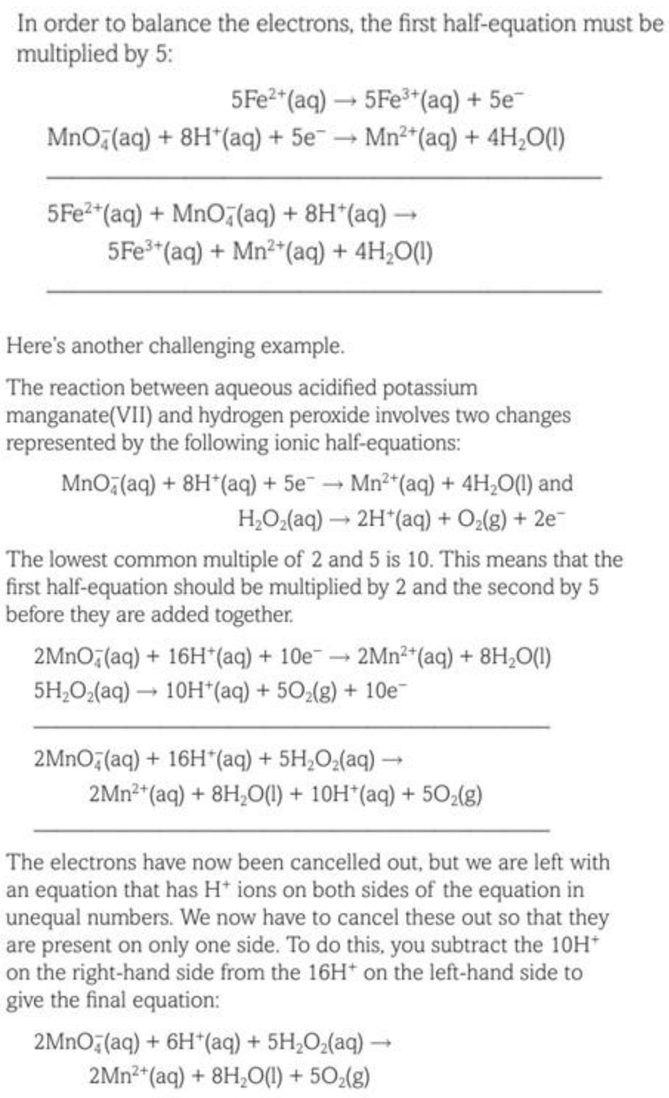
MORE COMPLICATED EXAMPLES

Here is something a little more difficult.

When an acidified aqueous solution of potassium manganate(VII) is added to an aqueous solution of iron(II) sulfate, the following two changes occur:

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$ and

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$



In order to balance the electrons, the first half-equation must be multiplied by 5:

$$5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e^-$$
$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$

Here's another challenging example.

The reaction between aqueous acidified potassium manganate(VII) and hydrogen peroxide involves two changes represented by the following ionic half-equations:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l) \text{ and}$$
$$H_2O_2(aq) \rightarrow 2H^+(aq) + O_2(g) + 2e^-$$

The lowest common multiple of 2 and 5 is 10. This means that the first half-equation should be multiplied by 2 and the second by 5 before they are added together.

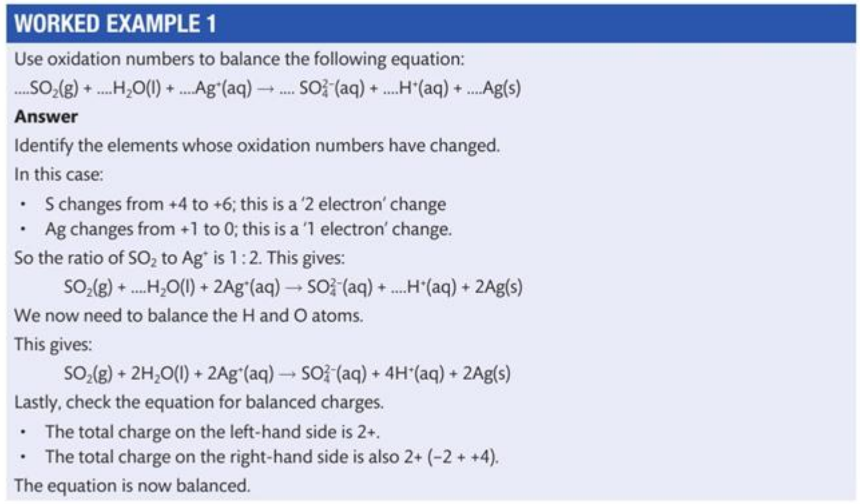
$$2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$$
$$5H_2O_2(aq) \rightarrow 10H^+(aq) + 5O_2(g) + 10e^-$$

$$2MnO_4^-(aq) + 16H^+(aq) + 5H_2O_2(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10H^+(aq) + 5O_2(g)$$

The electrons have now been cancelled out, but we are left with an equation that has H^+ ions on both sides of the equation in unequal numbers. We now have to cancel these out so that they are present on only one side. To do this, you subtract the $10H^+$ on the right-hand side from the $16H^+$ on the left-hand side to give the final equation:

$$2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$$

BALANCING USING OXIDATION NUMBERS



WORKED EXAMPLE 1

Use oxidation numbers to balance the following equation:

....$SO_2(g)$ + ...$H_2O(l)$ + ...$Ag^+(aq)$ → .... $SO_4^{2-}(aq)$ + ...$H^+(aq)$ + ...$Ag(s)$

Answer

Identify the elements whose oxidation numbers have changed.

In this case:

- S changes from +4 to +6; this is a '2 electron' change
- Ag changes from +1 to 0; this is a '1 electron' change.

So the ratio of SO_2 to Ag^+ is 1 : 2. This gives:

$SO_2(g)$ + ...$H_2O(l)$ + $2Ag^+(aq) \rightarrow SO_4^{2-}(aq)$ + ...$H^+(aq)$ + $2Ag(s)$

We now need to balance the H and O atoms.

This gives:

$$SO_2(g) + 2H_2O(l) + 2Ag^+(aq) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2Ag(s)$$

Lastly, check the equation for balanced charges.

- The total charge on the left-hand side is 2+.
- The total charge on the right-hand side is also 2+ (−2 + +4).

The equation is now balanced.

8B 1 Trends in groups 1 and 2

INTRODUCTION TO THE GROUP 1 AND 2 ELEMENTS

There are six elements in each of Groups 1 and 2. You are not likely to see samples of francium or radium, as all of their isotopes are radioactive. The other five elements in these groups look almost the same in appearance. You can describe all of them, when pure, as bright silvery solids. However, we have to keep them away from air to look like that. When exposed to air, they combine with oxygen to form oxides as surface layers, which makes them appear dull. Fig A shows the first five elements of Group 2 together.

▲ **fig A** From left to right: beryllium, magnesium, calcium, strontium and barium.

In this topic, we look at some trends in the properties of Group 1 and 2 elements.

TREND IN IONISATION ENERGY

We looked at ionisation energy in Topic 2. You may remember that it is a fundamental property that affects physical and chemical properties.

FIRST IONISATION ENERGIES IN GROUP 1

You should remember the definition of first ionisation energy. It is the energy required to remove an electron from each atom in one mole of atoms in the gaseous state. A general equation for this process, using M to represent an atom of any Group 1 element, is:

$$M(g) \rightarrow M^+(g) + e^-$$

Table A shows the metallic radius and the values of the first ionisation energies for the Group 1 elements.

ELEMENT	METALLIC RADIUS / nm	FIRST IONISATION ENERGY / kJ mol^{-1}
Lithium	0.152	519
Sodium	0.186	494
Potassium	0.231	418
Rubidium	0.244	402
Caesium	0.262	376

table A The metallic radii and the value of the first ionisation energies for the Group 1 elements.

FIRST AND SECOND IONISATION ENERGIES IN GROUP 2

Now we will consider the loss of two electrons from each atom, so we need to consider the second ionisation energy. This is the energy required to remove an electron from each singly charged ion in one mole of positive ions in the gaseous state. A general equation for this process is:

$$M^+(g) \rightarrow M^{2+}(g) + e^-$$

Table B shows the metallic radius and the values of the first and second ionisation energies for the Group 2 elements.

ELEMENT	METALLIC RADIUS / nm	IONISATION ENERGY / kJ mol^{-1}		
		FIRST	SECOND	1st + 2nd
Beryllium	0.112	900	1757	2657
Magnesium	0.160	738	1451	2189
Calcium	0.197	590	1145	1735
Strontium	0.215	550	1064	1614
Barium	0.224	503	965	1468

table B The metallic radii and the values of the first and second ionisation energies for the Group 2 elements.

FACTORS TO CONSIDER FOR GROUPS 1 AND 2

The factors to consider when explaining trends in ionisation energy are:

- the nuclear charge (or the number of protons in the nucleus)
- the orbital in which the electron exists

the shielding effect (sometimes called the 'screening effect'). This is the repulsion between filled inner shells and the electron being removed.

In Topic 2, we considered the subshell (or sublevel) from which the electron is being removed. For the Group 1 and 2 elements this is not necessary because in their reactions the electrons are always removed from an s subshell. You should be able to understand why the trend is a decrease down both Group 1 and Group 2.

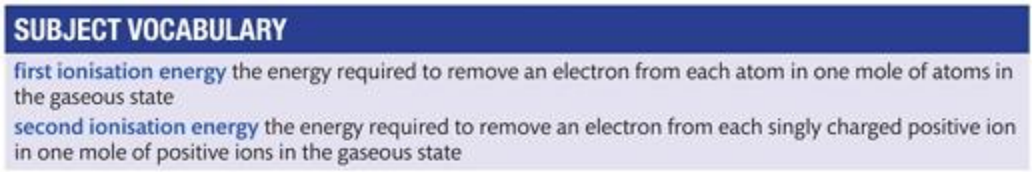
• As the nuclear charge increases, so the force of attraction for the electron being removed also increases. This means an increase in ionisation energy down the group.

• As each quantum shell is added, energy of the outermost electrons increases. This means a decrease in ionisation energy down the group.

• As the number of filled inner shells increases, their force of repulsion on the electron being removed increases. This means a decrease in ionisation energy down the group.

TREND IN REACTIVITY

We will look at the reactions of the elements of Groups 1 and 2 in Topics 8B.2 to 8B.6. In all these reactions, the element changes into either an M* ion or an M2+ ion, and there is a general increase in reactivity down the group. This can be explained by the decrease in energy needed to remove the electron from each atom of the element.



SUBJECT VOCABULARY

first ionisation energy the energy required to remove an electron from each atom in one mole of atoms in the gaseous state

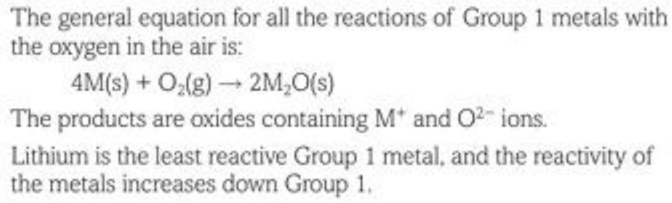
second ionisation energy the energy required to remove an electron from each singly charged positive ion in one mole of positive ions in the gaseous state

8B 2 Reactions of group 1 1elements

REACTIONS WITH OXYGEN

Group 1 metals, which are shiny when away from air, tarnish when exposed to oxygen. They can burn when heated in air or oxygen, but this isn't typically done in laboratories. Lithium batteries, commonly found in mobile phones and laptops, have been linked to fires due to rapid reactions with oxygen.

▲ **fig A** The lithium inside the battery of this mobile phone caught fire.



The general equation for all the reactions of Group 1 metals with the oxygen in the air is:

$$4M(s) + O_2(g) \rightarrow 2M_2O(s)$$

The products are oxides containing M^+ and O^{2-} ions.

Lithium is the least reactive Group 1 metal, and the reactivity of the metals increases down Group 1.

REACTIONS WITH CHLORINE

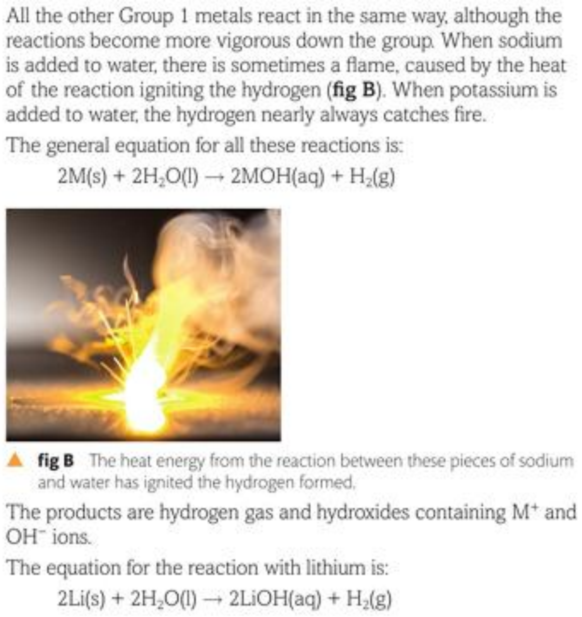
The Group 1 elements combine with chlorine when heated in chlorine gas. Just like the reactions with oxygen, the reactions with chlorine become more vigorous down the group, although this trend is harder to see than with the oxygen reactions.
The general equation for all of these reactions is:

$2M(s) + Cl_2(g) \rightarrow 2MCl(s)$

The products are chlorides containing M+ and Cl- ions.

REACTIONS WITH WATER

The reaction between lithium and water is vigorous. When a small piece of lithium is added to a beaker or trough of water, it reacts immediately and floats on the surface of the water. The fizzing is due to the formation of hydrogen gas and after a short while the lithium can no longer be seen. This is because it has reacted with the water to form a colourless solution of lithium hydroxide.



All the other Group 1 metals react in the same way, although the reactions become more vigorous down the group. When sodium is added to water, there is sometimes a flame, caused by the heat of the reaction igniting the hydrogen (**fig B**). When potassium is added to water, the hydrogen nearly always catches fire.

The general equation for all these reactions is:

$$2M(s) + 2H_2O(l) \rightarrow 2MOH(aq) + H_2(g)$$

fig B The heat energy from the reaction between these pieces of sodium and water has ignited the hydrogen formed.

The products are hydrogen gas and hydroxides containing M^+ and OH^- ions.

The equation for the reaction with lithium is:

$$2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$$

8B 3 Reactions of group 2 elements

REACTIONS WITH OXYGEN

Magnesium burns in air, resulting in a bright flame and white solid. Other Group 2 elements like calcium, strontium, and barium also react vigorously in air. These elements require heating for reactions to start, but even without heating, exposure to oxygen forms a coating of oxide, preventing further reactions. Barium is the most reactive and is often stored under oil.

The general equation for all these reactions is:

$2M(s) + O2(g) \rightarrow 2MO(s)$

The products are oxides containing M2+ and O2- ions.

REACTIONS WITH CHLORINE

The Group 2 elements combine with chlorine when heated in the gas. Just like the reactions with oxygen, the reactions with chlorine become more vigorous down the group. However, this trend is harder to see than with the oxygen reactions. Fig B shows what magnesium burning in a flask of chlorine gas looks like.
The general equation for all of these reactions is:

The products are chlorides containing M2+ and Cl- ions.

The general equation for all these reactions is:

$$2M(s) + O_2(g) \rightarrow 2MO(s)$$

REACTIONS WITH WATER

The reaction between magnesium and water is very slow and does not proceed completely. Calcium, strontium and barium react with increasing vigour (i.e. reactivity increases down the group), which can be seen by the increase in effervescence.

In fig C, you can see that a piece of magnesium in water is covered with bubbles of hydrogen gas, but that the reaction is not very vigorous.

Fig D shows piece of calcium in water is also covered with bubbles of hydrogen gas, but the reaction is more vigorous.

fig C Magnesium reacting very slowly with water.

fig D Calcium reacting vigorously with water.

The general equation for all of these reactions is:

$$M(s) + 2H_2O(l) \rightarrow M(OH)_2(aq) + H_2(g)$$

The products are hydrogen gas and hydroxides containing M^{2+} and OH^- ions.

The equation for the reaction with calcium is:

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$$

Calcium hydroxide is only slightly soluble in water, so the liquid in this experiment goes cloudy as a precipitate of calcium hydroxide forms.

The equation for the reaction with barium is:

$$Ba(s) + 2H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2(g)$$

Note the difference in the state symbol for the hydroxide in these equations, as barium hydroxide is soluble in water. You will learn more about the solubility of Group 2 hydroxides in the next topic.

MAGNESIUM AND STEAM

Magnesium reacts differently when heated in steam - it rapidly forms magnesium oxide (a white solid) and hydrogen gas in a vigorous reaction.

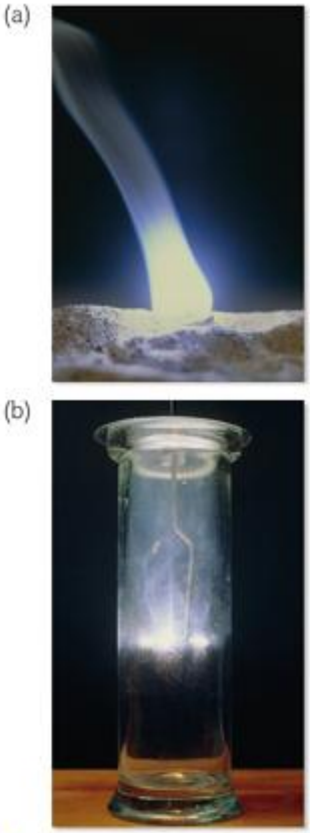
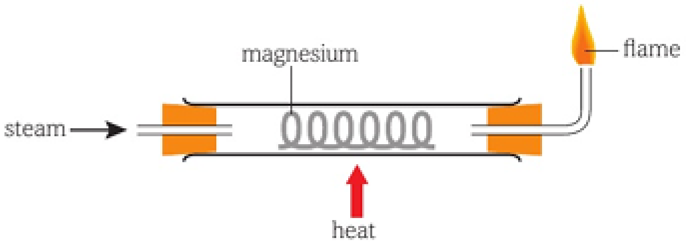


fig A (a) Burning magnesium in air. (b) Burning calcium in oxygen.

fig B Magnesium burning in chlorine.

The equation for this reaction is:

$$Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$$



REACTIONS OF BERYLLIUM AND RADIUM

You are not required to know any of the reactions of beryllium and radium.
In a similar way to Group 1, the trend is increasing reactivity down the group, so you should be able to predict that beryllium is less reactive than magnesium, and that radium is more reactive than barium.

8B 4 Oxides and hydroxides in groups 1 and 2

REACTIONS OF THE OXIDES WITH WATER

The Group 1 and 2 oxides are classed as basic oxides, which means that they can react with water to form alkalis. These reactions occur when the oxides are added to water. The only observation we can make is that the solids react to form colourless solutions. The general equations for these reactions are:

for Group 1 oxides: $M2O(s) + H_2O(l) \rightarrow 2MOH(aq)$
for Group 2 oxides: $MO(s) + H_2O(l) \rightarrow M(OH)_2(aq)$

These equations can be simplified because there is no change to the M* or M2* ion during the reactions.
$0^{-2} + H_2O \rightarrow 20H^-$
This equation shows the formation of hydroxide ions, which is why the resulting solutions are alkaline.

TRENDS IN SOLUBILITY OF THE GROUP 2 HYDROXIDES

The pH value of the alkaline solution formed depends partly on the relative amounts of oxide and water, but is also affected by differences in the solubility of the hydroxides.

TESTING FOR CARBON DIOXIDE

You may remember from your previous study of chemistry that limewater is used to test for carbon dioxide. It goes cloudy (or milky) as a white precipitate forms. Limewater is the name used for a saturated aqueous solution of calcium hydroxide. Carbon dioxide reacts to form calcium carbonate, the white precipitate, which is insoluble in water. The equation for the reaction is:

$CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + H_2O(1)$

As carbon dioxide is bubbled through limewater, the amount of precipitate increases (fig A).

MILK OF MAGNESIA

For over a century, a suspension of magnesium hydroxide in water has been sold as an indigestion remedy called milk of magnesia. A bottle of this contains a saturated solution of magnesium hydroxide mixed with extra solid magnesium hydroxide, which acts as an antacid.

The human stomach contains hydrochloric acid that is needed to digest food, but sometimes there is too much acid and the person develops symptoms of indigestion. Taking milk of magnesia neutralises some of the hydrochloric acid and relieves the symptoms. The equation for the reaction is:

$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$

Although hydroxide ions attack human tissue, the very low solubility of magnesium hydroxide means that the concentration of OH- ions in the medicine is also very low and is not a risk to health.

fig A As carbon dioxide is bubbled through limewater, the amount of precipitate increases.

REACTIONS OF THE OXIDES AND HYDROXIDES WITH ACIDS

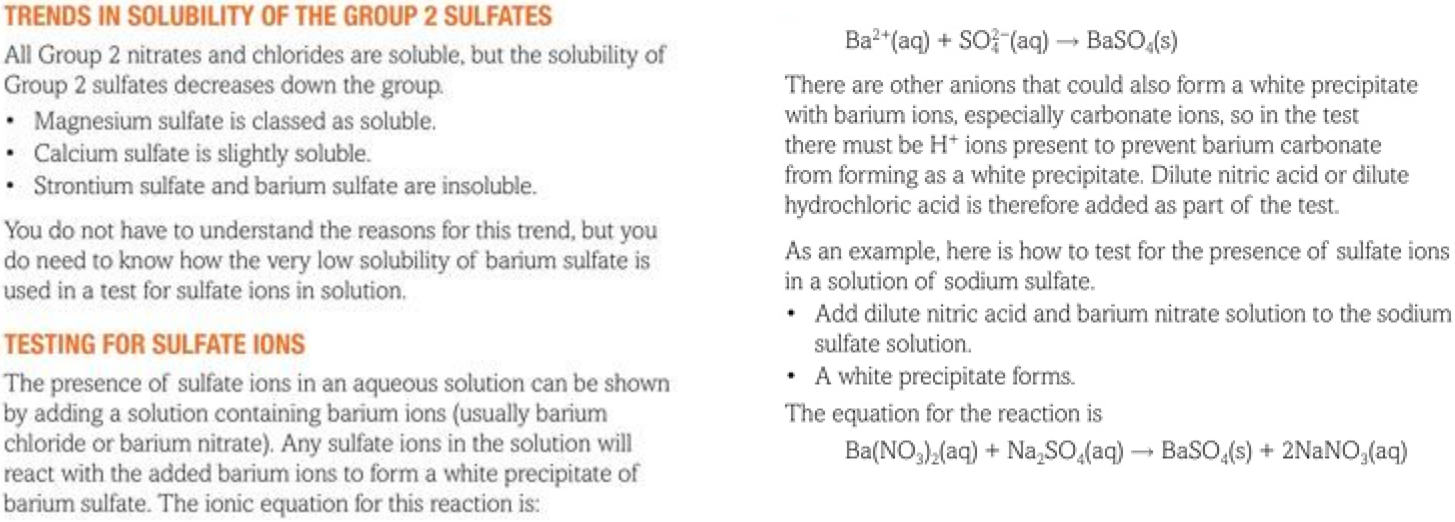
All of the Group 1 and 2 oxides and hydroxides react with acids to form salts and water. These reactions can be described as neutralisation reactions.
During the reactions, the only observations to be made are that a white solid reacts to form a colourless solution. The reactions are exothermic, so you may use some of them in experiments to measure energy changes.

fig B A bottle of milk of magnesia.

USE IN AGRICULTURE

For centuries, farmers have used lime to control soil acidity so that a greater yield of crops can be obtained.
fig C Lime being spread on a field.
Lime is mostly calcium hydroxide (obtained from limestone, which is calcium carbonate), and neutralises excess acidity in the soil. Using nitric acid to represent the acid in soil, the equation for this reaction is:

$Ca(OH)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_2O$



TRENDS IN SOLUBILITY OF THE GROUP 2 SULFATES

All Group 2 nitrates and chlorides are soluble, but the solubility of Group 2 sulfates decreases down the group.

- Magnesium sulfate is classed as soluble.
- Calcium sulfate is slightly soluble.
- Strontium sulfate and barium sulfate are insoluble.

You do not have to understand the reasons for this trend, but you do need to know how the very low solubility of barium sulfate is used in a test for sulfate ions in solution.

TESTING FOR SULFATE IONS

The presence of sulfate ions in an aqueous solution can be shown by adding a solution containing barium ions (usually barium chloride or barium nitrate). Any sulfate ions in the solution will react with the added barium ions to form a white precipitate of barium sulfate. The ionic equation for this reaction is:

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

There are other anions that could also form a white precipitate with barium ions, especially carbonate ions, so in the test there must be H^+ ions present to prevent barium carbonate from forming as a white precipitate. Dilute nitric acid or dilute hydrochloric acid is therefore added as part of the test.

As an example, here is how to test for the presence of sulfate ions in a solution of sodium sulfate.

- Add dilute nitric acid and barium nitrate solution to the sodium sulfate solution.
- A white precipitate forms.

The equation for the reaction is

$$Ba(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$$

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

There are other anions that could also form a white precipitate with barium ions, especially carbonate ions, so in the test there must be H+ ions present to prevent barium carbonate from forming as a white precipitate. Dilute nitric acid or dilute hydrochloric acid is therefore added as part of the test.

As an example, here is how to test for the presence of sulfate ions in a solution of sodium sulfate.
- Add dilute nitric acid and barium nitrate solution to the sodium sulfate solution.
- A white precipitate forms.

The equation for the reaction is

$$Ba(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$$

BARIUM MEALS

Solutions containing barium ions are poisonous to humans, however, barium sulfate is used in hospitals, where patients are sometimes given a barium 'meal'. This 'meal' contains barium sulfate, which is not poisonous because it is insoluble - although it contains barium ions, these ions are not free to move. Although bones can be seen clearly on X-rays, soft tissues cannot. If the patient has a barium meal before an X-ray, these soft tissues will show up more clearly because of the dense white solid.

SUBJECT VOCABULARY

basic oxides oxides of metals that react with water to form metal hydroxides, and with acids to form salts and water

fig D How a barium meal can help show up soft tissues on an X-ray.

8B 5 Thermal stability of compounds in groups 1 and 2

FACTORS AFFECTING THERMAL STABILITY

Thermal stability is a term that indicates how stable a compound is when it is heated. Does it not decompose at all (very thermally stable), or does it decompose as much as possible (not at all thermally stable), or somewhere in between?

The situation with Group 2 nitrates and carbonates is very different compared with a Group 1 chloride such as sodium chloride. There are three reasons for this.

1 The charge on a Group 2 cation is double that on a Group 1 cation (e.g. Ca2+ compared with Na*).

2 The size (ionic radius) of a Group 2 cation is smaller than that of the Group 1 cation in the same period.

3 The nitrate (NO3) and carbonate (CO) anions are more complex than the Cl-ion.

These differences mean that when Group 2 nitrates and carbonates are heated, they do not melt. Instead, they decompose. We need to look carefully at these factors to understand why this is.

- The larger, more complex nitrate ion can change into the smaller, more stable nitrite ion (NO2) or oxide ion (O2-) by decomposing and releasing oxygen gas and/or nitrogen dioxide gas.

- The larger, more complex carbonate ion can change into the smaller, more stable oxide ion (O2) by decomposing and releasing carbon dioxide gas, CO2.

- The stabilities of the nitrate and carbonate anions are influenced by the charge and size of the cations present. Smaller and more highly charged cations affect these anions more.

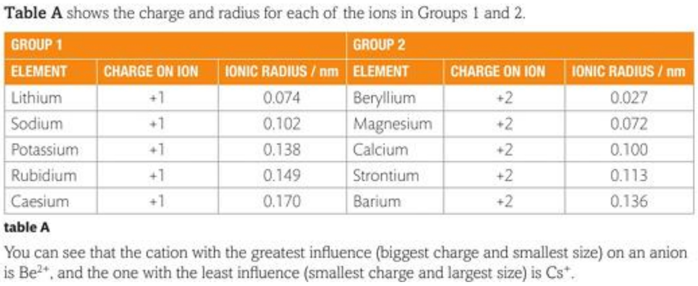


Table A shows the charge and radius for each of the ions in Groups 1 and 2.

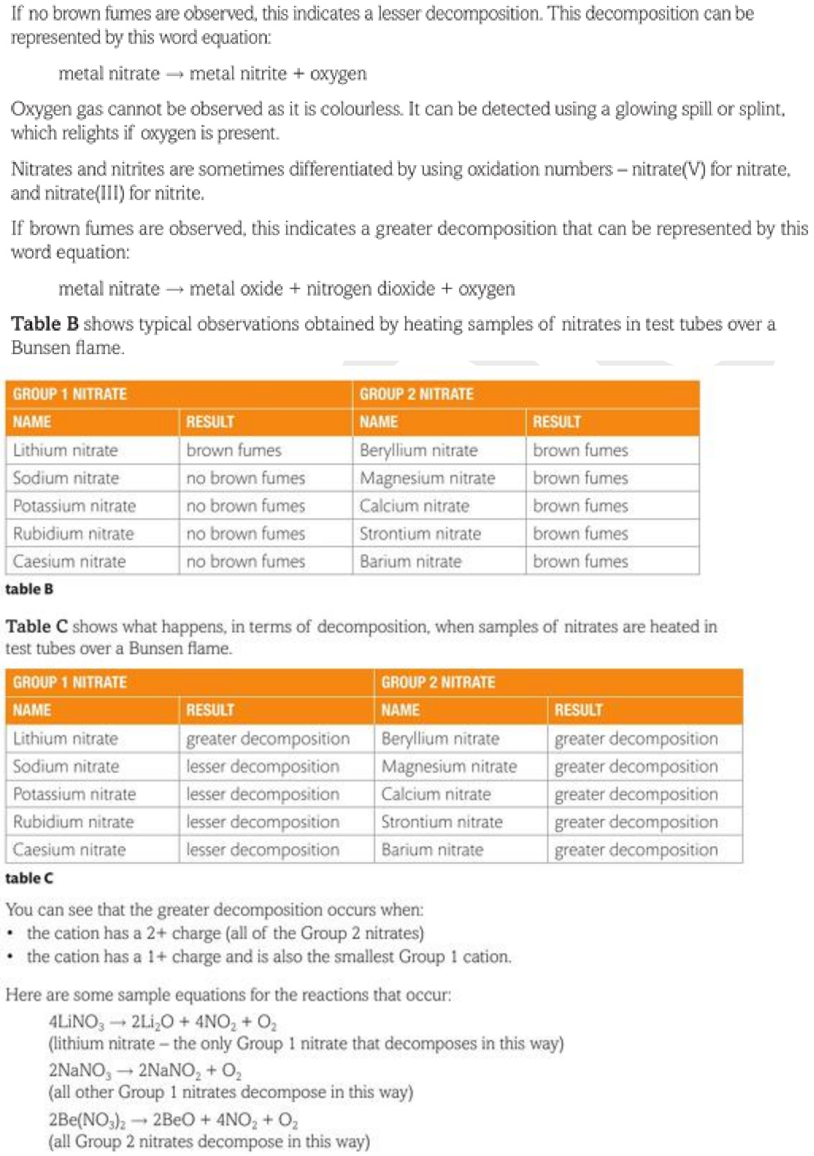
GROUP 1			GROUP 2		
ELEMENT	**CHARGE ON ION**	**IONIC RADIUS / nm**	**ELEMENT**	**CHARGE ON ION**	**IONIC RADIUS / nm**
Lithium	+1	0.074	Beryllium	+2	0.027
Sodium	+1	0.102	Magnesium	+2	0.072
Potassium	+1	0.138	Calcium	+2	0.100
Rubidium	+1	0.149	Strontium	+2	0.113
Caesium	+1	0.170	Barium	+2	0.136

table A

You can see that the cation with the greatest influence (biggest charge and smallest size) on an anion is Be^{2+}, and the one with the least influence (smallest charge and largest size) is Cs^+.

THERMAL STABILITY OF NITRATES

All of the nitrates of the Group 1 and Group 2 elements are white solids. When they are heated, they all decompose to nitrites or oxides, and give off nitrogen dioxide (brown fumes) and/or oxygen. If the nitrate contains water of crystallisation, then steam will also be observed.


If no brown fumes are observed, this indicates a lesser decomposition. This decomposition can be represented by this word equation:

metal nitrate → metal nitrite + oxygen

Oxygen gas cannot be observed as it is colourless. It can be detected using a glowing spill or splint, which relights if oxygen is present.

Nitrates and nitrites are sometimes differentiated by using oxidation numbers – nitrate(V) for nitrate, and nitrate(III) for nitrite.

If brown fumes are observed, this indicates a greater decomposition that can be represented by this word equation:

metal nitrate → metal oxide + nitrogen dioxide + oxygen

Table B shows typical observations obtained by heating samples of nitrates in test tubes over a Bunsen flame.

GROUP 1 NITRATE		GROUP 2 NITRATE	
NAME	**RESULT**	**NAME**	**RESULT**
Lithium nitrate	brown fumes	Beryllium nitrate	brown fumes
Sodium nitrate	no brown fumes	Magnesium nitrate	brown fumes
Potassium nitrate	no brown fumes	Calcium nitrate	brown fumes
Rubidium nitrate	no brown fumes	Strontium nitrate	brown fumes
Caesium nitrate	no brown fumes	Barium nitrate	brown fumes

table B

Table C shows what happens, in terms of decomposition, when samples of nitrates are heated in test tubes over a Bunsen flame.

GROUP 1 NITRATE		GROUP 2 NITRATE	
NAME	**RESULT**	**NAME**	**RESULT**
Lithium nitrate	greater decomposition	Beryllium nitrate	greater decomposition
Sodium nitrate	lesser decomposition	Magnesium nitrate	greater decomposition
Potassium nitrate	lesser decomposition	Calcium nitrate	greater decomposition
Rubidium nitrate	lesser decomposition	Strontium nitrate	greater decomposition
Caesium nitrate	lesser decomposition	Barium nitrate	greater decomposition

table C

You can see that the greater decomposition occurs when:

- the cation has a 2+ charge (all of the Group 2 nitrates)
- the cation has a 1+ charge and is also the smallest Group 1 cation.

Here are some sample equations for the reactions that occur:

$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$
(lithium nitrate – the only Group 1 nitrate that decomposes in this way)

$2NaNO_3 \rightarrow 2NaNO_2 + O_2$
(all other Group 1 nitrates decompose in this way)

$2Be(NO_3)_2 \rightarrow 2BeO + 4NO_2 + O_2$
(all Group 2 nitrates decompose in this way)

THERMAL STABILITY OF CARBONATES

All of the carbonates of the Group 1 and Group 2 elements are white solids. When they are heated, they either do not decompose, or decompose to oxides and give off carbon dioxide. As the gas given off is colourless and the carbonate and oxide are both white solids, there are no observations that can be made.

Table D shows what happens when samples of carbonates are heated in test tubes over a Bunsen flame.

GROUP 1 CARBONATE		GROUP 2 CARBONATE	
NAME	**RESULT**	**NAME**	**RESULT**
Lithium carbonate	decomposition	Beryllium carbonate	decomposition
Sodium carbonate	no decomposition	Magnesium carbonate	decomposition
Potassium carbonate	no decomposition	Calcium carbonate	decomposition
Rubidium carbonate	no decomposition	Strontium carbonate	decomposition
Caesium carbonate	no decomposition	Barium carbonate	decomposition

table D Results, in terms of decomposition, when samples of carbonates are heated.

SUBJECT VOCABULARY

thermal stability a measure of the extent to which a compound decomposes when heated

You can see that the pattern is similar to that of the nitrates. The lithium compound and all of the Group 2 compounds behave differently from the other Group 1 compounds.

Lithium carbonate decomposes at lower temperatures than the other Group 1 carbonates:

$$Li_2CO_3 \rightarrow Li_2O + CO_2$$

Other Group 1 carbonates do not decompose on heating, except at very high temperatures.

All Group 2 carbonates decompose in the same way, but with increasing difficulty down the group. A typical equation for one of these decompositions is:

$$CaCO_3 \rightarrow CaO + CO_2$$

You can see a similar pattern as with the nitrates. Decomposition occurs when:

- the cation has a 2+ charge (all of the Group 2 carbonates)
- the cation has a 1+ charge and is also the smallest Group 1 cation (only lithium carbonate).

▲ **fig A** Calcium oxide forms when calcium carbonate (limestone) is heated strongly. If the strong heating is continued, there is no further chemical change, but a very bright glow is seen. This is the origin of 'limelight' – it was formerly used in theatre lighting.

8B 6 Flame tests and the test for ammonium ions

INTRODUCTION TO FLAME TESTS

A flame test seems a very simple chemical test to identify the presence of a cation in a compound. However, it is important to know how to do one carefully, to know how to interpret the results, and to understand how the test works.

A flame test result can indicate the presence of some metals (in the form of cations) in Groups 1 and 2 of the Periodic Table. It does not work for all of them.

HOW TO DO A FLAME TEST

We will assume that a small quantity of a solid is available in a glass dish. This is how to do a flame test.

- Wear safety glasses and a lab coat. Within a fume cupboard, light a Bunsen burner.

- Using a dropper, add a few drops of concentrated hydrochloric acid to the solid and mix together so that the metal compound begins to dissolve.

Dip a clean metal wire (platinum or nichrome) or silica rod into the mixture to obtain a sample of the compound.

- Hold the end of the wire or rod in the flame and observe the colour.

PROBLEMS WITH A FLAME TEST

There are two main problems with a flame test.

- Many compounds contain small amounts of sodium compounds as impurities, so the intense colour of sodium can hide other colours.

- Describing colours with words is subjective - people have different levels of colour vision, and a word description of a colour may mean different colours to different people.

fig A A platinum wire loop with a sample of a strontium compound being held in a Bunsen flame.

COLOUR DESCRIPTIONS

Some traditional descriptions of colours are problematic. For example, what is the colour 'brick red"? It may depend on the bricks used in a particular location, and these are not the same throughout the world. Another example is the traditional colour description used for potassium. It is lilac, but can you tell the difference between lilac and lavender, magenta, mauve, pink, plum, puce, purple and violet?

Table A shows some traditional colour descriptions obtained when Group 1 and 2 compounds are tested in this way.

METAL CATION	FORMULA	COLOUR
Lithium	Li^+	red
Sodium	Na^+	yellow/orange
Potassium	K^+	lilac
Rubidium	Rb^+	red/purple
Caesium	Cs^+	blue/violet
Beryllium	Be^{2+}	(no colour)
Magnesium	Mg^{2+}	(no colour)
Calcium	Ca^{2+}	(brick) red
Strontium	Sr^{2+}	(crimson) red
Barium	Ba^{2+}	(apple) green

table A Colour descriptions obtained when Group 1 and 2 compounds undergo a flame test.

WHAT CAUSES THE COLOURS IN FLAME TESTS?

The simple answer is electron transitions. However, we need a more complete explanation than this.

Electrons in an atom occupy orbitals at specific energy levels, often represented by configurations like 2.8.1. They can absorb energy and move to higher levels, known as the 'ground state'. This is achieved during a flame test, where the electron returns to its ground state, releasing energy, which corresponds to visible light radiation.

The visible spectrum, covering 400-700 nm wavelengths, corresponds to the yellow-orange color of sodium in a flame test, while magnesium has no flame colour due to its electron transition outside the visible spectrum.

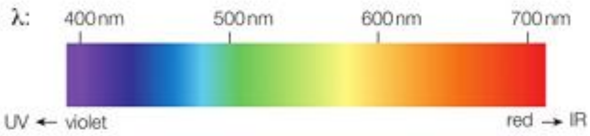


fig B The wavelengths of the spectrum of visible light.

THE TEST FOR AMMONIUM IONS

One cation that does not give a colour in a flame test is the ammonium ion. The usual test for ammonium ions in a solid or solution is to add sodium hydroxide solution and warm the mixture. The addition of sodium hydroxide causes this reaction:

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

and the warming releases ammonia gas. Ammonia can be recognised by its smell, but you can use damp litmus paper as a simple chemical test, which turns blue (ammonia is the only common alkaline gas). Alternatively, hydrogen chloride gas (from concentrated hydrochloric acid) reacts with ammonia to form white smoke of ammonium chloride:

$$NH_3 + HCl \rightarrow NH_4Cl$$

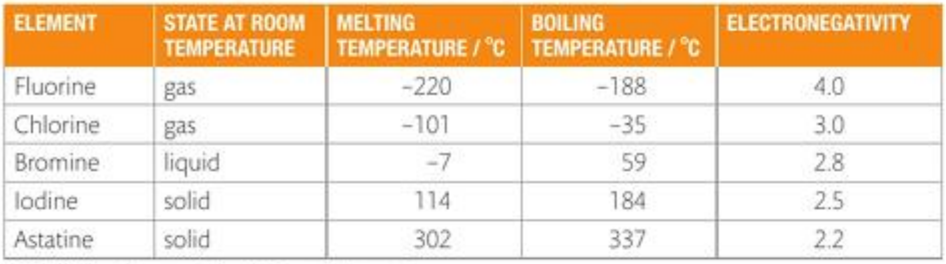
fig C The yellow-orange colour of sodium street lights is the same as the colour of sodium in a flame test.

8C 1 Trends in group 7

INTRODUCTION TO THE GROUP 7 ELEMENTS

Group 7 of the Periodic Table contains five elements. These elements are often known as halogens and they all form salts called halides. The term 'halogen' comes from Greek and means 'salt producer'. When considering the properties of the group, the elements at the top and bottom of the group (fluorine and astatine) are often ignored. Fluorine is ignored because it sometimes behaves differently from chlorine, bromine and iodine, and astatine is ignored because (like radium in Group 2) it only exists as radioactive isotopes.

Table A shows some information about the Group 7 elements.

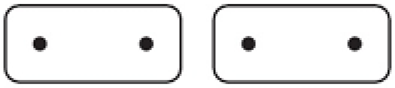


ELEMENT	STATE AT ROOM TEMPERATURE	MELTING TEMPERATURE / °C	BOILING TEMPERATURE / °C	ELECTRONEGATIVITY
Fluorine	gas	−220	−188	4.0
Chlorine	gas	−101	−35	3.0
Bromine	liquid	−7	59	2.8
Iodine	solid	114	184	2.5
Astatine	solid	302	337	2.2

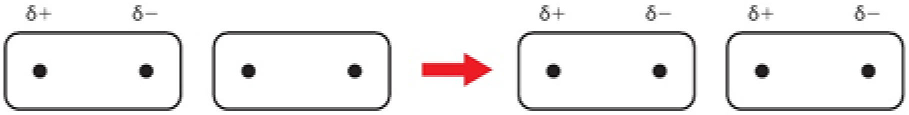
table A Physical properties of Group 7 elements.

TRENDS IN MELTING AND BOILING TEMPERATURE

Halogens, as diatomic molecules, have melting and boiling temperatures influenced by intermolecular forces of attraction, known as London forces. They are non-polar on average due to their identical atoms and equal electron pairs. However, when electron density fluctuates, the centers of positive and negative charge may not coincide, resulting in an instantaneous dipole. A rectangular shape represents a halogen molecule with two nuclei.



If the molecule on the left becomes an instantaneous dipole, then it will cause an induced dipole in the molecule on the right. This results in a force of attraction between the two molecules:



EQUATIONS FOR CHANGES OF STATE

You are probably used to writing equations for changes, but we use equations for physical changes less often. As well as using the correct state symbols, it is important to remember to write the formulae (not the symbols) of the halogens.

When bromine is left at room temperature, it gives off brown vapour, as its boiling point (59°C) is not much higher than room temperature. The equation for this change is:

$Br_2(1) \rightarrow Br_2(g)$

When iodine is warmed, most of it changes directly into a vapour without melting. This change is called sublimation.

The equation for this change is:

$I_2(S) \rightarrow I_2(g)$

TREND IN ELECTRONEGATIVITY

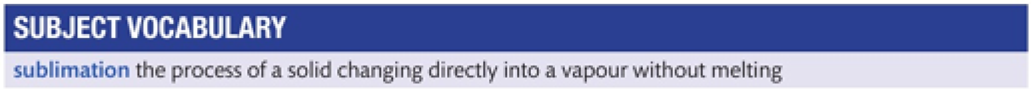
We have already seen in Topic 3B that electronegativity is the ability of an atom to attract the pair of electrons in a covalent bond. The 0-4 scale devised by Linus Pauling is still used. The electronegativity of an atom depends on:

- its nuclear charge - the bigger the nuclear charge, the higher the electronegativity
- the distance between the nucleus and the bonding pair of electrons - the shorter the distance, the higher the electronegativity
- the shielding effect of electrons in inner energy levels - the fewer energy levels, the higher the electronegativity.

The electronegativity of the Group 7 elements is the highest of any group in the Periodic Table. The electronegativity of fluorine is the highest of all elements.

TREND IN REACTIVITY

Fluorine is an extremely reactive element, and reactivity decreases down Group 7. Because of their high electronegativity, most reactions of the halogens involve them acting as oxidising agents and gaining electrons to form negative ions or becoming the slightly negative (8-) part of a polar molecule. The decreasing reactivity down the group can therefore be explained by reference to the same factors used to explain the decreasing electronegativity down the group.



SUBJECT VOCABULARY

sublimation the process of a solid changing directly into a vapour without melting

8C 2 Redox reactions in group 7

REACTIONS WITH METALS IN GROUPS 1 AND 2

There are 12 elements in Groups 1 and 2, and 5 elements in Group 7, so there are 60 possible reactions to consider. You do not need to know details of all of these reactions, but here are some useful generalisations that you should know.

• Reactions are most vigorous between elements at the bottom of Groups 1 and 2, and elements at the top of Group 7. The most vigorous reaction should be between caesium (or francium) and fluorine, and the least vigorous between beryllium and iodine (or astatine).
The products of these reactions are salts, ionic solids that are usually white.

• All of these reactions involve electron transfer to the halogen, so they are redox reactions in which the halogen acts as an oxidising agent.

• The oxidation number of the halogen decreases from 0 to -1, and the oxidation number of the metal increases from 0 to +1 or +2, depending on the group.

Here are a couple of sample equations:

- lithium reacting with chlorine $2Li + Cl_2 \rightarrow 2LiCl$
- barium reacting with bromine $Ba + Br_2 \rightarrow BaBr_2$

HALOGEN/HALIDE DISPLACEMENT REACTIONS

A more reactive halogen can displace a less reactive halogen from one of its compounds. So:

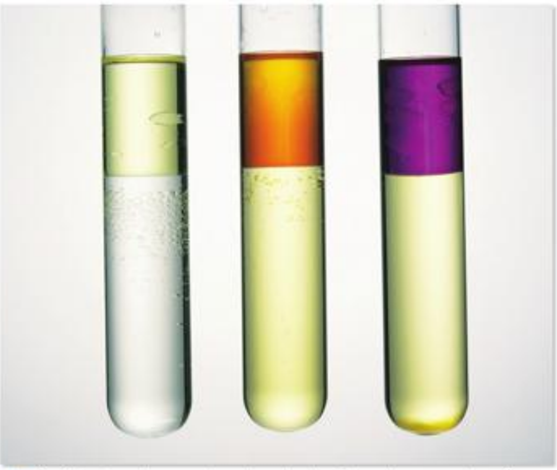
- chlorine displaces bromine and iodine
- bromine displaces iodine but not chlorine
- iodine does not displace either chlorine or bromine.

Reactions in aqueous solutions are indicated by color changes, but interpretation is challenging due to color similarity and concentration variation. For example, bromine in liquid form may appear red-brown, while iodine in water may appear brown. To better understand these reactions, add an organic solvent like cyclohexane, as halogens dissolve in this solvent.

Here are some sample equations:

- chlorine displacing bromine $Cl_2 + 2NaBr \rightarrow 2NaCl + Br_2$
- bromine displacing iodine $Br_2 + 2I^- \rightarrow 2Br^- + I_2$

These equations are examples of redox reactions. The reacting halogen decreases its oxidation number from 0 to -1, and the reacting halide increases its oxidation number from -1 to 0.



▲ **fig A** Look at the upper layer in each tube. The pale green colour of chlorine does not change much, the orange colour of bromine looks a bit darker, but the colour of iodine changes to purple or violet in cyclohexane.

The decreasing reactivity of chlorine, bromine and iodine in the reactions above can be explained using the same factors as in Topic 8C.1. Chlorine is the most reactive of the three because:

- it is the smallest atom, so the incoming electron gets closer to, and is more attracted by, the protons in the nucleus
- it has the smallest number of complete inner energy levels of electrons, so the incoming electron experiences the least repulsion.

DISPROPORTIONATION REACTIONS OF CHLORINE

Disproportionation is a more unusual type of reaction. In this reaction, one element undergoes both oxidation and reduction at the same time. We will look at three examples of this type of reaction, all involving chlorine.

CHLORINE WITH WATER

When chlorine is added to water, it dissolves to form a solution that is sometimes called 'chlorine water' (just as 'bromine water' is used to refer to bromine dissolved in water). Some of the dissolved chlorine also reacts to form a mixture of two acids.

You are familiar with one of the acids, hydrochloric acid, but the other acid is chloric(I) acid (its old name is hypochlorous acid). Its formula is shown in the equation below as HClO, but HOCl is also commonly used. Both acids are colourless solutions, so there is no visible change during the reaction.

fig B Chlorine can reduce the risk of transmitting infections in public swimming pools.

The disproportionation that occurs can be shown using oxidation numbers:

$Cl_2 + H_2O \rightarrow HCl + HClO$

0 −1 chlorine is reduced

0 +1 chlorine is oxidised

The addition of chlorine to disinfect water for drinking purposes has saved countless lives, and continues to do so today. It kills the pathogens responsible for water-borne diseases such as cholera.

CHLORINE WITH COLD ALKALI

When chlorine is added to cold dilute aqueous sodium hydroxide, it reacts to form the salts of the acids in the equation above. These salts are sodium chloride and sodium chlorate(I), which is also known as sodium hypochlorite.

Again, the disproportionation that occurs can be shown using oxidation numbers:

Again, the disproportionation that occurs can be shown using oxidation numbers:

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

0 −1 chlorine is reduced

0 +1 chlorine is oxidised

The sodium chlorate(I) formed is also a disinfectant, but it is mainly known for its bleaching action. It is used extensively in industry and is the active ingredient in household bleach.

CHLORINE WITH HOT ALKALI

When chlorine is added to hot concentrated sodium hydroxide solution, it reacts to form sodium chloride and a different product, sodium chlorate(V).

Again, the disproportionation that occurs can be shown using oxidation numbers:

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

0 −1 chlorine is reduced

0 +5 chlorine is oxidised

The sodium chlorate(V) formed is also used in bleaching, and as a weed killer.

Bromine and iodine react in similar ways.

REACTIONS OF FLUORINE AND ASTATINE

If you are asked to predict reactions of fluorine and astatine that you are not familiar with, then you can use information in this topic to help you. For example, you could write an equation to represent the reaction between sodium and astatine, based on your knowledge of the reaction between sodium and iodine.

SUBJECT VOCABULARY

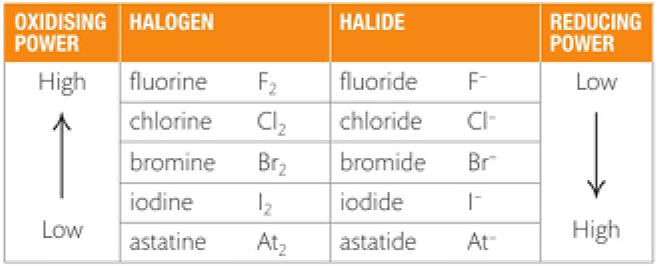
disproportionation reaction a reaction involving the simultaneous oxidation and reduction of an element in a single species

8C 3 Reactions of halides with sulfuric acids

REDOX REACTIONS AGAIN

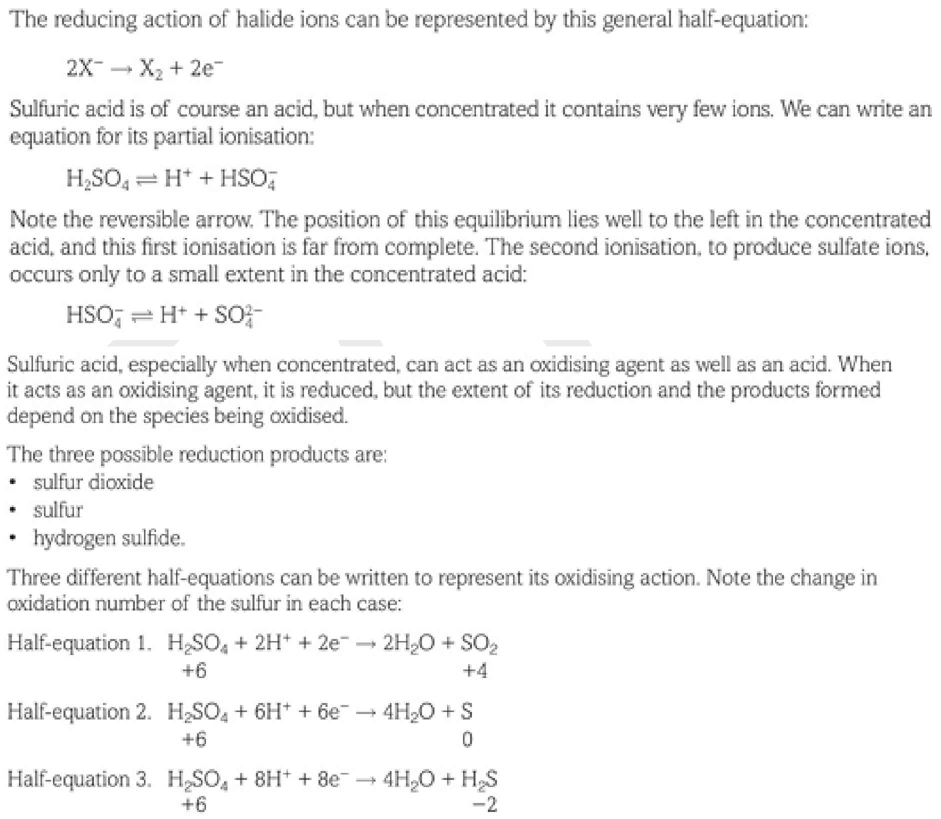
In Topics 8A.3, 8C.1 and 8C.2, you have learnt about several examples of the halogens acting as oxidising agents, and you know that this oxidising power decreases down the group.

In this topic, we will look at reactions of halide ions, not halogen molecules. It is important to realise that in these reactions, the halides act as reducing agents, and that the trend is different. This is shown in table A



OXIDISING POWER	HALOGEN		HALIDE		REDUCING POWER
High	fluorine	F_2	fluoride	F^-	Low
↑	chlorine	Cl_2	chloride	Cl^-	↓
	bromine	Br_2	bromide	Br^-	
	iodine	I_2	iodide	I^-	
Low	astatine	At_2	astatide	At^-	High

table A Notice that the decreasing trend down the group in oxidising power of halogens goes with the increasing trend in reducing power of halides.



The reducing action of halide ions can be represented by this general half-equation:

$$2X^- \rightarrow X_2 + 2e^-$$

Sulfuric acid is of course an acid, but when concentrated it contains very few ions. We can write an equation for its partial ionisation:

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

Note the reversible arrow. The position of this equilibrium lies well to the left in the concentrated acid, and this first ionisation is far from complete. The second ionisation, to produce sulfate ions, occurs only to a small extent in the concentrated acid:

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

Sulfuric acid, especially when concentrated, can act as an oxidising agent as well as an acid. When it acts as an oxidising agent, it is reduced, but the extent of its reduction and the products formed depend on the species being oxidised.

The three possible reduction products are:

- sulfur dioxide
- sulfur
- hydrogen sulfide.

Three different half-equations can be written to represent its oxidising action. Note the change in oxidation number of the sulfur in each case:

Half-equation 1. $\underset{+6}{H_2SO_4} + 2H^+ + 2e^- \rightarrow 2H_2O + \underset{+4}{SO_2}$

Half-equation 2. $\underset{+6}{H_2SO_4} + 6H^+ + 6e^- \rightarrow 4H_2O + \underset{0}{S}$

Half-equation 3. $\underset{+6}{H_2SO_4} + 8H^+ + 8e^- \rightarrow 4H_2O + \underset{-2}{H_2S}$

These half-equations may look complicated at first, but you should be able to see the pattern.

• In half-equation 1, the decrease in oxidation number (+6 to +4) is 2, which is the same as the numbers of H+ ions and electrons in the equation.

- The pattern is similar in the other two equations. The decrease in oxidation number of the sulfur is the same as the numbers of H+ ions and electrons in the half-equation (6 in reaction 2, 8 in reaction 3).

OBSERVATIONS AND PRODUCTS

Table B shows typical observations made, and products formed, when concentrated sulfuric acid is added to three sodium halides.

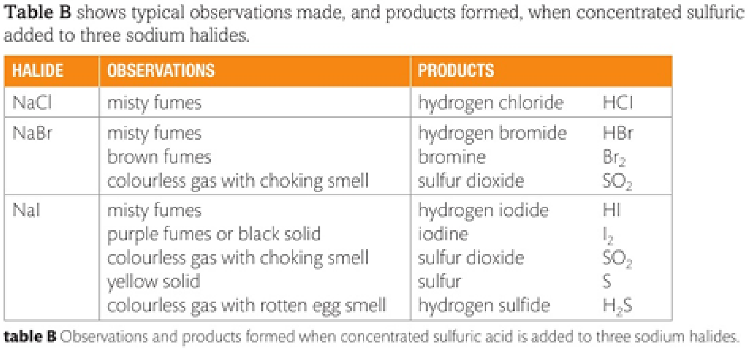
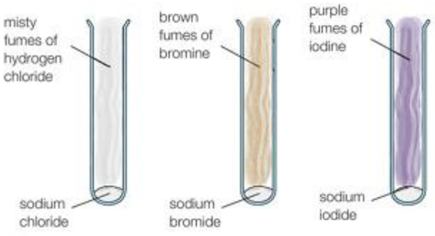


Table B shows typical observations made, and products formed, when concentrated sulfuric acid is added to three sodium halides.

HALIDE	OBSERVATIONS	PRODUCTS	
NaCl	misty fumes	hydrogen chloride	HCl
NaBr	misty fumes brown fumes colourless gas with choking smell	hydrogen bromide bromine sulfur dioxide	HBr Br_2 SO_2
NaI	misty fumes purple fumes or black solid colourless gas with choking smell yellow solid colourless gas with rotten egg smell	hydrogen iodide iodine sulfur dioxide sulfur hydrogen sulfide	HI I_2 SO_2 S H_2S

table B Observations and products formed when concentrated sulfuric acid is added to three sodium halides.



▲ **fig A** From left to right: tubes containing hydrogen chloride (formed from sodium chloride), bromine (formed from sodium bromide) and iodine (formed from sodium iodide).

In fig A, the tubes show misty fumes of hydrogen chloride, brown fumes of bromine, and purple fumes of iodine. The sulfuric acid behaves as an acid with sodium chloride, while bromide and iodide ions have different reducing powers, causing the reduction of sulfuric acid.

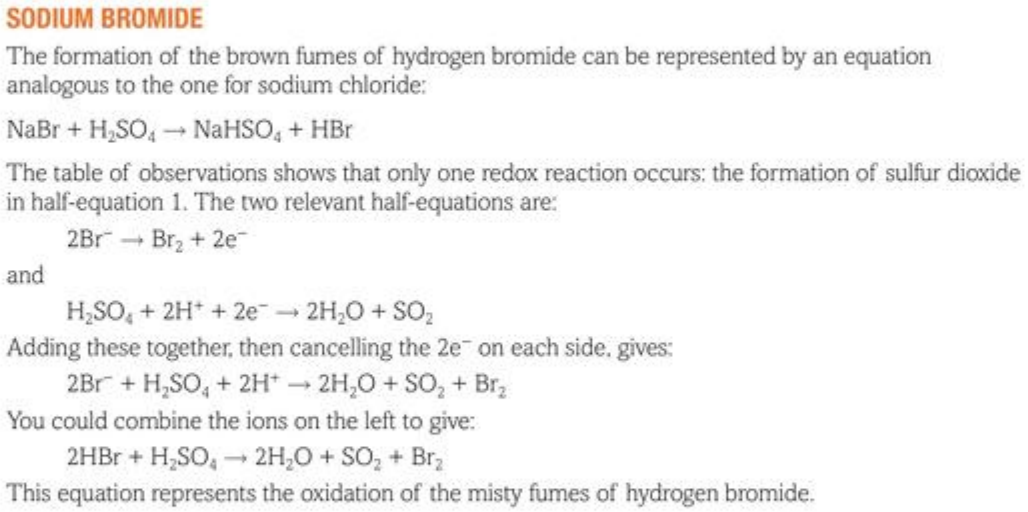
CONSTRUCTING EQUATIONS

Some of the equations you see, or are asked to write, may look very complicated and be hard to remember. It is better not to try to remember them, but to work them out by the addition of half-equations. This method is recommended for the redox equations of sodium bromide and sodium iodide.

SODIUM CHLORIDE

The reaction between sodium chloride and concentrated sulfuric acid can be represented by one equation, because no redox reactions are occurring:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$



SODIUM BROMIDE

The formation of the brown fumes of hydrogen bromide can be represented by an equation analogous to the one for sodium chloride:

$$NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr$$

The table of observations shows that only one redox reaction occurs: the formation of sulfur dioxide in half-equation 1. The two relevant half-equations are:

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

and

$$H_2SO_4 + 2H^+ + 2e^- \rightarrow 2H_2O + SO_2$$

Adding these together, then cancelling the $2e^-$ on each side, gives:

$$2Br^- + H_2SO_4 + 2H^+ \rightarrow 2H_2O + SO_2 + Br_2$$

You could combine the ions on the left to give:

$$2HBr + H_2SO_4 \rightarrow 2H_2O + SO_2 + Br_2$$

This equation represents the oxidation of the misty fumes of hydrogen bromide.

SODIUM IODIDE

The formation of the purple fumes of hydrogen iodide can be represented by an equation analogous to the one for sodium chloride:

$$NaI + H_2SO_4 \rightarrow NaHSO_4 + HI$$

The table of observations shows that three redox reactions occur, so the situation is more complicated. You could construct an equation showing the formation of sulfur dioxide in the same way as for sodium bromide.

Here is the result of applying the same method to the formation of sulfur in half-equation 2. The two relevant half-equations are:

$$2I^- \rightarrow I_2 + 2e^-$$

and

$$H_2SO_4 + 6H^+ + 6e^- \rightarrow 4H_2O + S$$

Before you add these together, you need to multiply the first one by three, so that the $6e^-$ on each side will cancel, giving:

$$6I^- + H_2SO_4 + 6H^+ \rightarrow 4H_2O + S + 3I_2$$

You could combine the ions on the left to give:

$$6HI + H_2SO_4 \rightarrow 4H_2O + S + 3I_2$$

This equation represents the oxidation of the misty fumes of hydrogen iodide.

You should now be able to use the same method to construct an equation to represent the oxidation of the misty fumes of hydrogen iodide to form hydrogen sulfide.

8C 4 Other reactions of halides

TESTING FOR HALIDE IONS IN SOLUTION

These tests depend on the very low solubility of silver halides in water and their different solubility in aqueous ammonia.

The reagent is silver nitrate solution, but dilute nitric acid is added first to make sure that any other anions (especially carbonate ions) are removed, as they would also form precipitates.

If a precipitate is obtained, it is then usual to add some ammonia solution. This solution can be dilute or concentrated.

Table A and fig A show the results obtained. This test cannot be used to detect fluoride ions in aqueous solution, because silver fluoride is soluble.

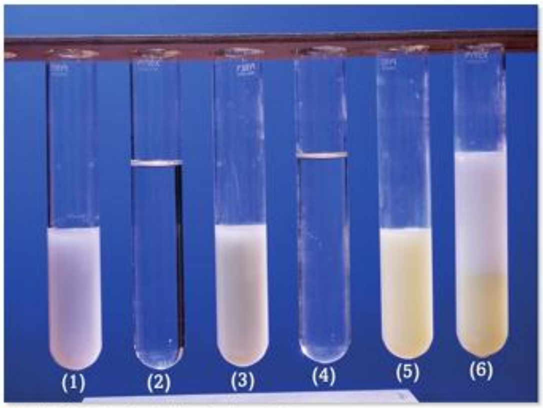


fig A Testing for halide ions in solution.

	CHLORIDE IONS	BROMIDE IONS	IODIDE IONS
add silver nitrate solution	white precipitate	cream precipitate	yellow precipitate
add dilute aqueous ammonia	soluble	insoluble	insoluble
add concentrated aqueous ammonia	soluble	soluble	insoluble

table A Results obtained from precipitation reactions of the aqueous anions Cl^-, Br^- and I^- with silver nitrate solution, followed by aqueous ammonia.

From left to right in fig A:

- tube 1 shows the white precipitate formed from a chloride
- tube 2 shows the result of adding dilute aqueous ammonia to the white precipitate
- tube 3 shows the cream precipitate formed from a bromide
- tube 4 shows the result of adding concentrated aqueous ammonia to the cream precipitate tube 5 shows the yellow precipitate formed from an iodide

tube 6 shows the result of adding concentrated aqueous ammonia to the yellow precipitate - it has not dissolved.

The general ionic equation for the formation of the precipitates is:

$$Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$$

You can write a specific equation, such as:

$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$

The results in table A suggest that a halide ion could be identified without using aqueous ammonia. However, the colours of the three precipitates are similar. Even when all three are seen together, it is not easy to be sure which is which. In a single test, where only one precipitate is seen, this would be even more difficult.
Aqueous ammonia is a useful solvent because the precipitates have different solubilities in it.

- Silver chloride dissolves readily in both dilute and concentrated aqueous ammonia.

- Silver bromide dissolves readily in concentrated aqueous ammonia, but not in dilute aqueous ammonia.

- Silver iodide dissolves in neither dilute nor concentrated aqueous ammonia.

Dissolving of the precipitates occurs because of the formation of a complex ion. In the case of silver chloride, the equation for the reaction is:

$$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$$

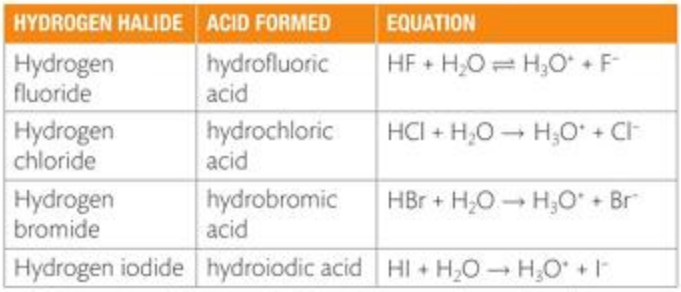
HYDROGEN HALIDES ACTING AS ACIDS

All of the hydrogen halides are colourless gases and exist as polar diatomic molecules.

REACTIONS WITH WATER

The hydrogen halides readily react with water to form acidic solutions, all of which are colourless.

Table B shows these reactions.



HYDROGEN HALIDE	ACID FORMED	EQUATION
Hydrogen fluoride	hydrofluoric acid	$HF + H_2O \rightleftharpoons H_3O^+ + F^-$
Hydrogen chloride	hydrochloric acid	$HCl + H_2O \rightarrow H_3O^+ + Cl^-$
Hydrogen bromide	hydrobromic acid	$HBr + H_2O \rightarrow H_3O^+ + Br^-$
Hydrogen iodide	hydroiodic acid	$HI + H_2O \rightarrow H_3O^+ + I^-$

table B Reactions of hydrogen halides with water to form acidic solutions.

REACTIONS WITH AMMONIA

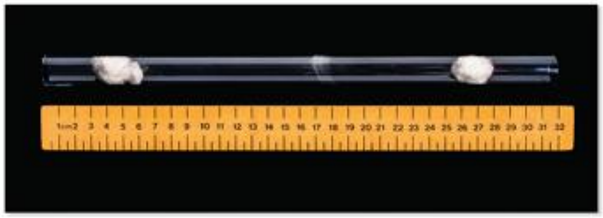
Hydrogen halides all react with ammonia gas to form salts, all of which are white ionic solids.

Cotton wool absorbs concentrated aqueous ammonia and hydrochloric acid, releasing ammonia and hydrogen chloride gases. These gases move through a tube, forming ammonium chloride, which forms closer to the hydrochloric acid side due to faster movement.

For example, when ammonia and hydrogen chloride gases are mixed together, they react to form ammonium chloride:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

You may be familiar with the use of the reaction in **fig B** to illustrate diffusion and the different rates of diffusion of ammonia and hydrogen chloride.



▲ **fig B** The different rates of diffusion of ammonia (from the left) and hydrogen chloride (from the right).

FLUORIDES AND ASTATIDES

This chapter discusses reactions involving fluorides and astatides, but cannot predict their reactions using chlorides, bromides, and iodides. To predict unfamiliar reactions, use information on these topics, such as creating an equation for acid formation when adding hydrogen astatide to water, based on hydrogen iodide's equation.

8D 1 Making standard solutions

WHAT ARE STANDARD SOLUTIONS AND PRIMARY STANDARDS?

The next topic, Topic 8D.2, is about doing titrations. One substance needed in a titration is a standard solution, which we will look at in this topic.

A standard solution is a solution whose concentration is accurately known. One obvious way to prepare a standard solution is to take a known mass of a substance and dissolve it in water to make a known volume of solution.

These substances are known as primary standards. Ideally, primary standards should:

- be solids with high molar masses
- be available in a high degree of purity
- be chemically stable (neither decompose nor react with substances in the air)
- not absorb water from the atmosphere
- be soluble in water
- react rapidly and completely with other substances when used in titrations.

Unfortunately, several substances that are often used in titrations are not suitable as primary standards.

MAKING A STANDARD SOLUTION OF SULFAMIC ACID

Sulfamic acid is probably unfamiliar to you. It is a readily available primary standard for use in acid-base titrations that has the necessary characteristics. Its formula can be shown in more than one way, including NH2SOH, and it has a molar mass of 97.1 gmol"1.
We will look in detail at a method used to obtain an accurately known value for the concentration of this solution. The method used is known as 'weighing by difference'. In your practical work, you may use a different method.

CALCULATING ROUGHLY HOW MUCH TO WEIGH

You need some idea of the approximate concentration and volume of the solution to be made. Typical values are 0.1 mol dm3 and 250 cm3.
Using the calculation method given in Topic 1E.2, the approximate amount of sulfamic acid, n = cx V= 0.1 x 0.25 0.025 mol, so the approximate mass needed is m = n x M=0.025 x 97.1 = 2g Note that even though we are going to do a very accurate weighing, we only need to know an approximate mass at this stage.

APPARATUS

The apparatus you need is:

- safety glasses and a lab coat
- an accurate balance (we will assume one reading to 3 decimal places)
- a weighing bottle (or weighing boat)
- a spatula
- a 250 cm3 beaker
- a 250 cm3 volumetric flask

- a wash bottle containing deionised water (or distilled water) a small funnel
- a glass stirring rod.

METHOD

1 Add between 2.3 and 2.5 g of sulfamic acid to the weighing bottle and weigh accurately.

2 Transfer as much as possible of the acid to a clean beaker and reweigh the weighing bottle.

3 Add about 100 cm3 of deionised water to the beaker and stir until all of the sulfamic acid has dissolved.

4 Remove the stirring rod, washing traces of solution from the rod into the beaker using the wash bottle.

5 Place a funnel in the neck of the volumetric flask and pour the solution from the beaker into the flask.

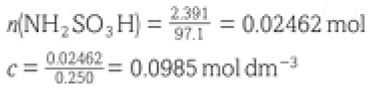
6 Rinse the inside of the beaker several times using the wash bottle and transfer the rinsings to the flask.

7 Add deionised water to the flask and fill up exactly to the graduation mark.

8 Stopper the flask and invert it several times to make a uniform solution.

You can now calculate an accurate value for the concentration of the solution, using these example values.

mass of weighing bottle+sulfamic acid=19.542g
mass of weighing bottle + any traces of sulfamic acid = 17.151g
mass of sulfamic acid added = 2.391g



$$n(NH_2SO_3H) = \frac{2.391}{97.1} = 0.02462 \text{ mol}$$

$$c = \frac{0.02462}{0.250} = 0.0985 \text{ mol dm}^{-3}$$

SUBJECT VOCABULARY

standard solution a solution whose concentration is accurately known
primary standards substances used to make a standard solution by weighing

8D 2 Doing titrations

WHAT IS A TITRATION?

Titration is a practical method for measuring the volume of two reacting solutions to calculate their concentration. It is often referred to as volumetric analysis. In this book, we will focus on acid-base titrations, where bases are soluble in water, making them alkalis. The colorless acids and bases are used, and an indicator is used to indicate the reaction's completion. The method assumes a sodium hydroxide solution with a concentration of 0.1 mol dm3.

OUTLINE OF THE TITRATION METHOD

Here is an outline of the titration method that introduces some key terms.
- Add the acid to the alkali until the equivalence point of the titration and the end point of the indicator is reached.
- Record the burette readings using the lowest part of the meniscus.
- Calculate the titre.

- Repeat the titration until concordant titres are obtained.

APPARATUS

The apparatus likely to be used is:

- a conical flask (usually 250 cm3)
- a burette (usually 50 cm3) and stand
- a pipette (usually 25 cm3) and pipette filler
- a wash bottle containing deionised water (or distilled water)
- a small funnel
- a white tile.

METHOD

1 Rinse the conical flask with deionised water and place it on a white tile.

2 Using a pipette filler, rinse the pipette with deionised water and then with some of the sodium hydroxide solution.

3 Use the pipette to transfer 25.0 cm^3 of the sodium hydroxide solution to the conical flask.

4Add about 3 drops of methyl orange indicator.

5 Rinse the burette with deionised water and then with some of the sulfamic acid solution.

6 Fill the burette with the sulfamic acid solution and set it up in the stand above the conical flask.

7 Record the burette reading

8 Add the sulfamic acid solution to the conical flask until the indicator just changes colour, and again record the burette reading.

9 Empty and rinse the conical flask with deionised water, and repeat the titration until concordant titres have been obtained.

CHOOSING AN INDICATOR

Two common indicators are:

- methyl orange
- phenolphthalein.

Sometimes it is important to use one of these and not the other, but in other titrations it does not matter which one you use. Table A shows the colours of these indicators and which combination of acid and base they should be used with.

INDICATOR	COLOUR IN ACID	COLOUR IN ALKALI	ACID–BASE COMBINATION
methyl orange	red	yellow	strong acid – weak base and strong acid – strong base
phenolphthalein	colourless	pink	weak acid – strong base and strong acid – strong base

table A Information about methyl orange and phenolphthalein.

Examples of strong acids are:

- hydrochloric acid
- nitric acid.

Examples of strong bases are:

- sodium hydroxide
- potassium hydroxide.

The commonest weak base is ammonia.

The commonest weak acid is ethanoic acid.

fig C This shows the burette after the titration has been done. Note the white tile and the colour of the phenolphthalein indicator. The pink colour shows that an acid has been neutralised and there is an excess of an alkali.

SUBJECT VOCABULARY

equivalence point the point at which there are exactly the right amounts of substances to complete the reaction

end point the point at which the indicator just changes colour; ideally, the end point should coincide with the equivalence point

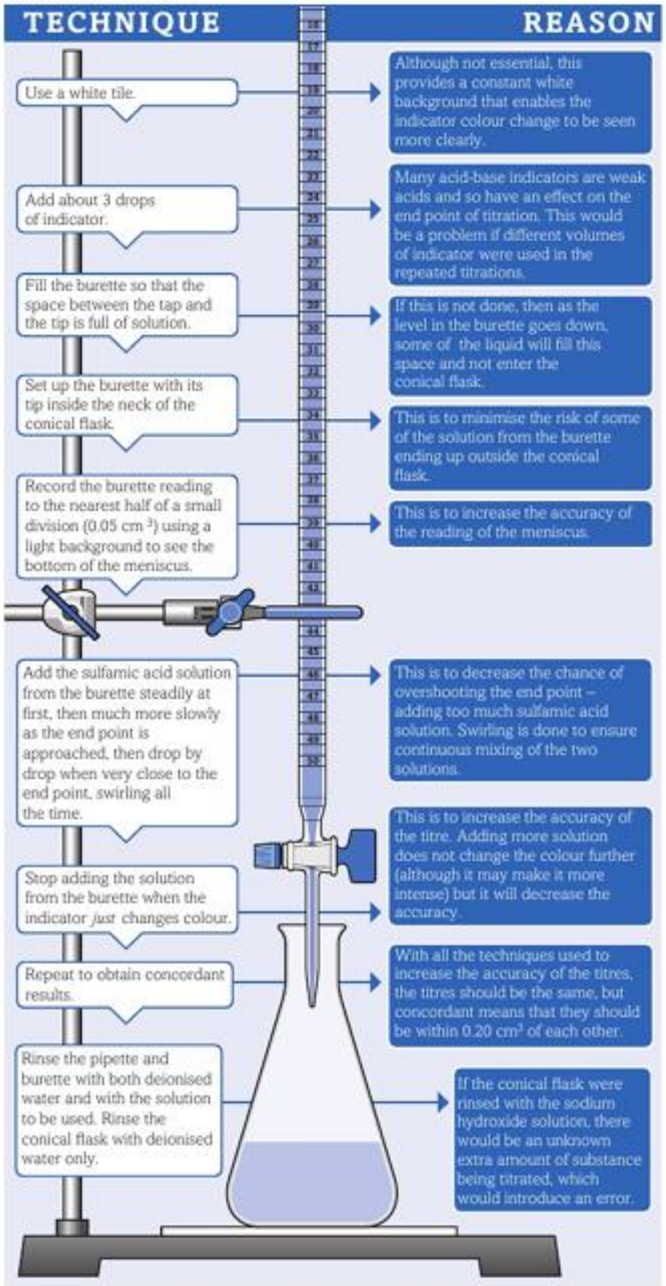
meniscus the curving of the upper surface of a liquid in a container; the lowest (horizontal) part of the meniscus should be read

titre the volume added from the burette during a titration

concordant titres titres that are close together (usually within 0.20 cm^3 of each other)

TITRATION TECHNIQUES

To obtain accurate results in a titration, it is important to work carefully. The diagram shows some important techniques and the reasons for them.



TECHNIQUE	REASON
Use a white tile.	Although not essential, this provides a constant white background that enables the indicator colour change to be seen more clearly.
Add about 3 drops of indicator.	Many acid-base indicators are weak acids and so have an effect on the end point of titration. This would be a problem if different volumes of indicator were used in the repeated titrations.
Fill the burette so that the space between the tap and the tip is full of solution.	If this is not done, then as the level in the burette goes down, some of the liquid will fill this space and not enter the conical flask.
Set up the burette with its tip inside the neck of the conical flask.	This is to minimise the risk of some of the solution from the burette ending up outside the conical flask.
Record the burette reading to the nearest half of a small division (0.05 cm^3) using a light background to see the bottom of the meniscus.	This is to increase the accuracy of the reading of the meniscus.
Add the sulfamic acid solution from the burette steadily at first, then much more slowly as the end point is approached, then drop by drop when very close to the end point, swirling all the time.	This is to decrease the chance of overshooting the end point – adding too much sulfamic acid solution. Swirling is done to ensure continuous mixing of the two solutions.
Stop adding the solution from the burette when the indicator *just* changes colour.	This is to increase the accuracy of the titre. Adding more solution does not change the colour further (although it may make it more intense) but it will decrease the accuracy.
Repeat to obtain concordant results.	With all the techniques used to increase the accuracy of the titres, the titres should be the same, but concordant means that they should be within 0.20 cm^3 of each other.
Rinse the pipette and burette with both deionised water and with the solution to be used. Rinse the conical flask with deionised water only.	If the conical flask were rinsed with the sodium hydroxide solution, there would be an unknown extra amount of substance being titrated, which would introduce an error.

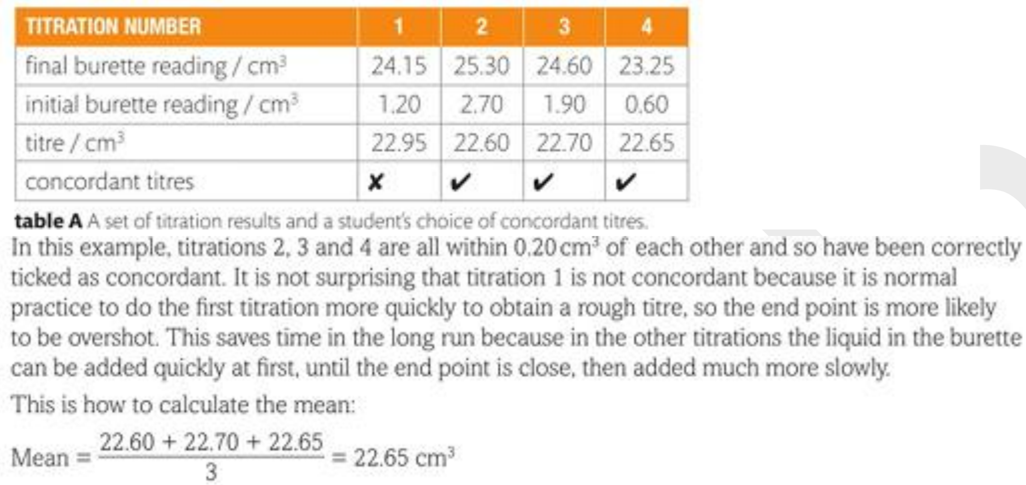
fig B Titration techniques and the reasons for them.

8D 3 Calculations from titrations

CALCULATING THE MEAN (AVERAGE) TITRE

The terms 'average' and 'mean' are often used interchangeably, but in scientific work you should take care to use the proper word. 'Average' has more than one mathematical meaning - it can represent the mean, the median or the mode. For these calculations you should use the mean: a set of values added to give a total, which is then divided by the number of values.

Before calculating a mean titre, only the concordant values must be selected, i.e. those that are within 0.20 cm3 of each other. Table A shows some typical titration results and a student's choice of concordant titres.



TITRATION NUMBER	1	2	3	4
final burette reading / cm^3	24.15	25.30	24.60	23.25
initial burette reading / cm^3	1.20	2.70	1.90	0.60
titre / cm^3	22.95	22.60	22.70	22.65
concordant titres	✗	✓	✓	✓

table A A set of titration results and a student's choice of concordant titres.

In this example, titrations 2, 3 and 4 are all within 0.20 cm^3 of each other and so have been correctly ticked as concordant. It is not surprising that titration 1 is not concordant because it is normal practice to do the first titration more quickly to obtain a rough titre, so the end point is more likely to be overshot. This saves time in the long run because in the other titrations the liquid in the burette can be added quickly at first, until the end point is close, then added much more slowly.

This is how to calculate the mean:

$$\text{Mean} = \frac{22.60 + 22.70 + 22.65}{3} = 22.65\ cm^3$$

8D 4 Mistakes, errors, accuracy and precision

USING THE CORRECT TERMINOLOGY

In science, it is sometimes difficult to find the correct words to use when considering the results of experiments and the calculations based on these results. This is because in the non-scientific world, words are often used with less care. You have already seen the idea that 'amount' has a specific meaning in chemistry (amount of substance, in moles) and should not be used to refer to mass or volume.

We will look at terminology in this topic.

- Mistakes and errors are not the same thing.
- Accuracy and precision have different meanings.
- Systematic errors and random errors have different causes.

Here, we look at the differences in meaning between some of the more important terms.

To do this, we will refer back to previous sections in Topic 8D, which involve measuring masses and volumes using different methods and apparatus.

MISTAKES ARE NOT ERRORS

Put very simply, an error is something that even a skilled operator would find difficult to avoid, and is a consequence of the way the apparatus has been constructed and how readings can be made using it. A mistake is something that a skilled operator can avoid by being careful.

Here are some examples of mistakes.

1 A chemist weighs a beaker on a balance without making sure the balance is tared (set to zero) beforehand. The reading on the balance could be very different from the actual mass of the beaker, so the reading should not be used, although this careless chemist may not realise this.

2 A student sees a burette reading of 27.35 cm3 but writes it down as 23.75 cm3. This is the student's mistake, and has nothing to do with the apparatus.

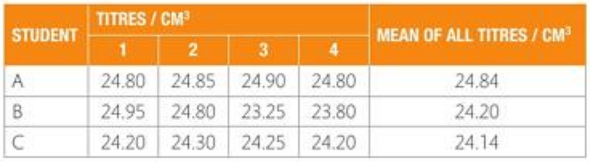
3 A student fills a burette using a funnel and forgets to remove the funnel before adding the liquid to the flask. During the addition, some of the liquid in the funnel drips into the burette, and this causes an incorrect burette reading to be recorded. This is due to the student's faulty technique. Again, it has nothing to do with the actual apparatus, only his careless use of it.

ACCURACY AND PRECISION, AND SYSTEMATIC AND RANDOM ERRORS

The most important terms to consider are:

- error
- accuracy
- precision.

Consider the titres in **table A**, which were recorded by students doing the same titration as the teacher.



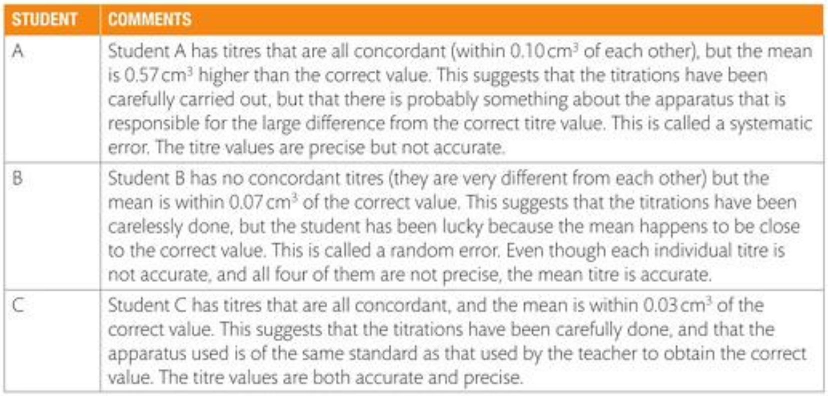
STUDENT	TITRES / CM^3				MEAN OF ALL TITRES / CM^3
	1	2	3	4	
A	24.80	24.85	24.90	24.80	24.84
B	24.95	24.80	23.25	23.80	24.20
C	24.20	24.30	24.25	24.20	24.14

table A Titres recorded by Students A, B and C doing the same titration as their teacher.

All the mean titres have been calculated correctly.

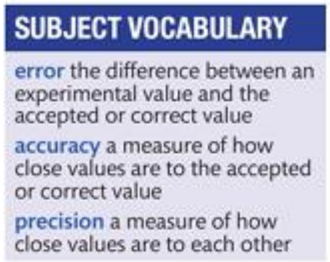
Now for the archery competition. The aim of an archery competition is to win by managing to land all the arrows as close as possible to the centre of the target. These diagrams show how well the three students have done at archery using their titre values.

Table B provides commentary on these values.



STUDENT	COMMENTS
A	Student A has titres that are all concordant (within 0.10 cm^3 of each other), but the mean is 0.57 cm^3 higher than the correct value. This suggests that the titrations have been carefully carried out, but that there is probably something about the apparatus that is responsible for the large difference from the correct titre value. This is called a systematic error. The titre values are precise but not accurate.
B	Student B has no concordant titres (they are very different from each other) but the mean is within 0.07 cm^3 of the correct value. This suggests that the titrations have been carelessly done, but the student has been lucky because the mean happens to be close to the correct value. This is called a random error. Even though each individual titre is not accurate, and all four of them are not precise, the mean titre is accurate.
C	Student C has titres that are all concordant, and the mean is within 0.03 cm^3 of the correct value. This suggests that the titrations have been carefully done, and that the apparatus used is of the same standard as that used by the teacher to obtain the correct value. The titre values are both accurate and precise.

table B Comments explaining how Students A, B and C have done with their titre values.



SUBJECT VOCABULARY

error the difference between an experimental value and the accepted or correct value

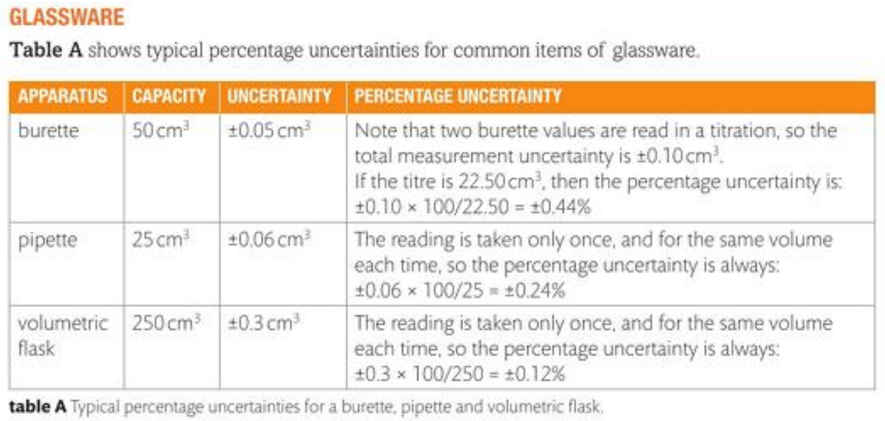
accuracy a measure of how close values are to the accepted or correct value

precision a measure of how close values are to each other

8D 6 Overall measurements uncertainty

PERCENTAGE MEASUREMENT UNCERTAINTIES

Each piece of apparatus you use to record a value (such as mass, volume, temperature or time) has a measurement uncertainty associated with it, which depends on the way it has been manufactured and calibrated.
The actual measurement uncertainty may be fixed. However, in many cases the percentage uncertainty when you use the apparatus depends on the value you measure. This mostly depends on whether you use the apparatus to record only one value or two values, and on how big the value is compared to the capacity of the apparatus.



GLASSWARE

Table A shows typical percentage uncertainties for common items of glassware.

APPARATUS	CAPACITY	UNCERTAINTY	PERCENTAGE UNCERTAINTY
burette	50 cm^3	±0.05 cm^3	Note that two burette values are read in a titration, so the total measurement uncertainty is ±0.10 cm^3. If the titre is 22.50 cm^3, then the percentage uncertainty is: ±0.10 × 100/22.50 = ±0.44%
pipette	25 cm^3	±0.06 cm^3	The reading is taken only once, and for the same volume each time, so the percentage uncertainty is always: ±0.06 × 100/25 = ±0.24%
volumetric flask	250 cm^3	±0.3 cm^3	The reading is taken only once, and for the same volume each time, so the percentage uncertainty is always: ±0.3 × 100/250 = ±0.12%

table A Typical percentage uncertainties for a burette, pipette and volumetric flask.

BALANCES

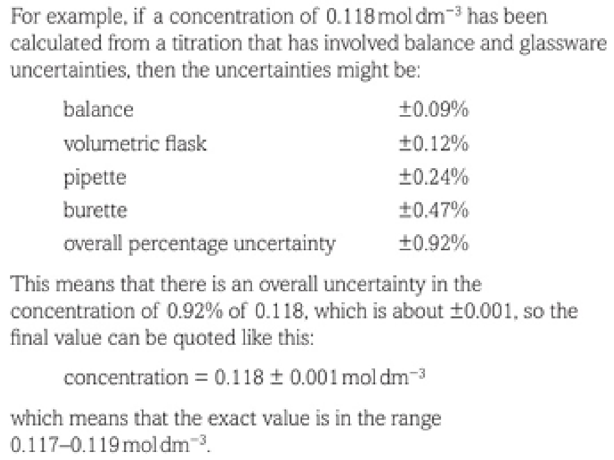
The percentage uncertainty in using a balance depends on:

- the precision of the balance, i.e. the number of decimal places to which the balance can be read
- the mass being weighed, as the percentage uncertainty will be greater for a smaller mass.

The percentage uncertainty is greater in Worked example 2, even though the balance reads to one more decimal place. This is because the balance is used twice and also because the mass being weighed is much smaller.

ADDING MEASUREMENT UNCERTAINTIES

If a final answer has been obtained using more than one piece of apparatus, then the approximate total measurement uncertainty is obtained by adding together the individual uncertainties.



For example, if a concentration of 0.118 mol dm^{-3} has been calculated from a titration that has involved balance and glassware uncertainties, then the uncertainties might be:

balance	±0.09%
volumetric flask	±0.12%
pipette	±0.24%
burette	±0.47%
overall percentage uncertainty	±0.92%

This means that there is an overall uncertainty in the concentration of 0.92% of 0.118, which is about ±0.001, so the final value can be quoted like this:

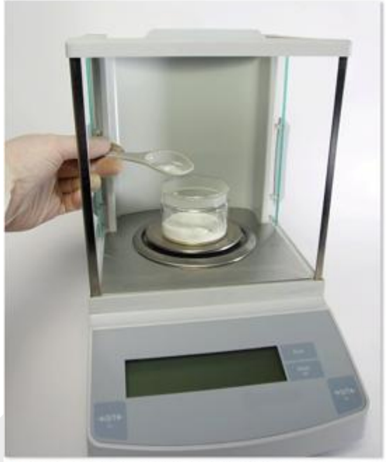
concentration = 0.118 ± 0.001 mol dm^{-3}

which means that the exact value is in the range 0.117–0.119 mol dm^{-3}.

MINIMISING ERROR AND UNCERTAINTY

How can errors and uncertainties be minimised in an experiment? This depends on a number of factors, some of which are easier to control than others.

For example, in a thermochemistry experiment carried out in the laboratory using standard equipment, there will always be transfer of heat energy to the surroundings. This heat transfer creates a random error in the measurement of the temperature change. In this type of experiment, using a balance that reads to three decimal places (instead of a balance that reads to two decimal places) will have no significant effect on the overall uncertainty of the final value. Minimising heat energy losses will have a much greater effect.



▲ **fig A** This balance is tared (set to zero) and ready to use. The pan is enclosed; this is necessary on a four-decimal place balance because of fluctuations in the reading caused by draughts of air.

SUBJECT VOCABULARY

percentage uncertainty the actual measurement uncertainty in an experiment multiplied by 100 and divided by the value recorded

Revision questions

1.a)

This question is about the forces between molecules and ions.

Some data for three small molecules are shown.

Molecule	M_r	Boiling temperature / °C
Fluorine	38.0	–188
Hydrogen chloride	36.5	–85
Methanol	32.0	65

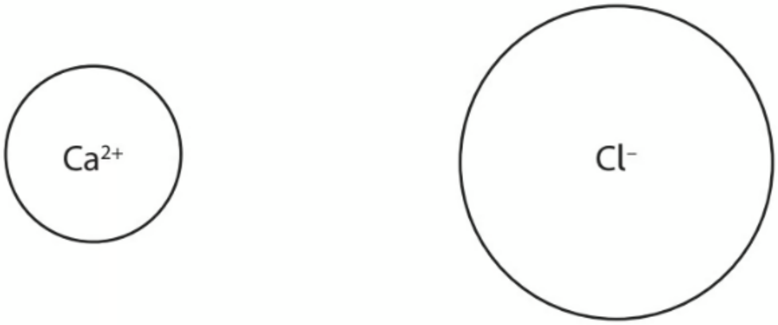
Explain the large variation in boiling temperatures, given the small range in M_r values.

Detailed descriptions of the forces involved are not required.

b.

Calcium chloride is soluble in water.

Complete the diagram to show how water molecules interact with each ion.
You may use  to represent a water molecule.



c.

Explain why bromine is a liquid but iodine is a solid at room temperature.

Detailed explanations of the forces involved are not required.

2.

Potassium chlorate(V), $KClO_3$, is a crystalline solid used in fireworks. It is produced by the Liebig Process in two stages.

Stage 1	Chlorine gas is passed through hot calcium hydroxide solution forming calcium chlorate(V), $Ca(ClO_3)_2$.

$$6Ca(OH)_2(aq) + 6Cl_2(g) \rightarrow Ca(ClO_3)_2(aq) + 5CaCl_2(aq) + 6H_2O(l)$$

Stage 2	Potassium chloride solution is then added to form potassium chlorate(V).

$$Ca(ClO_3)_2(aq) + 2KCl(aq) \rightarrow 2KClO_3(aq) + CaCl_2(aq)$$

The solution is heated to reduce its volume and then allowed to crystallise. The crystals are filtered off.
The remaining filtrate is evaporated further to obtain more crystals.

i) Write the **overall** equation for the Liebig Process. State symbols are not required.

(1)

ii) Calculate the **overall** atom economy by mass for the production of potassium chlorate(V), $KClO_3$, using your equation in (a)(i).

b.

Explain the type of reaction that takes place in Stage 1 of the Liebig Process, using oxidation numbers.

$$6Ca(OH)_2(aq) + 6Cl_2(g) \rightarrow Ca(ClO_3)_2(aq) + 5CaCl_2(aq) + 6H_2O(l)$$

c.

The crystals of potassium chlorate(V) formed also contain some halide ion impurities.

i) Describe a chemical test on a solution of these crystals to **confirm** that the impurities present are chloride ions rather than bromide ions. Include the expected results.

(3)

ii) 1.52 g of impure potassium chlorate(V), formed in the Liebig Process, was heated until the mass of solid remaining was constant at 1.02 g.

The reaction that occurred was

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

The impurities present did not decompose on heating.

Calculate the percentage purity of the sample. Give your answer to an appropriate number of significant figures.

3. a)

This question is about Group 1 metals.

When potassium is placed into a beaker of cold water, potassium hydroxide and hydrogen are formed.

i) Write the equation for this reaction. Include state symbols.

(2)

ii) This is a redox reaction.

State which element is oxidised and which is reduced.

Justify your answer by giving the initial and final oxidation numbers of any element that changes oxidation state.

(2)

iii) The reaction of potassium with water is very vigorous and a flame is seen.

State the colour of the flame.

b.

The label has come off a bottle known to contain **M**, a Group 1 metal which is stored in oil. A student carried out an experiment to determine the identity of **M.**

Procedure

Step **1**

A small piece of **M** was wiped with tissue paper to remove the oil.
The piece of **M** was weighed and placed in a beaker of distilled water.

Step **2**

After the reaction had finished, the contents of the beaker and washings were transferred to a 250.0 cm^3 volumetric flask. The solution was made up to the mark with distilled water and mixed thoroughly.

Step **3**

A pipette was used to transfer 25.0 cm^3 portions of this solution to conical flasks. Each portion was then titrated with hydrochloric acid of concentration 0.400 mol dm^{-3}.

c.

Results

Mass of metal, M	0.37 g
Mean titre of hydrochloric acid	12.80 cm^3

The reaction taking place is shown.

$$\mathbf{M}OH\,(aq) + HCl\,(aq) \rightarrow \mathbf{M}Cl\,(aq) + H_2O\,(l)$$

i) The indicator used was phenolphthalein. State the colour **change** at the end-point.

(2)

from .... to ....

ii) Calculate the relative atomic mass of **M** and use it to identify the Group 1 metal, **M.**

(4)

4.a)

Magnesium oxalate, MgC_2O_4, decomposes on heating to form magnesium carbonate and carbon monoxide.

$$MgC_2O_4\,(s) \rightarrow MgCO_3\,(s) + CO\,(g)$$

A 6.0 g sample of magnesium oxalate was heated for three minutes but the decomposition was only 70% complete.

Calculate the total mass of solid that remains.

b.

In practice, magnesium carbonate also decomposes on stronger heating.

Describe and explain the trend in the thermal decomposition of Group 2 carbonates.

c.

Suggest why a pure sample of magnesium carbonate will **not** be produced from the decomposition of magnesium oxalate even if the sample is heated for longer.

5. a.

Magnesium ethanedioate (MgC_2O_4) decomposes on gentle heating to form magnesium carbonate and carbon monoxide.

$$MgC_2O_4 \rightarrow MgCO_3 + CO$$

i) State why the thermal decomposition of magnesium ethanedioate should be carried out in a fume cupboard.

(1)

ii) After heating a 6.0 g sample of magnesium ethanedioate for three minutes, the decomposition was 70% complete.

Calculate the total mass of the solid mixture that remains.

(4)

b.

Magnesium carbonate undergoes thermal decomposition at a higher temperature than magnesium ethanedioate.

$$MgCO_3 \rightarrow MgO + CO_2$$

Explain the trend in the thermal decomposition of Group 2 carbonates going down the group.

6.a)

This question is about the elements in Group 7.

Use your knowledge of the trends in the properties of Group 7 elements to predict the colour and physical state of astatine at room temperature.

b.

i) State the meaning of the term electronegativity.

(1)

ii) Explain the trend in electronegativity down Group 7.

(2)

c.

Compare and contrast the reactions of chlorine with

- water
- cold, dilute aqueous alkali
- hot, concentrated aqueous alkali

Include an equation for each reaction, stating the type of reaction and the oxidation numbers of the chlorine involved. State symbols are not required.