

TOPIC 8 REDOX CHEMISTRY AND GROUPS 1, 2 AND 7

A REDOX CHEMISTRY | B THE ELEMENTS OF GROUPS 1 AND 2 | C INORGANIC CHEMISTRY OF GROUP 7 | D QUANTITATIVE CHEMISTRY

Redox reactions are among the most common and most important chemical reactions in everyday life. Here are two examples of redox reactions that occur in our daily lives:

- 1 One of the most common chemical reactions, *combustion*, is a classic redox reaction. For example, when petrol burns within the internal combustion engine of a car, carbon atoms in the fuel are oxidised to carbon dioxide and carbon monoxide. As this is happening, oxygen in the air is reduced when it combines with the hydrogen atoms of the fuel to form water.
- 2 *Photosynthesis* is probably the single most important process on the planet. It uses the energy of sunlight to grow plants and so provide food for all higher organisms. Photosynthesis is accomplished through a series of redox reactions in which energy from light is finally converted into carbohydrates on which animals and humans can feed. Oxygen is also a vital by-product of photosynthesis.

The Periodic Table of elements is a familiar feature in any study of chemistry. It helps us to make sense of the variety of chemical elements and their different reactions, some of which are redox reactions. It also helps us to make sense of the even greater variety of chemical compounds of the elements. In this topic, we will focus mostly on three groups (columns) of the Periodic Table to illustrate the trends within the groups and several features of the elements and compounds in them.

In these groups, you will meet familiar elements such as magnesium and chlorine, but also less familiar elements such as barium and bromine. For example, you will learn how the limewater test for carbon dioxide works, how milk of magnesia relieves indigestion and why farmers spread lime on their fields. You will learn that although barium compounds are very poisonous, you can safely eat a 'barium meal' before having an X-ray.

By learning how flame tests work, you will also understand how fireworks can have flames of different colours. The use of chlorine and its compounds in disinfectants and bleaches has saved many lives, and you will learn something of the chemistry involved in how these products work.

You will also learn about titrations, especially how to do them accurately, and carry out calculations from results.

MATHS SKILLS FOR THIS TOPIC

- Carry out calculations using numbers in ordinary form
- Use appropriate units in calculations including measurement of ionic radius and ionisation energy
- Use ratios to construct and balance equations
- Understand the connection between frequency and wavelength, and their use in representing the colour of light

What prior knowledge do I need?

Topic 1

- Calculations involving moles and concentrations

Topic 1B

- Balancing equations for charge using electrons

Topic 2B

- The structure of the Periodic Table

Topic 7

- Intermolecular forces

What will I study in this topic?

- Oxidation and reduction in terms of electron loss and gain
- Using oxidation numbers
- Reaction trends in Groups 1, 2 and 7
- Tests for anions and cations
- Practical techniques and calculations in volumetric analysis
- Accuracy, precision, errors and uncertainties

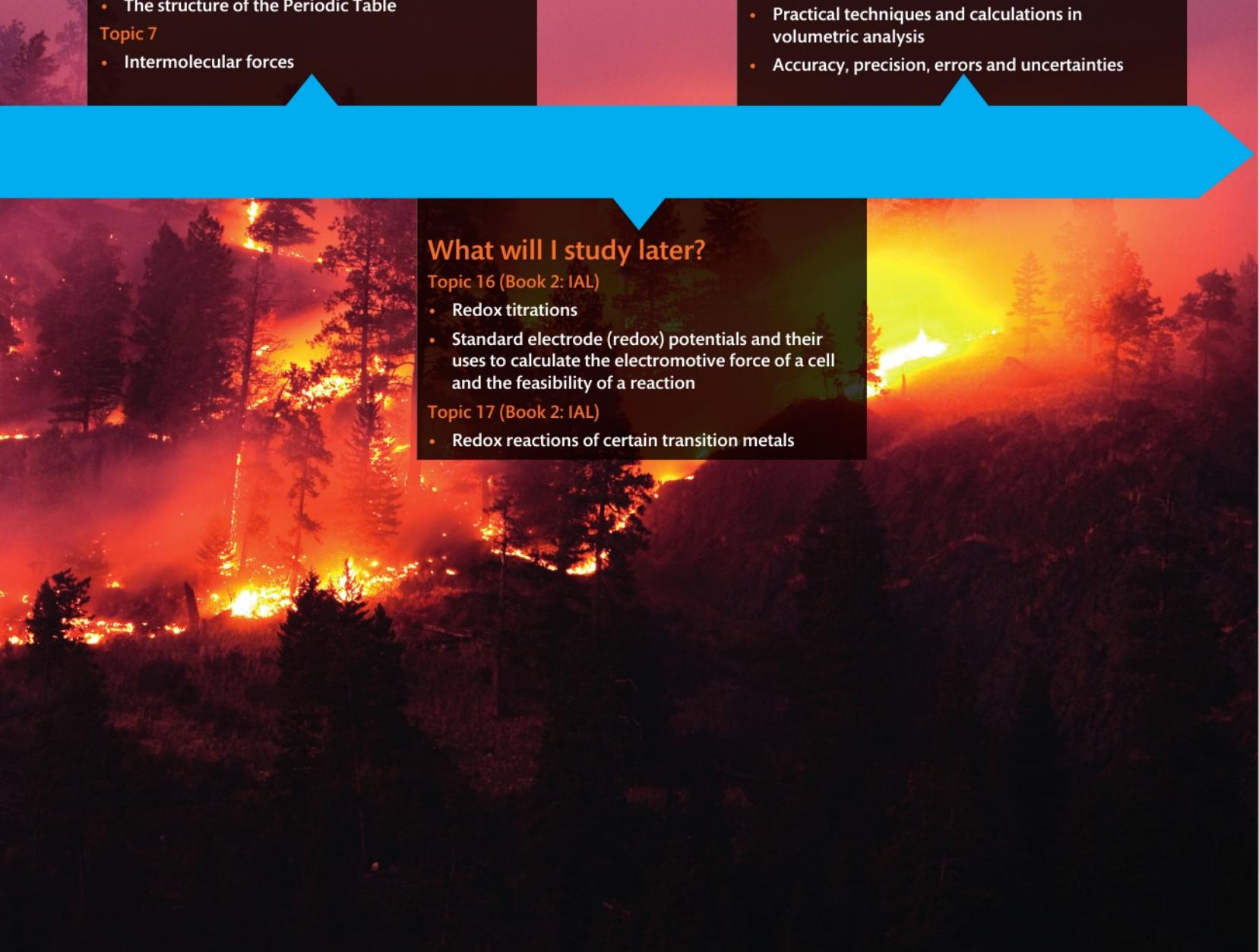
What will I study later?

Topic 16 (Book 2: IAL)

- Redox titrations
- Standard electrode (redox) potentials and their uses to calculate the electromotive force of a cell and the feasibility of a reaction

Topic 17 (Book 2: IAL)

- Redox reactions of certain transition metals



8A 1 ELECTRON LOSS AND GAIN

8.5 8.6 8.7

LEARNING OBJECTIVES

- Understand oxidation and reduction in terms of electron transfer and changes in oxidation number.
- Understand the application of these ideas to reactions of s-block and p-block elements.
- Know that oxidising agents gain electrons and that reducing agents lose electrons.
- Understand that a disproportionation reaction involves an element in a single species being simultaneously oxidised and reduced.

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).

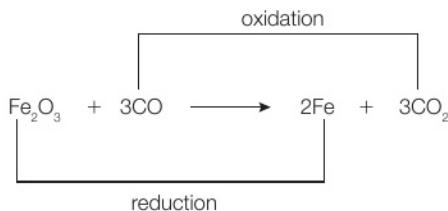


fig A Example of oxidation and reduction during the reaction between iron(III) oxide and carbon monoxide.

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).

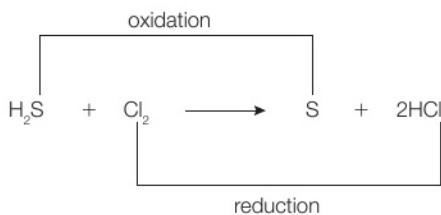


fig B Example of oxidation and reduction during the reaction between chlorine and hydrogen sulfide.

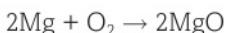
A reaction that involves both reduction and oxidation is called a **redox reaction**.

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:

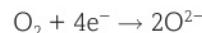


The magnesium has been oxidised because it has gained oxygen. The oxygen must have been reduced, but by what definition?

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



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



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:



The carbon monoxide must have been oxidised (it gains oxygen), but it is not easy to see how it has lost electrons because carbon monoxide and carbon dioxide are both covalent compounds.

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**.

EXAM HINT

An oxidising agent is reduced.

DISPROPORTIONATION

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



One of the Cu^+ ions in copper(I) oxide has lost an electron to become Cu^{2+} . At the same time, the other Cu^+ 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**.

CHECKPOINT

1. In the reaction:



- (a) Which species has been oxidised and which species has been reduced?
- (b) Write ionic half-equations to represent both the oxidation and the reduction reactions.

2. In each of the following reactions identify whether the underlined species has been oxidised, reduced or neither.

- (a) Al(s) + $1\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{AlCl}_3(\text{s})$
- (b) 4Na(s) + TiO₂(s) → 2Na₂O(s) + Ti(s)
- (c) Ag⁺(aq) + Cl⁻(aq) → AgCl(s)
- (d) Cl₂(aq) + 2Br⁻(aq) → 2Cl⁻(aq) + Br₂(aq)
- (e) CuO(s) + 2H⁺(aq) → Cu²⁺(aq) + H₂O(l)
- (f) MnO₂(s) + 4HCl(aq) → MnCl₂(aq) + Cl₂(aq) + 2H₂O(l)

3. In each of the following reactions, identify the species that has been oxidised. In each case, justify your answer.

- (a) Fe(s) + H₂SO₄(aq) → FeSO₄(aq) + H₂(g)
- (b) Na(s) + $\frac{1}{2}\text{H}_2(\text{g}) \rightarrow \text{NaH}(\text{s})$
- (c) CuO(s) + Cu(s) → Cu₂O(s)
- (d) 2Fe(OH)₂(s) + $\frac{1}{2}\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Fe}(\text{OH})_3(\text{s})$
- (e) 2V³⁺(aq) + Zn(s) → 2V²⁺(aq) + Zn²⁺(aq)

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

8.1

8.2

8.9

LEARNING OBJECTIVES

- Know what is meant by the term oxidation number and understand the rules for assigning oxidation numbers.
- Be able to calculate the oxidation number of elements in compounds and ions, including in peroxides and metal hydrides.
- Understand that metals, in general, form positive ions by loss of electrons with an increase in oxidation number whereas non-metals, in general, form negative ions by gain of electrons with a decrease in oxidation number.

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.

For example, in MgO the oxidation number of magnesium is +2, since the charge on the magnesium ion is 2^+ . Similarly, the oxidation number of oxygen is -2 .

In SO_2 , the oxidation number of the sulfur is +4 because if the compound were fully ionic the sulfur ion would have a charge of 4^+ . The oxidation number of oxygen is once again -2 .

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.

WORKED EXAMPLE 1

Deduce the oxidation number of chlorine in:

- (a) NaCl
- (b) NaClO
- (c) NaClO₃

Answers

- (a) The oxidation number of Na is $+1$. The two oxidation numbers must add up to zero, so the oxidation number of Cl must be -1 .
- (b) The oxidation number of Na is $+1$ and the oxidation number of O is -2 . The oxidation numbers must add up to zero, so the oxidation number of Cl must be $+1$.
- (c) The oxidation number of Na is $+1$ and the oxidation number of O is -2 . The oxidation numbers must add up to zero, so the oxidation number of Cl must be $+5$.

$$+1 + (3 \times -2) + x = 0$$

$$x = 0 - 1 - (-6) = +5$$

WORKED EXAMPLE 2

Deduce the oxidation number of nitrogen in:

- (a) NH₃
- (b) NO₂⁻
- (c) NO₃⁻.

Answers

(a) N is more electronegative than H and must therefore have a negative oxidation number. The oxidation number of H is therefore +1. The oxidation numbers must add up to zero, so the oxidation number of N is -3.

$$x + (3 \times 1) = 0$$

$$x = -3$$

(b) O is more electronegative than N, so the oxidation number of O is -2. The oxidation numbers must add up to -1 (the charge on the ion), so the oxidation number of N is +3.

$$x + (2 \times -2) = -1$$

$$x = +3$$

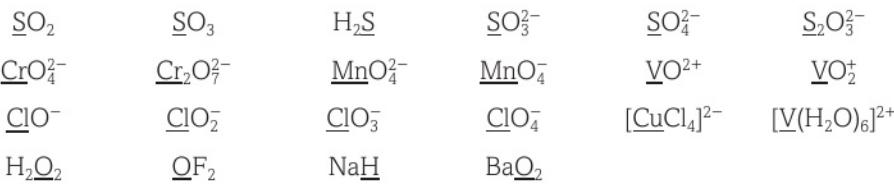
(c) O is more electronegative than N, so the oxidation number of O is -2. The oxidation numbers must add up to -1 (the charge on the ion), so the oxidation number of N is +5.

$$x + (3 \times -2) = -1$$

$$x = +5$$

CHECKPOINT

1. Calculate the oxidation number of the underlined element in each of the following species.

**SUBJECT VOCABULARY**

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

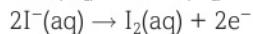
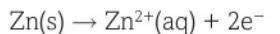
8A 3 RECOGNISING REACTIONS USING OXIDATION NUMBERS

LEARNING OBJECTIVES

- Understand oxidation and reduction in terms of electron transfer and changes in oxidation number, and the application of these ideas to reactions of s-block and p-block elements.
- Know that the oxidation number is a useful concept in terms of the classification of reactions as redox and as disproportionation.

USING OXIDATION NUMBERS TO CLASSIFY REACTIONS

Consider the following ionic half-equations:

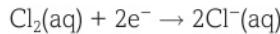


In all three cases, electrons have been lost so the reactions are oxidations. But also notice that the oxidation number of the element has increased in each case.

- 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**.

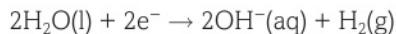
Consider the following ionic half-equations:



Cl changes from 0 to -1



Mn changes from +7 to +2



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.

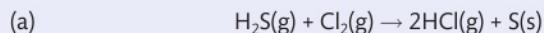
This concept can now be applied to full equations.

EXAM HINT

Notice that the higher oxidation numbers for metal ions in solution are always in the form of oxyions, e.g., in CrO_4^{2-} , Cr has an oxidation number of +6.

WORKED EXAMPLE

Use oxidation numbers to show whether the following reactions are examples of redox reactions.



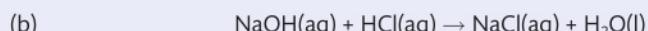
Oxidation numbers: +1 -2 0 +1 -1 0

Answer

The oxidation number of S has increased (-2 to 0), so it has been oxidised.

The oxidation number of Cl has decreased (0 to -1), so it has been reduced.

Since both oxidation and reduction have taken place, the reaction is classified as a redox reaction.



Oxidation numbers: +1 -2 +1 +1 -1 +1 -1 +1 -2

Answer

There is no change in oxidation number for any of the elements involved in the reaction, so this is not an example of a redox reaction.



Oxidation numbers: +1 -2 +1 0 +1 -1 +1 +1 -2 +1 -2

Answer

The oxidation number of Cl has both increased (0 in Cl_2 to +1 in NaClO) and decreased (0 in Cl_2 to -1 in NaCl), so this is an example of a redox reaction.

It is also an example of a **disproportionation reaction**.

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:



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:



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

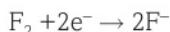
We can also make some predictions about the reactions of p-block elements in terms of redox.

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:



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

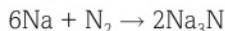
Now consider the Group 7 element fluorine, which is the most reactive halogen. The half-equation for its reaction is:



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

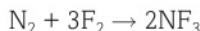
Nitrogen is a p-block element in Group 5, with an electronegativity higher than aluminium, but lower than fluorine. What predictions can we make about the change in oxidation number in its reactions? This depends on which element it reacts with.

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



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:



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**.

CHECKPOINT

- Copy the following table. Use oxidation numbers to complete it. The first example has been done for you.

EQUATION	REDOX REACTION (✓ OR X)	DISPROPORTIONATION (✓ OR X)	ELEMENT OXIDISED	ELEMENT REDUCED
$\text{Mg} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2$ 0 +1 -1 +2 -1 0	✓	X	Mg	H
$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$				
$2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$				
$\text{KOH} + \text{HNO}_3 \rightarrow \text{KNO}_3 + \text{H}_2\text{O}$				
$\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HClO}$				

SUBJECT VOCABULARY

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

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

8A 4 OXIDATION NUMBERS AND NOMENCLATURE

8.3

8.4

LEARNING OBJECTIVES

- Be able to indicate the oxidation number of an element in a compound or ion, using a Roman numeral.
- Be able to write formulae given oxidation numbers.

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 ₂ MnO ₄	Mn +6	potassium manganate(VI)
CrO ₄ ²⁻	Cr +6	chromate(VI) ion
Cr ₂ O 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:

- the systematic name for Na₂SO₄ is sodium sulfate(VI), but it is often just called sodium sulfate
- Na₂SO₃ should be labelled sodium sulfate(IV), but the name sodium sulfite is still commonly used
- SO₂ and SO₃ 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.

WORKED EXAMPLE 1

Deduce the formula for iron(II) sulfate.

Answer

The formula of the iron(II) ion is Fe²⁺.

The formula of the sulfate ion is SO₄²⁻.

So the two ions are present in a 1 : 1 ratio to produce a neutral compound, giving the formula FeSO₄.

WORKED EXAMPLE 2

Deduce the formula for iron(III) sulfate.

Answer

The formula of the iron(III) ion is Fe^{3+} .

The formula of the sulfate ion is SO_4^{2-} .

So the two ions are present in a 2:3 ratio to give a neutral compound, giving the formula $\text{Fe}_2(\text{SO}_4)_3$.

CHECKPOINT

1. Give the systematic name for each of the following compounds:

- (a) PCl_3
- (b) PCl_5
- (c) V_2O_5
- (d) NaClO
- (e) NaClO_3

2. Give the systematic name for each of the following ions:

- (a) NO_3^-
- (b) NO_2^-
- (c) ClO_4^-
- (d) VO_2^+
- (e) VO_2^{2+}

3. Deduce the formula for each of the following compounds:

- (a) copper(I) oxide
- (b) copper(II) oxide
- (c) chromium(III) sulfate(VI)
- (d) lead(IV) iodide
- (e) cobalt(III) nitrate(V)

4. Why is it not necessary to refer to sodium chloride as sodium(I) chloride, or magnesium oxide as magnesium(II) oxide?

8A 5 CONSTRUCTING FULL IONIC EQUATIONS

LEARNING OBJECTIVES

- Be able to write ionic half-equations and use them to construct full ionic equations.

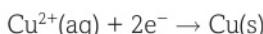
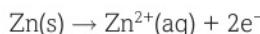
BALANCING BY COUNTING ELECTRONS

STRAIGHTFORWARD EXAMPLES

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



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:



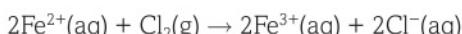
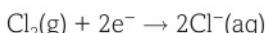
Now let's try an example where the electrons are not the same in the two ionic half-equations.

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:



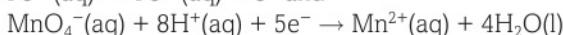
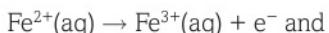
This time, one of the half-equations contains one electron, while the other contains two electrons. Before these can be added together to produce a full equation, the equation containing Fe^{2+} must be multiplied by 2.



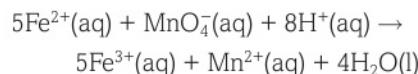
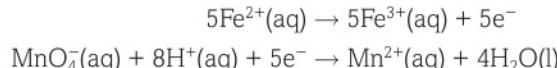
MORE COMPLICATED EXAMPLES

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:



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

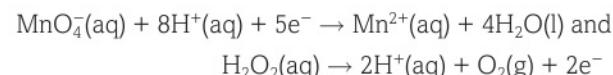


EXAM HINT

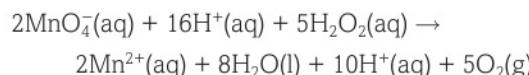
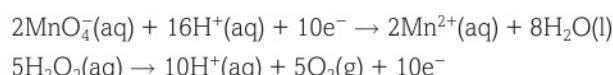
Acidified potassium manganate(VII) is very commonly used as an oxidising agent in analytical chemistry. It will be useful to learn this half equation by heart.

Here's another challenging example.

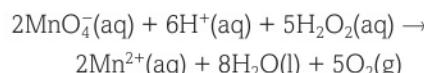
The reaction between aqueous acidified potassium manganate(VII) and hydrogen peroxide involves two changes represented by the following ionic half-equations:



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.



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:



EXAM HINT

This final equation shows that this reaction takes place in acid conditions. Many redox reactions are pH sensitive.

BALANCING USING OXIDATION NUMBERS**WORKED EXAMPLE 1**

Use oxidation numbers to balance the following equation:

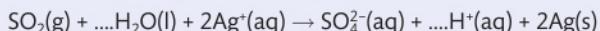
**Answer**

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 SO₂ to Ag⁺ is 1 : 2. This gives:



We now need to balance the H and O atoms.

This gives:



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.

WORKED EXAMPLE 2

Use oxidation numbers to balance the following equation:

**Answer**

Identify the elements whose oxidation numbers have changed.

In this case:

Fe changes from +2 to +3; this is a '1 electron' change

Cl changes from +5 to -1; this is a '6 electron' change.

So the ratio of Fe to ClO₃⁻ is 6 : 1. This gives:



Once again, balance the H and O atoms.

This gives:



Check the charges.

- The total charge on the left-hand side is +17((6 × +2) + -1 + (6 × +1)).
- The total charge on the right-hand side is +17((6 × +3) + -1).

The equation is now balanced.

CHECKPOINT

1. Use each pair of ionic half-equations to construct a full ionic equation. Include state symbols.

- Zn(s) → Zn²⁺(aq) + 2e⁻ and Fe³⁺(aq) + e⁻ → Fe²⁺(aq)
- $\frac{1}{2}\text{I}_2(\text{aq}) + \text{e}^- \rightarrow \text{I}^-(\text{aq})$ and $2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightarrow \text{S}_4\text{O}_6^{2-}(\text{aq}) + 2\text{e}^-$
- MnO₄⁻(aq) + 8H⁺(aq) + 5e⁻ → Mn²⁺(aq) + 4H₂O(l) and Ce³⁺(aq) → Ce⁴⁺(aq) + e⁻
- Cr₂O₇²⁻(aq) + 14H⁺(l) + 6e⁻ → 2Cr³⁺(aq) + 7H₂O(l) and Fe²⁺(aq) → Fe³⁺(aq) + e⁻
- FeO₄²⁻(aq) + 8H⁺(aq) + 3e⁻ → Fe³⁺(aq) + 4H₂O(l) and C₂O₄²⁻(aq) → 2CO₂(g) + 2e⁻

2. Use oxidation numbers to balance each of the following equations.

- Cu(s) + H⁺(aq) + NO₃⁻(aq) → Cu²⁺(aq) + H₂O(l) + NO(g)
- Cu(s) + H⁺(aq) + NO₃⁻(aq) → Cu²⁺(aq) + H₂O(l) + NO₂(g)
- Cl₂(g) + OH⁻(aq) → Cl⁻(aq) + ClO₃⁻(g) + H₂O(l)

LEARNING OBJECTIVES

- Understand the reasons for the trend in ionisation energy down Groups 1 and 2.
- Understand the reasons for the trend in reactivity of the elements down Group 1 (Li to K) and Group 2 (Mg to Ba).

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:



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.

The energy needed for ionisation is used to overcome the electrostatic attraction between the electron being removed and the protons in the nucleus.

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:



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.

The energy needed for ionisation is used to overcome the electrostatic attraction between the electron being removed and the protons in the nucleus.

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.

You can see that the first factor causes an increase, but the second and third factors cause a decrease. The combined effect of the second and third factors outweighs the effect of the first factor. This means that there is a decrease 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 M^{2+} 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.

LEARNING TIP

When writing an equation for an ionisation, you should always include the state symbol (g) after each atom and ion.

CHECKPOINT

- Write equations to represent the first ionisation of beryllium and the second ionisation of barium.
- Explain fully why beryllium is less reactive than barium.

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 ELEMENTS

LEARNING OBJECTIVES

- Know the reactions of the elements of Group 1 (Li to K) with oxygen, chlorine and water.

REACTIONS WITH OXYGEN

You know that the Group 1 metals are only shiny when kept out of air. When they are exposed to air, they tarnish. This means that they form a dull, dark layer on the surface as they are oxidised by oxygen in the air.

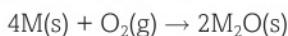
Group 1 metals can burn when heated in air or oxygen, but you would not normally do this in the laboratory because the reactions are extremely vigorous.

Many people are now aware of one problem to do with batteries containing lithium. Such batteries are common in mobile phones and laptops, but there have been a small number of cases where the battery has caught fire. **Fig A** shows a mobile phone on fire, caused by the lithium in the battery reacting rapidly with the oxygen in the air.



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:



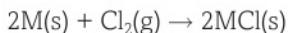
The products are oxides containing M^+ and O^{2-} ions.

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:



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.

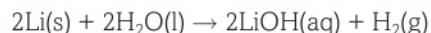
The general equation for all these reactions is:



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:



EXAM HINT

Make sure that you remember to use the correct symbols for reactants and products if asked to do so in an exam question.

REACTIONS OF OTHER GROUP 1 METALS

You are not required to know any of the reactions of rubidium or caesium. However, because you know that the trend is increasing reactivity down the group, you can predict that both rubidium and caesium are more reactive than potassium.

LEARNING TIP

Practise writing equations for reactions of Group 1 elements with oxygen, chlorine and water.

CHECKPOINT

1. Write an equation for each of these reactions:

- lithium with oxygen
- sodium with chlorine
- potassium with water.

2. Soon after sodium is added to water, a colourless solution is formed. Explain why it is wrong to write that sodium is soluble in water.

8B 3 REACTIONS OF GROUP 2 ELEMENTS

8.12
PART8.13
PART

LEARNING OBJECTIVES

- Know the reactions of the elements of Group 2 (Mg to Ba) with oxygen, chlorine and water.

REACTIONS WITH OXYGEN

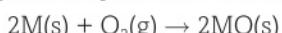
You should be familiar with the reaction that occurs when magnesium burns in air – there is a very bright flame and the formation of a white solid.

Similar observations can be made when other Group 2 elements burn in air, but they are qualitatively different, that is, you should be able to recognise that when calcium, strontium and barium are heated in air, the reactions are more vigorous. However, this may be hard to see if the metals are not fresh samples. If the burning metal is placed in a gas jar of oxygen, then the same reaction occurs, although more vigorously.

For all these elements, the element needs to be heated for the reaction to start. However, even without heating, there is a slow reaction between the element and oxygen when the element is exposed to air. This forms a surface coating of oxide which helps to prevent the element from further reaction.

Barium is the most reactive. It is often stored under oil to keep it from reacting with oxygen and water vapour in the air.

The general equation for all these reactions is:

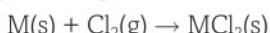


The products are oxides containing M^{2+} and O^{2-} ions.

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 M^{2+} and Cl^{-} ions.

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.

(a)



(b)



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



▲ **fig B** Magnesium burning in chlorine.



▲ **fig C** Magnesium reacting very slowly with water.



▲ **fig D** Calcium reacting vigorously with water.

The general equation for all of these reactions is:



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

The equation for the reaction with calcium is:



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

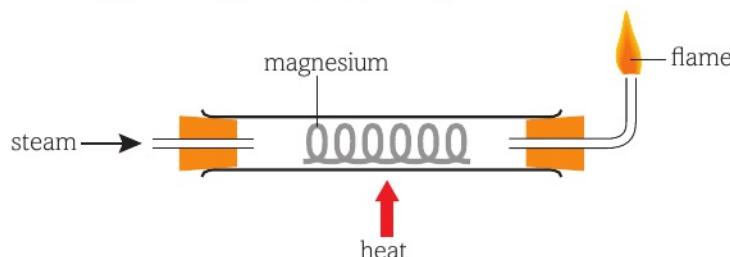
The equation for the reaction with barium is:



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. The equation for this reaction is:



The hydrogen formed is burned as it leaves the tube. This is for safety reasons, to prevent the escape of a highly flammable gas into the laboratory.

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.

LEARNING TIP

Practise writing equations for reactions of Group 2 elements with oxygen, chlorine and water.

CHECKPOINT

1. Write an equation for each of these reactions:

- (a) calcium with oxygen
- (b) strontium with chlorine
- (c) barium with water.

2. Suggest why it is not a good idea to use water to put out a fire involving burning magnesium.

8B 4 OXIDES AND HYDROXIDES IN GROUPS 1 AND 2

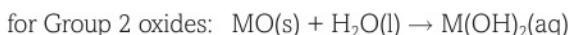
8.14 8.15 8.19(i,ii)

LEARNING OBJECTIVES

- Know the reactions of the oxides of Group 1 and 2 elements with water and dilute acid, and their hydroxides with dilute acid.
- Know the trends in solubility of the hydroxides and sulfates of Group 2 elements.
- Know the reactions, including ionic equations where appropriate, for identifying carbonate and sulfate ions.

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:



These equations can be simplified because there is no change to the M^+ or M^{2+} ion during the reactions.



This equation shows the formation of hydroxide ions, which is why the resulting solutions are alkaline.

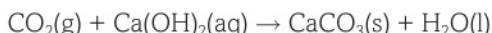
TRENDS IN SOLUBILITY OF THE GROUP 2 HYDROXIDES

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.

For example, when magnesium oxide reacts with water, the magnesium hydroxide formed has a very low solubility in water. The solubility of the Group 2 hydroxides increases down the group. Therefore, the maximum alkalinity (pH value) of the solutions formed also increases down the group.

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:



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



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

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:



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.



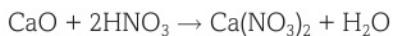
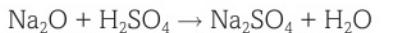
fig B A bottle of milk of magnesia.

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.

Here are some sample equations:



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:



TRENDS IN SOLUBILITY OF THE GROUP 2 SULFATES

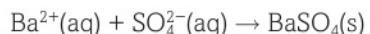
All Group 2 nitrates and chlorides are soluble, but the solubility of Group 2 sulfates decreases down the group.

- 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:

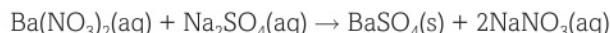


There are other anions that could also form a white precipitate with barium ions, especially carbonate ions, so in the test there must be H^+ ions present to prevent barium carbonate from forming as a white precipitate. Dilute nitric acid or dilute hydrochloric acid is therefore added as part of the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



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.



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

LEARNING TIP

There is no trend in reactivity with water for the Group 1 and 2 oxides, because they already contain metal ions, not metal atoms.

CHECKPOINT

1. Limewater is used to test for carbon dioxide. Why should limewater not be left exposed to air before using it in this test?
2. Why is an acid added when using barium chloride or barium nitrate solution to test for sulfate ions?

SUBJECT VOCABULARY

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

8B 5 THERMAL STABILITY OF COMPOUNDS IN GROUPS 1 AND 2

LEARNING OBJECTIVES

- Understand the reasons for the trends in thermal stability of the nitrates and the carbonates of the elements in Groups 1 and 2 in terms of the size and charge of the cations involved.
- Know experimental procedures used to show patterns in the thermal decomposition of Group 1 and 2 nitrates and carbonates.

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?

You are familiar with ionic bonding in compounds and you know that the bond strength is responsible for physical properties such as the melting temperature. For example, the high melting temperature of sodium chloride (NaCl) can be explained in terms of the strong electrostatic forces of attraction between the large numbers of oppositely charged Na^+ and Cl^- ions. When sodium chloride melts, the ions change from being regularly arranged in a giant lattice to moving freely in a liquid. There is no decomposition occurring in this change of state.

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.

- The charge on a Group 2 cation is double that on a Group 1 cation (e.g. Ca^{2+} compared with Na^+).
- The size (ionic radius) of a Group 2 cation is smaller than that of the Group 1 cation in the same period.
- The nitrate (NO_3^-) and carbonate (CO_3^{2-}) 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 (NO_2^-) or oxide ion (O^{2-}) 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 (O^{2-}) by decomposing and releasing carbon dioxide gas, CO_2 .
- 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:



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:



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

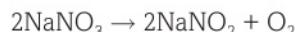
You can see that the greater decomposition occurs when:

- 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:



(lithium nitrate – the only Group 1 nitrate that decomposes in this way)



(all other Group 1 nitrates decompose in this way)



(all Group 2 nitrates decompose in this way)

EXAM HINT

Previous exam questions suggest that many students are poor at reproducing these equations under exam conditions so be sure to learn them.

EXAM HINT

Note that these reactions involving decompositions of nitrates are redox reactions. Check by assigning oxidation numbers to nitrogen and oxygen in each reaction.

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.

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:



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:



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).

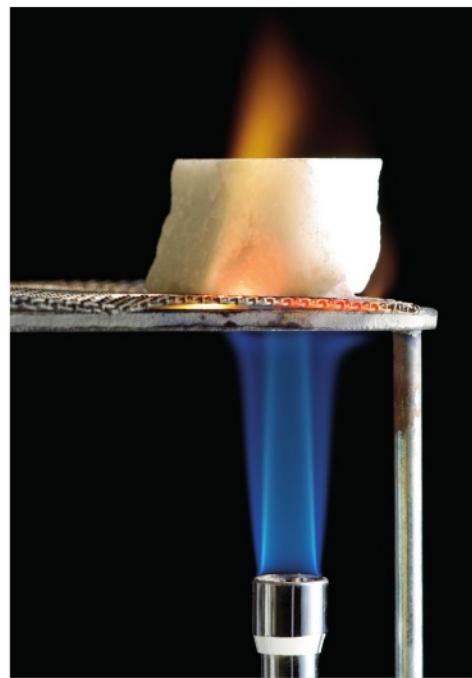


fig A Calcium oxide forms when calcium carbonate (limestone) is heated strongly. If the strong heating is continued, there is no further chemical change, but a very bright glow is seen. This is the origin of 'limelight' – it was formerly used in theatre lighting.

LEARNING TIP

Look for the similar patterns in the thermal stability of Group 1 and Group 2 nitrates and carbonates. Although the reactions are different, the lithium compound behaves like the Group 2 compounds and not like the other Group 1 compounds.

CHECKPOINT

1. What observations would be made when these compounds are heated in a test tube over a Bunsen flame?
 - (a) calcium nitrate
 - (b) sodium carbonate.
2. Write a chemical equation for each of these reactions.
 - (a) the decomposition of potassium nitrate
 - (b) the decomposition of strontium carbonate.

SUBJECT VOCABULARY

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

LEARNING OBJECTIVES

- Know experimental procedures used to show flame colours in compounds of Group 1 and 2 elements.
- Understand the formation of characteristic flame colours by Group 1 and 2 compounds in terms of electron transitions.
- Know how to identify 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. (One reason for using hydrochloric acid is to convert any metal compound to a chloride – chlorides are more volatile than other salts so are more likely to give better results.)
- 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.

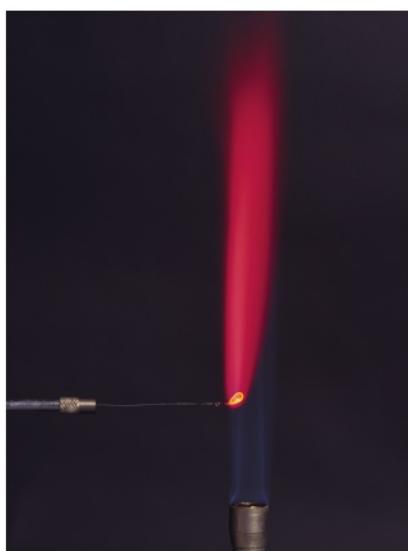


fig A A platinum wire loop with a sample of a strontium compound being held in a Bunsen flame.

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.

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.

There are also some metal cations with characteristic flame colours that are not in Groups 1 or 2. For example, copper compounds produce a blue-green colour in 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.

You know from **Topic 2** that electrons occupy orbitals in specific energy levels in an atom. These are often represented using electron configurations such as 2.8.1 (for sodium).

Electrons can absorb energy and move to higher energy levels. Sometimes the term ‘ground state’ is used to describe an atom with all its electrons in their lowest possible energy levels. If an electron moves to a higher energy level, then the new situation can be described as an ‘excited state’. This movement of an electron to an excited state occurs during a flame test.

However, this movement is immediately followed by the return of the electron to its ground state, which releases energy. If this energy corresponds to radiation in the visible light spectrum, then a characteristic colour appears – this is the flame test colour.

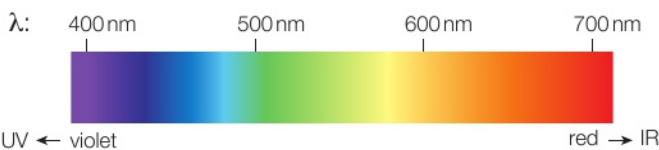


fig B The wavelengths of the spectrum of visible light.

For example, the visible spectrum covers the part of the electromagnetic spectrum in the wavelength range 400–700 nm. The electron transition in sodium corresponds to a wavelength of about 590 nm, which is in the yellow-orange part of the spectrum, so this is the colour of a sodium compound in a flame test. The electron transition in magnesium corresponds to a wavelength outside the visible spectrum, so there is no flame colour for magnesium.



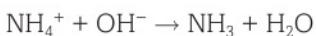
fig C The yellow-orange colour of sodium street lights is the same as the colour of sodium in a flame test.

LEARNING TIP

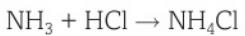
Remember that doing a flame test on a magnesium compound has nothing to do with burning magnesium metal in a Bunsen flame. When magnesium metal burns, it changes from Mg atoms to Mg²⁺ ions. Magnesium compounds already contain Mg²⁺ ions.

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:



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:



EXAM HINT

If you are asked for a safety precaution for these reactions, it is worth saying that they should be carried out in a fume cupboard.

CHECKPOINT

1. Why is concentrated hydrochloric acid used in flame tests?
2. Explain why barium compounds give a characteristic flame colour but magnesium compounds do not.

LEARNING OBJECTIVES

- Understand reasons for the trends in melting and boiling temperatures, physical state at room temperature, electronegativity and reactivity down the group.
- Be able to make predictions about fluorine and astatine and their compounds, in terms of knowledge of trends in halogen chemistry.

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

All of the halogens exist as diatomic molecules, so their melting and boiling temperatures depend on the strengths of the intermolecular forces of attraction between these molecules. We looked at these forces, known as London forces, in **Topic 7**. Here is a reminder of how they happen.

As the two atoms in the diatomic molecule are identical, the pair of electrons forming the covalent bond between them is shared equally between the two atoms. This means that the halogen molecules are non-polar, at least on average. However, as the positive charges of the protons in the two nuclei are in fixed positions, but the electron density in a halogen molecule continuously fluctuates, sometimes the centres of positive and negative charge do not coincide. This situation results in a temporary dipole, which is often referred to as an instantaneous dipole.

We will use a rectangular shape to represent a halogen molecule. The two dots represent the nuclei of the two halogen atoms. When two molecules are close together, you would expect no interaction between the two because they are both non-polar.



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:



This force of attraction is described as an instantaneous dipole-induced dipole attraction, and these are the intermolecular forces of attraction that exist between halogen molecules. These weak forces increase as the number of electrons and therefore the size of the electron cloud increases. The forces increase in strength down Group 7 as the number of electrons in the molecules increases. This explains the increase in both melting temperature and boiling temperature down Group 7.

EQUATIONS FOR CHANGES OF STATE

You are probably used to writing equations for chemical 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:



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:



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 ($\delta-$) 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.

We will see examples of reactions in **Topics 8C.2 to 8C.4**.

LEARNING TIP

Write a brief summary to help you understand the difference between intermolecular forces involving permanent dipoles and temporary dipoles.

CHECKPOINT

1. Why does bromine have a higher boiling temperature than chlorine?
2. Why is fluorine the most electronegative element of all?

SUBJECT VOCABULARY

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

8C 2 REDOX REACTIONS IN GROUP 7

LEARNING OBJECTIVES

- Understand the trend in reactivity of Group 7 elements in terms of the redox reactions of chlorine, bromine and iodine with halide ions in aqueous solution, followed by the addition of an organic solvent.
- Understand, in terms of changes in oxidation number, oxidation reactions of the halogens with Group 1 and 2 metals and disproportionation reactions of chlorine with water, and with cold and hot alkali.

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 $2\text{Li} + \text{Cl}_2 \rightarrow 2\text{LiCl}$
- barium reacting with bromine $\text{Ba} + \text{Br}_2 \rightarrow \text{BaBr}_2$

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.

These reactions occur in aqueous solution, so any reaction that occurs is indicated by a colour change. One problem in interpreting colour changes in these reactions is the similarity of some colours and the variation in colour with concentration. For example, bromine in its liquid state is red-brown, but bromine dissolved in water might be orange or yellow, depending on the concentration. Iodine dissolved in water may also appear brown at some concentrations.

When doing these reactions, it is a good idea to add an organic solvent (such as cyclohexane) after the reaction, and then shake the tube. Halogens are more soluble in cyclohexane than in water, so the halogen dissolves in the organic upper layer, where its colour can more easily be seen. **Fig A** shows the colours of the halogens dissolved in cyclohexane.

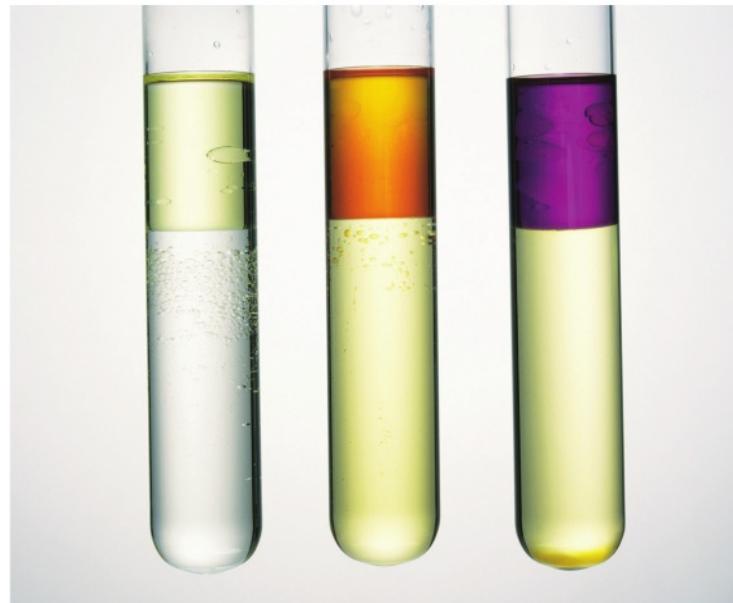


fig A Look at the upper layer in each tube. The pale green colour of chlorine does not change much, the orange colour of bromine looks a bit darker, but the colour of iodine changes to purple or violet in cyclohexane.

Here are some sample equations:

- chlorine displacing bromine $\text{Cl}_2 + 2\text{NaBr} \rightarrow 2\text{NaCl} + \text{Br}_2$
- bromine displacing iodine $\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$

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.

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

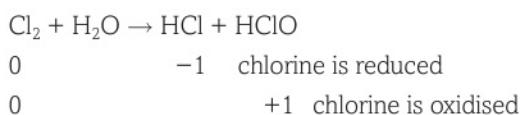
Disproportionation is a more unusual type of reaction. In this reaction, one element undergoes both oxidation and reduction at the same time. We will look at three examples of this type of reaction, all involving chlorine.

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.

The disproportionation that occurs can be shown using oxidation numbers:



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.

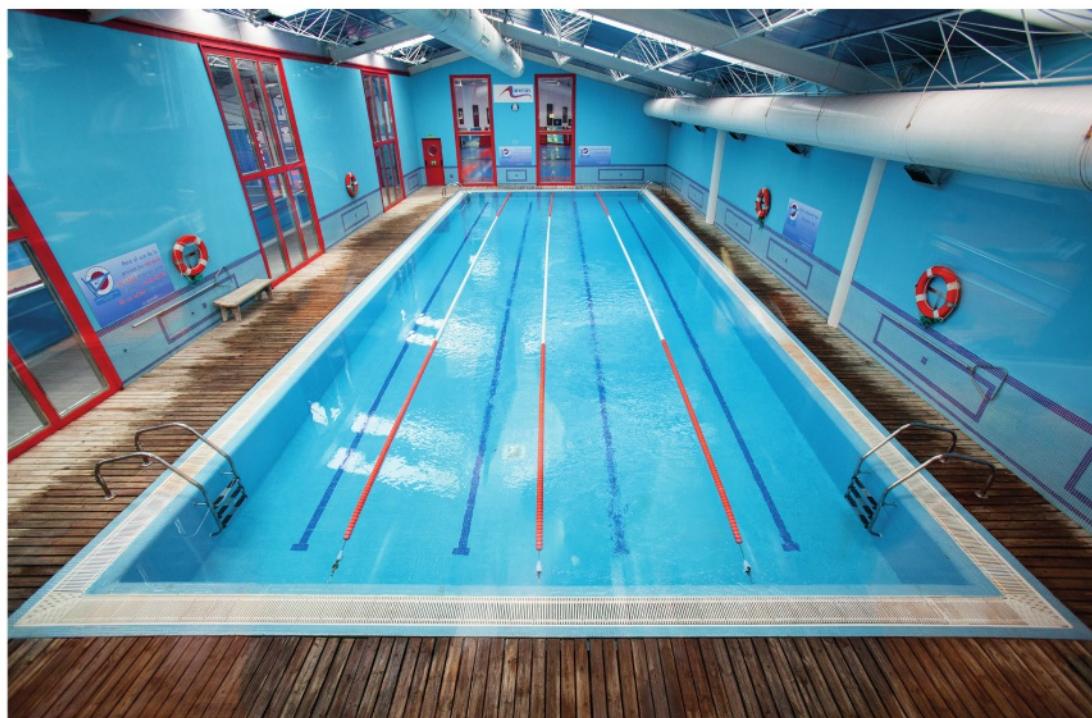
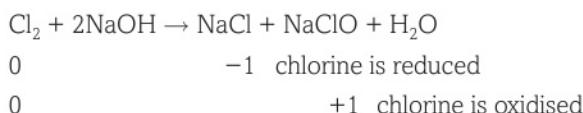


fig B Chlorine can reduce the risk of transmitting infections in public swimming pools.

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:

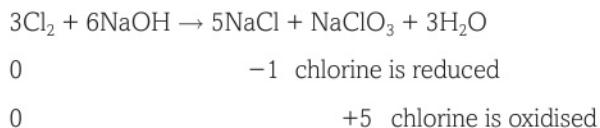


The sodium chlorate(I) formed is also a disinfectant, but it is mainly known for its bleaching action. It is used extensively in industry and is the active ingredient in household bleach.

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:



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.

LEARNING TIP

Read the explanation for chlorine being more reactive than the other halogens (except for fluorine) at the end of **Topic 8C.1**. Now try to explain why astatine is the least reactive halogen.

CHECKPOINT

1. (a) Write a chemical equation for the reaction between chlorine and potassium iodide.
(b) Write an ionic equation for the reaction between bromine and sodium astatide.
2. Write equations and name the products of the reactions between bromine and:
 - (a) cold dilute aqueous sodium hydroxide
 - (b) hot concentrated sodium hydroxide solution.

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 ACID

LEARNING OBJECTIVES

- Understand the reactions of solid Group 1 halides with concentrated sulfuric acid, to illustrate the trend in reducing ability of the hydrogen halides.

REDOX REACTIONS AGAIN

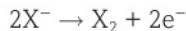
In **Topics 8A.3, 8C.1** and **8C.2**, you have learnt about several examples of the halogens acting as oxidising agents, and you know that this oxidising power decreases down the group.

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 ↓ High
	chlorine Cl ₂	chloride Cl ⁻	
	bromine Br ₂	bromide Br ⁻	
	iodine I ₂	iodide I ⁻	
	astatine At ₂	astatide At ⁻	

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:



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



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:

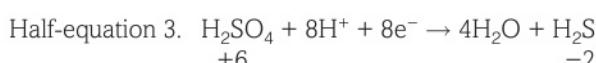
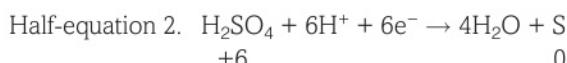
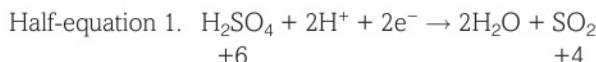


Sulfuric acid, especially when concentrated, can act as an oxidising agent as well as an acid. When it acts as an oxidising agent, it is reduced, but the extent of its reduction and the products formed depend on the species being oxidised.

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:



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

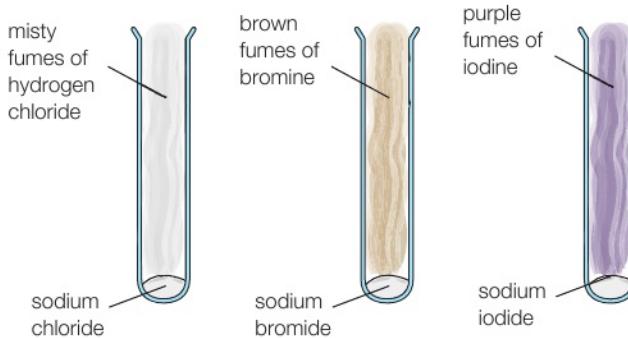
- In half-equation 1, the decrease in oxidation number (+6 to +4) is 2, which is the same as the numbers of H⁺ ions and electrons in the equation.
- The pattern is similar in the other two equations. The decrease in oxidation number of the sulfur is the same as the numbers of H⁺ ions and electrons in 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.

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
Nal	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 ₂ S

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).

The tube on the left in **fig A** shows no colour. These are the misty fumes of hydrogen chloride, formed from sodium chloride. The tube in the middle contains brown fumes. This is bromine, formed from sodium bromide. The tube on the right contains purple fumes. This is iodine, formed from sodium iodide.

With sodium chloride, the sulfuric acid behaves only as an acid, and not as an oxidising agent. This is because chloride ions have low reducing power.

With sodium bromide, the greater reducing power of bromide ions causes the sulfuric acid to be reduced, as in half-equation 1 above.

With sodium iodide, the much greater reducing power of iodide ions causes the sulfuric acid to be reduced, as in half-equations 1, 2 and 3.

CONSTRUCTING EQUATIONS

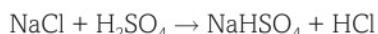
Some of the equations you see, or are asked to write, may look very complicated and be hard to remember. It is better not to try to remember them, but to work them out by the addition of half-equations. This method is recommended for the redox equations of sodium bromide and sodium iodide.

EXAM HINT

The chloride ion is behaving as a base in this reaction.

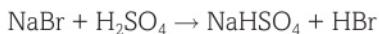
SODIUM CHLORIDE

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



SODIUM BROMIDE

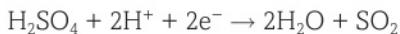
The formation of the brown fumes of hydrogen bromide can be represented by an equation analogous to the one for sodium chloride:



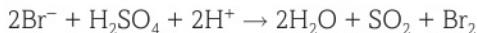
The table of observations shows that only one redox reaction occurs: the formation of sulfur dioxide in half-equation 1. The two relevant half-equations are:



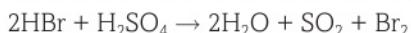
and



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



You could combine the ions on the left to give:



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:



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.

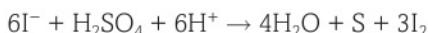
Here is the result of applying the same method to the formation of sulfur in half-equation 2. The two relevant half-equations are:



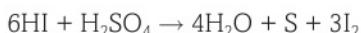
and



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



You could combine the ions on the left to give:



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.

LEARNING TIP

Look carefully at all of the equations in this topic. Make sure you can identify whether they are redox reactions and, if so, what the extent of the reaction is.

CHECKPOINT

- Explain what kind of reaction occurs when concentrated sulfuric acid is added to sodium fluoride.
- Use half-equations to construct an overall equation for the reaction between iodide ions and concentrated sulfuric acid that results in the formation of hydrogen sulfide.

LEARNING OBJECTIVES

- Understand precipitation reactions of the aqueous anions Cl^- , Br^- and I^- with aqueous silver nitrate solution and nitric acid, and the solubility of the precipitates in aqueous ammonia solutions.
- Understand reactions of hydrogen halides with ammonia and with water.

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.

EXAM HINT

Make sure that you can write an ionic equation for the reaction of acid with carbonate ions to produce carbon dioxide and water.

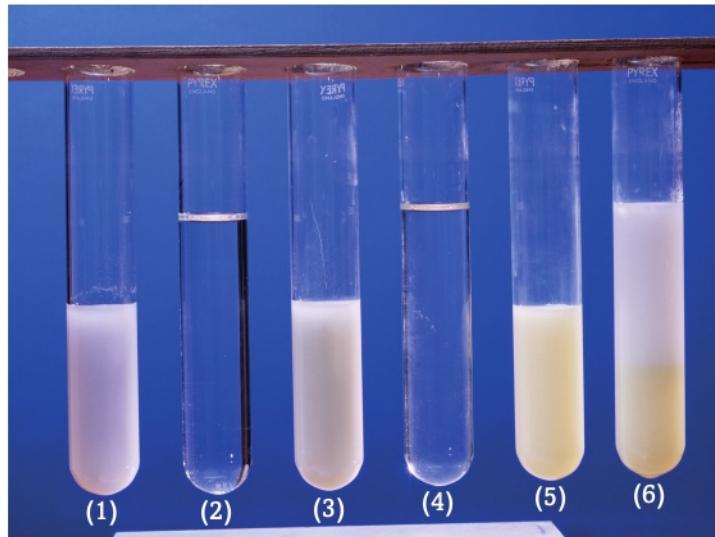
The reagent is silver nitrate solution, but dilute nitric acid is added first to make sure that any other anions (especially carbonate ions) are removed, as they would also form precipitates.

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.

	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.

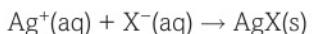


▲ fig A Testing for halide ions in solution.

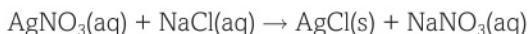
From left to right in **fig A**:

- 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:



You can write a specific equation, such as:



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:



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	$\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$
Hydrogen chloride	hydrochloric acid	$\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$
Hydrogen bromide	hydrobromic acid	$\text{HBr} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Br}^-$
Hydrogen iodide	hydroiodic acid	$\text{HI} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{I}^-$

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

LEARNING TIP

Note the reversible arrow in the first equation. Although hydrogen fluoride is very soluble in water, it is only a weak acid, whereas the other acids formed are strong.

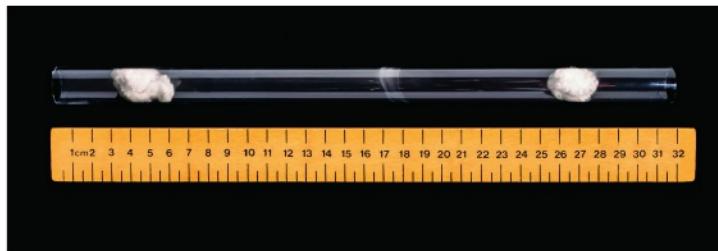
REACTIONS WITH AMMONIA

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

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



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).

Ammonia and hydrogen chloride gases are given off from the cotton wool pieces soaked in concentrated aqueous ammonia (on the left) and concentrated hydrochloric acid (on the right). These colourless gases move through the tube until they meet and react to form ammonium chloride. Ammonia gas molecules ($M_r = 17.0$) move more quickly and therefore travel further in the same time as hydrogen chloride molecules ($M_r = 36.5$). This means that the ammonium chloride does not form exactly halfway down the tube, it forms closer to the hydrochloric acid side.

FLUORIDES AND ASTATIDES

Fluorides and astatides have been mentioned in some of the reactions in this chapter, especially when it is not possible to make predictions about their reactions using trends in the chlorides, bromides and iodides. For example, you might predict that silver nitrate would form a white precipitate with sodium fluoride because sodium chloride does, but this is not the case.

If you are asked to predict reactions of fluorides and astatides that you are not familiar with, you can use information in this topic to help you. For example, you could write an equation to show the formation of an acid when hydrogen astatide is added to water, based on the equation for hydrogen iodide.

DID YOU KNOW?

None of the reactions in this topic involve redox. This is because the oxidation number of every halogen in a halogen compound in this topic remains unchanged at -1.

CHECKPOINT

1. Write equations to show:
 - the formation of the cream precipitate in the test for bromide ions
 - the precipitate dissolving in concentrated aqueous ammonia.
2. (a) Describe what happens when ammonia and hydrogen bromide gases are mixed together.
 (b) Name the product of the reaction and write an equation for its formation.

8D 1 MAKING STANDARD SOLUTIONS

LEARNING OBJECTIVES

- Be able to calculate solution concentrations, including simple acid-base titrations.

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. For example, hydrochloric acid does not exist as a solid, but only as HCl(g) and HCl(aq). Sodium hydroxide is a solid, but it readily absorbs water vapour and reacts with carbon dioxide from the atmosphere. A sample of sodium hydroxide can be accurately weighed, but it is not certain what is being weighed, as there will be unknown masses of water and sodium carbonate mixed with it. You may remember seeing a white powder around the neck of a bottle of sodium hydroxide solution. This white powder is sodium carbonate.

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 NH₂SO₃H, and it has a molar mass of 97.1 g mol⁻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 dm⁻³ and 250 cm³.

Using the calculation method given in **Topic 1E.2**, the approximate amount of sulfamic acid, $n = c \times V = 0.1 \times 0.25 = 0.025$ mol, so the approximate mass needed is $m = n \times M = 0.025 \times 97.1 = 2$ g.

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

- Add between 2.3 and 2.5 g of sulfamic acid to the weighing bottle and weigh accurately.
- Transfer as much as possible of the acid to a clean beaker and reweigh the weighing bottle.
- Add about 100 cm³ of deionised water to the beaker and stir until all of the sulfamic acid has dissolved.
- Remove the stirring rod, washing traces of solution from the rod into the beaker using the wash bottle.
- Place a funnel in the neck of the volumetric flask and pour the solution from the beaker into the flask.
- Rinse the inside of the beaker several times using the wash bottle and transfer the rinsings to the flask.
- Add deionised water to the flask and fill up exactly to the graduation mark.
- 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.

$$\text{mass of weighing bottle + sulfamic acid} = 19.542 \text{ g}$$

$$\text{mass of weighing bottle + any traces of sulfamic acid} = 17.151 \text{ g}$$

$$\text{mass of sulfamic acid added} = 2.391 \text{ g}$$

$$n(\text{NH}_2\text{SO}_3\text{H}) = \frac{2.391}{97.1} = 0.02462 \text{ mol}$$

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

LEARNING TIP

Look carefully at each step of the method. How does each step contribute to the accuracy of the final value of the concentration?



When making a standard solution in a volumetric flask, it is important to ensure that the lowest part of the liquid (the meniscus) is aligned with the graduation mark.

CHECKPOINT

1. A student used the method described but made two mistakes.

- (a) In Step 6, he poured the rinsings down the sink instead of transferring them to the flask.
- (b) In Step 7, he added water above the graduation mark.

Explain how each mistake affected the calculated concentration.

2. A student used the method to make 500 cm³ of a solution of sodium carbonate ($M = 106.0 \text{ g mol}^{-1}$).

These are her weighings:

$$\text{mass of weighing bottle + sodium carbonate} = 23.382 \text{ g}$$

$$\text{mass of weighing bottle} = 18.218 \text{ g}$$

Calculate the concentration of the solution made.

SKILLS CRITICAL THINKING

SKILLS PROBLEM SOLVING

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

8.20
PART

CP3

CP4

LEARNING OBJECTIVES

- Be able to calculate solution concentrations, including simple acid-base titrations.

WHAT IS A TITRATION?

A titration is a practical method with the aim of measuring the volumes of two solutions that react together, and using the results to calculate the concentration of one of the solutions. Because the method involves measuring volumes, it is sometimes known as volumetric analysis.

You may come across different titration types (redox titrations and complexometric titrations), but in this book we will consider only acid–base titrations. Many, but not all, bases are soluble in water, which makes them alkalis. They are often referred to as acid–alkali titrations.

All of the acids and bases you will use in titrations are colourless, as are the products, so there is nothing to see when the reaction is complete. This problem is solved by using an indicator, a substance which has different colours in acids and bases/alkalis.

In the method described in this topic, we will assume that a solution of sodium hydroxide of approximate concentration 0.1 mol dm^{-3} is available and that the standard solution of sulfamic acid referred to in **Topic 8D.1** will be used. The aim is to calculate an accurate value for the concentration of the sodium hydroxide solution. The method will be described in some detail, and we will focus on avoiding common errors in technique.

In some titrations, it is important to choose which way round to do the titration (which solution goes in the pipette and which solution in the burette). In other titrations, it does not matter.

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 cm^3)
- a burette (usually 50 cm^3) and stand
- a pipette (usually 25 cm^3) and pipette filler
- a wash bottle containing deionised water (or distilled water)
- a small funnel
- a white tile.

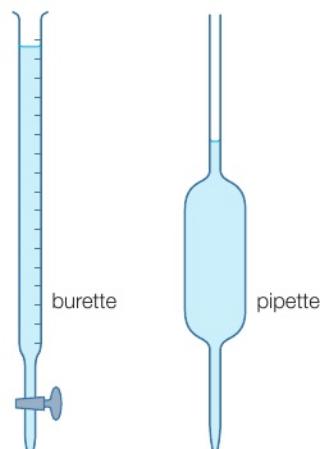


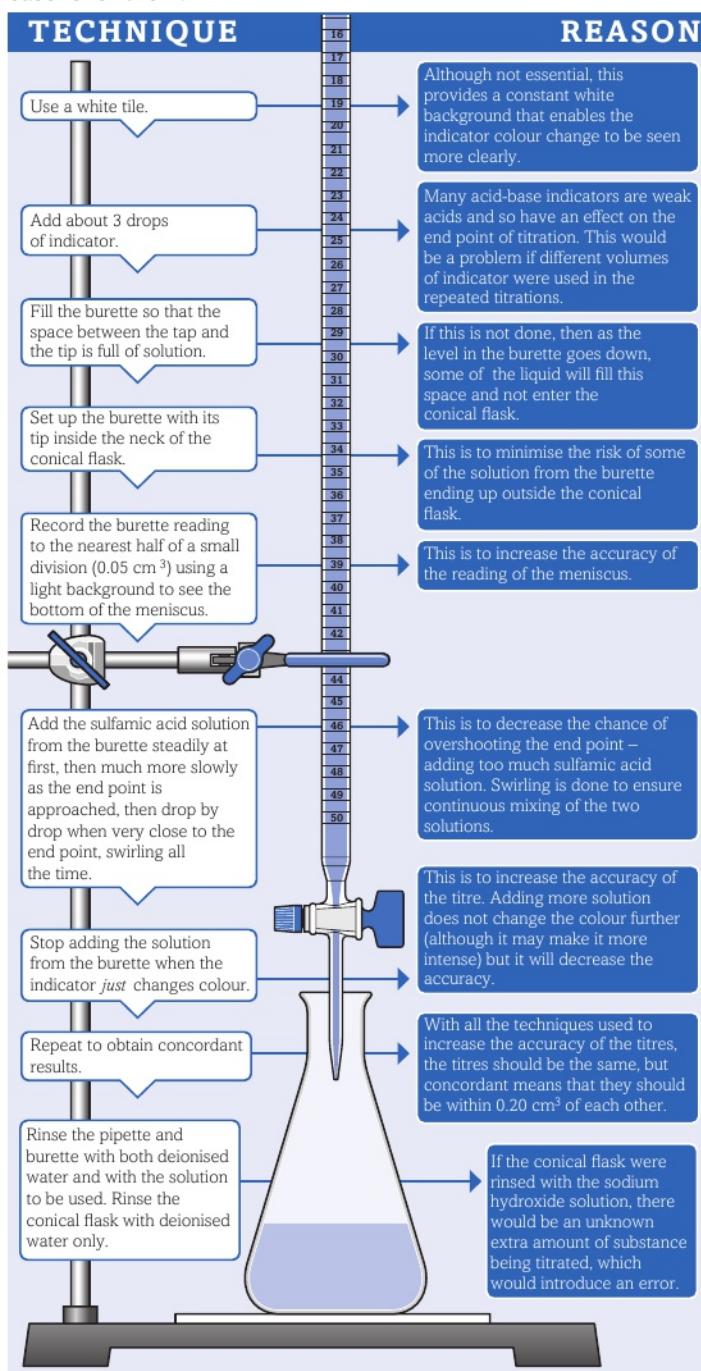
Fig A Note that the space between the tap and the tip of the burette is full of solution.

METHOD

- Rinse the conical flask with deionised water and place it on a white tile.
- Using a pipette filler, rinse the pipette with deionised water and then with some of the sodium hydroxide solution.
- Use the pipette to transfer 25.0 cm^3 of the sodium hydroxide solution to the conical flask.
- Add about 3 drops of methyl orange indicator.
- Rinse the burette with deionised water and then with some of the sulfamic acid solution.
- Fill the burette with the sulfamic acid solution and set it up in the stand above the conical flask.
- Record the burette reading.
- Add the sulfamic acid solution to the conical flask until the indicator just changes colour, and again record the burette reading.
- Empty and rinse the conical flask with deionised water, and repeat the titration until concordant titres have been obtained.

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.



▲ **fig B** Titration techniques and the reasons for them.

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.

LEARNING TIP

The best way to understand all the features of successful titrations is to do several titrations yourself.

CHECKPOINT

SKILLS CRITICAL THINKING

- A student does not fill the burette space between the tap and the tip in a titration. Explain the effect of this mistake on the value of the titre.
- A student rinses out the conical flask with deionised water, then with the solution used in the pipette. Explain the effect of this mistake on the value of the titre.

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)

LEARNING OBJECTIVES

- Be able to calculate solution concentrations, including simple acid-base 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 cm^3 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:

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

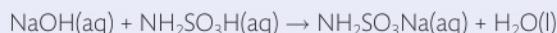
CALCULATING A CONCENTRATION

WORKED EXAMPLE 1

Here is a typical set of titration results from the method given in **Topic 8D.2**.

volume of sodium hydroxide solution used	= 25.0 cm^3
volume of sulfamic acid solution used	= 22.65 cm^3
concentration of sulfamic acid solution	= $0.0985\text{ mol dm}^{-3}$

The equation for the reaction is:



You may be shown a shorter method than the following one, but this method, using moles, is more versatile and can be used in more difficult examples.

Step 1: calculate the amount of one substance, in this case the sulfamic acid.

$$n(\text{NH}_2\text{SO}_3\text{H}) = c \times V = 0.0985 \times \frac{22.60}{1000} = 0.00223 \text{ mol}$$

Step 2: calculate the amount of the other substance using the reacting ratio in the equation.

As the reacting ratio is 1 : 1, $n(\text{NaOH}) = 0.00223 \text{ mol}$

Step 3: calculate the concentration of sodium hydroxide solution.

$$c = \frac{n}{V} = \frac{0.00223}{0.0250} = 0.0892 \text{ mol dm}^{-3}$$

WORKED EXAMPLE 2

A titration is done to calculate the concentration of a solution of nitric acid, using a standard solution of sodium carbonate. The equation for the reaction is:



The titration results are:

volume of sodium carbonate solution used	= 25.0 cm ³
volume of nitric acid solution used	= 27.25 cm ³
concentration of sodium carbonate solution	= 0.108 mol dm ⁻³

Step 1: calculate the amount of sodium carbonate.

$$n = 0.108 \times \frac{25}{1000} = 0.00270 \text{ mol}$$

Step 2: calculate the amount of the other substance using the reacting ratio in the equation (1 : 2 in this example).

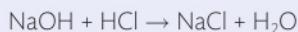
$$n = 0.00270 \times 2 = 0.00540 \text{ mol}$$

Step 3: calculate the concentration of the nitric acid.

$$c = \frac{0.00540}{0.02725} = 0.198 \text{ mol dm}^{-3}$$

WORKED EXAMPLE 3

A titration is done to calculate the concentration of a solution of hydrochloric acid, using the sodium hydroxide solution from Worked example 1. The equation for the reaction is:



The titration results are:

volume of sodium hydroxide solution used	= 25.0 cm ³
volume of hydrochloric acid used	= 22.68 cm ³
concentration of sodium hydroxide solution	= 0.0892 mol dm ⁻³

This time, we will use the shorter method of calculation, using the expression

$$V_1 \times \frac{M_1}{n_1} = V_2 \times \frac{M_2}{n_2}$$

where V is the volume, M is the molar concentration and n is the coefficient in the equation. The subscript 1 refers to the first substance in the equation, and the subscript 2 to the second substance.

In this example, the unknown is M_2 , so rearranging the expression and substituting the values gives the answer.

$$M_2 = \frac{V_1 \times M_1 \times n_2}{V_2 \times n_1} = \frac{25.0 \times 0.0892 \times 1}{22.68 \times 1} = 0.0983 \text{ mol dm}^{-3}$$

LEARNING TIP

Practise the calculation method. Make sure that you use the reacting ratio the right way round.

CHECKPOINT

1. A student records these readings during a titration:

final burette reading / cm ³	28.0	27.8	27.4	27.0
initial burette reading / cm ³	2.7	2.8	2.8	2.8
titre / cm ³	25.3	25.0	24.6	24.2

$$\text{mean titre} = 24.4 \text{ cm}^3$$

What mistakes has the student made in recording these results?

2. A student does a titration using this reaction:



She records these results:

$$\text{volume of KOH solution} = 25.0 \text{ cm}^3$$

$$\text{volume of H}_2\text{SO}_4 = 19.83 \text{ cm}^3$$

$$\text{concentration of H}_2\text{SO}_4 = 0.0618 \text{ mol dm}^{-3}$$

What is the concentration of the KOH solution, in mol dm⁻³?

SKILLS CRITICAL THINKING

SKILLS PROBLEM SOLVING

4 MISTAKES, ERRORS, ACCURACY AND PRECISION

LEARNING OBJECTIVES

- Understand the difference between a mistake and an error.
- Understand the difference between accuracy and precision.
- Comment on sources of error in experimental procedures.

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 cm^3 but writes it down as 23.75 cm^3 . 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**.

The last two terms are often confused. We will try to understand the difference between them by considering some burette readings and an archery competition.

A teacher and some students do a titration using the same solutions. The teacher works carefully and obtains a mean titre of 24.27 cm^3 , which we will assume is the 'correct' value.

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.

LEARNING TIP

Comparing the archery competition and the titrations should help you to understand the difference between accuracy and precision.

CHECKPOINT

SKILLS CRITICAL THINKING

- An experimental method requires a 25.0 cm³ pipette to be used to measure a volume of liquid in different experiments. A student uses a 25 cm³ measuring cylinder instead in each case. Explain whether the student has made a mistake or has introduced a random error or a systematic error.
- Consider these titres recorded in cm³.

Student 1	27.60	27.70	27.70	27.65
Student 2	26.15	26.82	26.60	26.30
Student 3	24.40	26.50	26.50	26.40

The teacher's mean titre was 26.50 cm³, which can be assumed to be correct.

Explain whether the students' titres indicate accuracy, precision, both or neither.

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

5 MEASUREMENT ERRORS AND MEASUREMENT UNCERTAINTIES

LEARNING OBJECTIVES

- Understand how to minimise the sources of measurement uncertainty in volumetric analysis.

RANDOM AND SYSTEMATIC ERRORS

Consider the accepted meanings of two terms briefly mentioned in **Topic 8D.4 (table A)**.

TERM	MEANING
random error	This is an error caused by unpredictable changes in conditions such as temperature or pressure, or by a difference in recording that is difficult to get exactly right.
systematic error	This is an error caused by the apparatus, and leads to the recorded value being either too low or too high.

table A

RANDOM ERRORS

Here are examples of random errors.

- The volume of a gas collected in a syringe is measured in different experiments done on the same day. The atmospheric pressure and the temperature of the laboratory may vary during the day, and this will cause an unpredictable change in the value recorded.
- The mass of an object is measured using the same balance but at different times during the day. The values may differ slightly, as a result of changes in temperature, draughts or condensation of water vapour on the balance pan.
- An experiment is done with a flask in an electric water bath. The thermostat is set to 50 °C, but as the heater automatically switches on, the actual temperature rises slightly above 50 °C, and then falls to slightly less than 50 °C after the thermostat switches off.

Repeating an experiment should lead to a more accurate final value being recorded because these random fluctuations become less important when values are averaged.

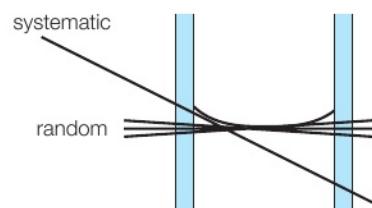


fig A When recording a liquid level, the operator should view the meniscus at eye level (horizontally). This diagram shows that minor variations from the horizontal can be considered as random errors. If the meniscus is consistently viewed from above, then the error can be described as systematic.

SYSTEMATIC ERRORS

Here are examples of systematic errors.

- A 25.0 cm³ pipette has been wrongly calibrated during its manufacture, so that the graduation mark is lower than it should be. This means that no matter how carefully it is used, the volume of solution added from this pipette will always be less than 25.0 cm³.
- The amount of liquid in a thermometer is more than it should be, so that the height of the liquid at all temperatures is higher than it should be. This means that the temperature recorded will always be greater than the correct temperature.
- A measuring cylinder has markings on it from 0 to 10 cm³, but the diameter of the cylinder is smaller than the manufacturer intended. This means that when the liquid level shows 10 cm³, the volume is less than 10 cm³.

Repeating an experiment using the same apparatus will not lead to a more accurate value being recorded.

LEARNING TIP

Think about how using a burette could involve both random and systematic errors.

MEASUREMENT UNCERTAINTY

When using apparatus, there is always a potential error, known as **measurement uncertainty**. The size of the measurement uncertainty is determined by the precision of the apparatus.

BALANCES

Digital balances can have various degrees of precision. A balance that measures to three decimal places is more precise than one that measures to only one decimal place. This means that the measurement uncertainty involved in using the three-decimal place balance is lower than in using the one-decimal place balance. This is illustrated in **table B**. The greater the degree of precision of the balance, the smaller the measurement uncertainty in the recorded mass.

NUMBER OF DECIMAL PLACES	MEASUREMENT UNCERTAINTY	EXAMPLE
1	±0.05 g	A reading of 17.1 g could be between 17.05 and 17.15 g
2	±0.005 g	A reading of 17.10 g could be between 17.095 g and 17.105 g
3	±0.0005 g	A reading of 17.100 g could be between 17.0995 g and 17.1005 g

table B Examples of measurement uncertainties when using a balance.



fig B The scale on a beaker is there only as a guide and should not be used to record values to be used in calculations. A measuring cylinder is better for this purpose.

GLASSWARE

Most laboratory glassware is manufactured to Class A and Class B (or Grade A and Grade B) standards. Class A apparatus is much more expensive than Class B apparatus, and the extra cost reflects the way in which the apparatus is calibrated, rather than the quality of the actual apparatus.

You will almost certainly use Class B apparatus, which is still capable of giving measurements to a high degree of accuracy. If you look carefully, you should be able to see the manufacturer's statement about level of precision marked on the apparatus. You should see a temperature quoted (usually 20 °C). At higher temperatures, the glass and the solution it contains will expand to different extents, and the value of the volume will no longer be accurate within the given tolerances.

Table C shows information about typical pieces of Class B glassware that are used to measure volumes.

APPARATUS	CAPACITY	MEASUREMENT UNCERTAINTY
burette	50 cm ³	±0.05 cm ³ (but the burette is read twice in a titration, so the total measurement uncertainty is ±0.10 cm ³)
pipette	25 cm ³	±0.06 cm ³
volumetric flask	250 cm ³	±0.3 cm ³

table C Examples of measurement uncertainties in glassware.

LEARNING TIP

Remember that, assuming you have used the piece of apparatus correctly, you still cannot say for certain that any measurement made with the apparatus is accurate. It is only possible to know if there has been an error if you happen to know the true value of the measurement made. The best you can say is that there is a potential error involved, which is given by the *measurement uncertainty* of using the apparatus.

CHECKPOINT

SKILLS

CRITICAL THINKING

1. A student carries out a titration and obtains a titre of 23.40 cm³. She repeats the titration the next day using different apparatus and obtains a titre of 24.50 cm³.
 - (a) What is the total measurement uncertainty of the first titre?
 - (b) Identify a potential source of random error that may have affected her results.
 - (c) Identify a potential source of systematic error that may have affected her results.
2. A student uses a pipette and a burette to add 50.0 cm³ of a liquid to a flask in different experiments. Use the table of measurement uncertainties (**table C** above) to calculate which piece of apparatus is the better one to use in this experiment.

SUBJECT VOCABULARY

random error an error caused by unpredictable variations in conditions

systematic error an error that is constant or predictable, usually because of the apparatus used

measurement uncertainty the potential error involved when using a piece of apparatus to make a measurement

6 OVERALL MEASUREMENT UNCERTAINTY

LEARNING OBJECTIVES

- Understand how to estimate the overall uncertainty of the calculated result in volumetric analysis.

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: $\pm0.10 \times 100/22.50 = \pm0.44\%$
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: $\pm0.06 \times 100/25 = \pm0.24\%$
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: $\pm0.3 \times 100/250 = \pm0.12\%$

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.

WORKED EXAMPLE 1

- mass of a marble chip = 3.57 g

The measurement uncertainty in a two-decimal place balance is ±0.005 g. We have to count this uncertainty twice. This is because there is a ±0.005 g uncertainty when calibrating the balance to zero, as well as a ±0.005 g uncertainty when measuring the mass.

So the percentage uncertainty is:

$$\pm\frac{2 \times 0.005 \times 100}{3.57} = \pm0.28\%$$

WORKED EXAMPLE 2

- mass of weighing bottle + solid = 20.354 g
- mass of weighing bottle = 19.816 g
- mass of solid = 0.538 g

The measurement uncertainty in a three-decimal place balance is ± 0.0005 g. We have to count this uncertainty twice for each measurement and we have two measurements, so we need to count it four times. The percentage uncertainty is:

$$\pm \frac{4 \times 0.0005 \times 100}{0.538} = \pm 0.37\%$$

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 $0.118 \text{ mol dm}^{-3}$ has been calculated from a titration that has involved balance and glassware uncertainties, then the uncertainties might be:

balance	$\pm 0.09\%$
volumetric flask	$\pm 0.12\%$
pipette	$\pm 0.24\%$
burette	$\pm 0.47\%$
overall percentage uncertainty	$\pm 0.92\%$

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:

$$\text{concentration} = 0.118 \pm 0.001 \text{ mol dm}^{-3}$$

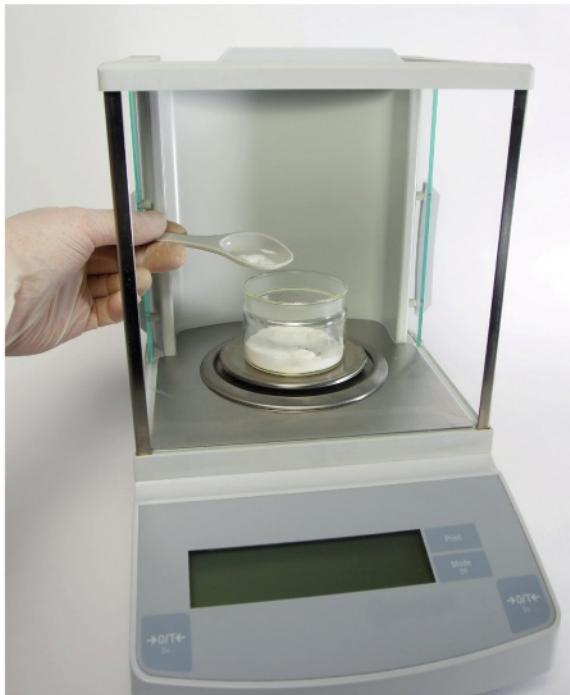
which means that the exact value is in the range 0.117 – $0.119 \text{ mol dm}^{-3}$.

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.

Where a measuring instrument can be used for a range of values, the percentage uncertainty can be minimised by using a higher value rather than a lower one. For example, when using a balance, weighing a sample of 5 g will lead to a much lower percentage uncertainty than weighing a 0.5 g sample. In a titration, it is not a good idea to have a titre value of 10 cm^3 instead of 30 cm^3 , as the larger titre has the lower percentage uncertainty.



▲ **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.

LEARNING TIP

Practise calculating measurement uncertainties and percentage uncertainties for different pieces of apparatus.

CHECKPOINT

1. A student uses a one-decimal place balance to weigh a piece of zinc. He records a mass of 2.8 g. What is the percentage uncertainty?
2. A thermometer has a measurement uncertainty of 1°C . A student uses it to measure a temperature rise and records these values:
start temperature = 15°C
final temperature = 28°C
What is the percentage uncertainty in the temperature rise?

SUBJECT VOCABULARY

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

NUTS ABOUT SELENIUM

SKILLS

INITIATIVE, SELF DIRECTION

Selenium is an essential dietary element in trace quantities, but it can be toxic in higher concentrations. The extract below describes one technique used to reduce discharge of selenium salts into the San Francisco Bay, USA.

SOME OF OUR SELENIUM IS MISSING



fig A Wetlands are an important habitat for birds and other wildlife.

From an article in *New Scientist* magazine

In 1989, the multinational oil company Chevron discovered that it had reduced its discharge of toxic selenium salts into the San Francisco Bay by almost three-quarters. The company should have been very pleased with itself. After all, the six oil companies in the area flush up to 3000 kilograms of selenium into the bay each year, and it seemed that by simply planting a 35-hectare wetland between its outfall and the bay, Chevron had found a practical answer to the problem.

But officials from the State Regional Water Quality Control Board were not so sanguine. They wanted to know where all the selenium was going and told Chevron to find out. The company searched in the sediment at the bottom of the wetland, dug up the wetland plants, and checked for a build-up of selenium compounds in the water. But despite all the effort, half of the selenium was still missing.

Alarm bells started to ring. Perhaps the local wildlife was eating the missing selenium. But there were no telltale signs – no dead or maimed animals. Then a team of biologists from the University of California at Berkeley made an educated guess. Norman Terry, Adel Zayed and their colleagues had been studying the way that some plants take toxic selenium salts from soil and water and turn them into the volatile gas dimethyl selenide. They suggested that Chevron's selenium could literally be vanishing into thin air.

SCIENCE COMMUNICATION

1. The article was written for *New Scientist* and was based on research presented in a scientific paper.
 - (a) Read the article and comment on the type of writing being used. Think about whether this is a scientist reporting the results of their experiments, a scientific review of a paper or a newspaper or magazine article for a specific audience.
 - (b) Is there any bias present in the report? What type of words would make you think that was the case?
 - (c) Criticise how the use of language has been adapted for the audience. Would the wording be different if this was aimed at an audience of 14–16 year olds? How would it be different if written by the press officer of the company Chevron?

WRITING SCIENTIFICALLY

Note that when the word criticise is given in this context it does not mean that you should be negative. Instead, your comments should show reasoned judgement. Try to be constructive.

CHEMISTRY IN DETAIL

2. Calculate the number of moles of selenium present in 3000 kg of selenium.
3. Give the electronic configuration, using s, p, d notation, of the Se atom and the Se^{2-} ion.
4. Give the oxidation number of selenium in the following compounds:
 - (a) Na_2SeO_3
 - (b) Ag_2Se
 - (c) H_2SeO_4
5. Selenium is in Group 6 of the Periodic Table. Give some reasons why selenium chemistry is likely to be similar to sulfur chemistry.
6. Suggest a shape for the molecule SeF_6 .
7. Give the formula for the molecule dimethyl selenide. Use your knowledge of Group 6 chemistry to suggest a shape for the molecule.
8. Dimethyl sulfide has a boiling temperature of 38 °C and dimethyl telluride has a boiling temperature of 82 °C. By drawing a suitable plot, suggest a boiling temperature for dimethyl selenide and explain your choice. What assumptions have you made?

THINKING BIGGER TIP

Consider the position of selenium relative to sulfur and tellurium in Group 6 when you are drawing your plot. Make sure you use suitable axes and scale in order to obtain a reasonable suggestion for the boiling point.

ACTIVITY

In our world today there is an increasing need to communicate scientific ideas and concepts to people who consider themselves to be 'non-scientists'. Researchers may not always be the best people to communicate science (even their own!), but there are many occupations where this is an essential skill.

Imagine you need to give a 5–10 minute presentation to the chief executive officer (CEO) of an oil company to argue the case for the use of genetically engineered plants to deal with selenium waste. How might you convince the CEO that the benefits are outweighed by any perceived concerns about genetic engineering?

INTERPRETATION NOTE

Refer back to the article's final paragraph. You might also like to do some research. If you do, make sure you carefully consider the nature of the source.

DID YOU KNOW?

Brazil nuts are a particularly rich source of selenium, but don't go overboard! Too much selenium in the diet can cause the body to break down and excrete excess selenium in the form of gaseous hydrogen selenide (H_2Se). This can leave the unwitting consumer of too many brazil nuts breathing out an odour not unlike garlic.



8

EXAM PRACTICE

- 1 The equation for a reaction is:



Which description is correct for this reaction?

- A oxidation only
- B reduction only
- C oxidation and reduction
- D neither oxidation nor reduction

[1]

(Total for Question 1 = 1 mark)

- 2 What is the oxidation number of chlorine in the compound KClO_4 ?

- A -1
- B +1
- C +4
- D +7

[1]

(Total for Question 2 = 1 mark)

- 3 Which equation represents a disproportionation reaction?

- A $2\text{LiOH} + \text{H}_2\text{SO}_4 \rightarrow \text{Li}_2\text{SO}_4 + 2\text{H}_2\text{O}$
- B $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$
- C $2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3$
- D $\text{KF} + \text{H}_2\text{SO}_4 \rightarrow \text{KHSO}_4 + \text{HF}$

[1]

(Total for Question 3 = 1 mark)

- 4 Which equation represents the process that occurs when the second ionisation energy of strontium is measured?

- A $\text{Sr(s)} \rightarrow \text{Sr}^+(g) + e^-$
- B $\text{Sr}^+(s) \rightarrow \text{Sr}^{2+}(g) + e^-$
- C $\text{Sr(g)} \rightarrow \text{Sr}^+(g) + e^-$
- D $\text{Sr}^+(g) \rightarrow \text{Sr}^{2+}(g) + e^-$

[1]

(Total for Question 3 = 1 mark)

- 5 A combination of reagents that can be used to test for sulfate ions in solution is $\text{Ba(NO}_3)_2$ and HNO_3 .

Which other combination of reagents can also be used in this test?

- A $\text{BaO} + \text{NaOH}$
- B $\text{BaCO}_3 + \text{NaOH}$
- C $\text{BaSO}_4 + \text{HCl}$
- D $\text{BaCl}_2 + \text{HCl}$

[1]

(Total for Question 5 = 1 mark)

- 6 A mass of 830 mg of KOH is dissolved in water to make 150 cm^3 of solution.

What is the concentration of hydroxide ions in this solution?

- A 0.0148 g dm^{-3}
- B $0.0986\text{ mol dm}^{-3}$
- C 0.325 mol dm^{-3}
- D 5.53 mg dm^{-3}

[1]

(Total for Question 6 = 1 mark)

- 7 Most chlorine-based bleaches contain the ClO^- ion.

- (a) (i) State the oxidation number of the chlorine in the ClO^- ion. [1]
- (ii) Give the systematic name of the ClO^- ion. [1]

- (b) The ClO^- ion is produced when chlorine gas is reacted with water.

Write an ionic equation for this reaction and explain why chlorine is said to undergo 'disproportionation'. [3]

- (c) Chlorine forms another ion with the formula ClO_3^- . This ion exists in the compound KClO_3 .

KClO_3 decomposes on heating according to the equation:



Comment on the change in oxidation number of the chlorine in this reaction. [3]

(Total for Question 7 = 8 marks)

- 8 Bromine is present in sea water as aqueous bromide ions, $\text{Br}^-(\text{aq})$. Bromine can be extracted from sea water by adding chlorine. The ionic equation for the reaction is:

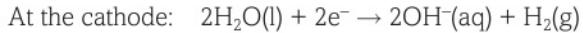


- (a) (i) State what is meant by oxidation and reduction in terms of electron transfer. [1]

- (ii) State which species is acting as an oxidising agent. Justify your answer. [2]

- (b) The chlorine required for extraction of bromine is manufactured from a concentrated solution of sodium chloride using electrolysis.

The ionic half-equations for the reactions at the electrodes are:



Use these two half-equations to produce an overall ionic equation for the reaction taking place during the electrolysis. [2]

(Total for Question 8 = 5 marks)

- 9** This question is about the chemistry of the elements in Groups 1 and 2 of the Periodic Table.
- (a) When magnesium burns in air it forms a mixture of magnesium oxide and magnesium nitride.
Give the formula of both magnesium oxide and magnesium nitride. [2]
- (b) (i) Write an equation for the reaction between calcium and water. Include state symbols. [2]
- (ii) Explain how the reactivity of the Group 2 metals with water changes down the group. [3]
- (iii) State how the solubility of the hydroxides of the Group 2 metals changes down the group. [1]
- (c) Explain the trend in thermal stability of the carbonates of the Group 2 metals. [3]
- (d) The nitrates of most of the Group 1 metals decompose on heating as shown in the equation:



where M represents a Group 1 metal.

However, lithium nitrate decomposes further.

Write an equation for the thermal decomposition of lithium nitrate. State symbols are not required. [2]

(Total for Question 9 = 13 marks)

- 10** This question is about halides.

- (a) Group 1 halides react with concentrated sulfuric acid in different ways.

Sodium chloride reacts to give hydrogen chloride as the only gaseous product.

Sodium bromide reacts to give both hydrogen bromide and bromine as gaseous products.

- (i) Write an equation for the reaction of both sodium chloride and sodium bromide with concentrated sulfuric acid. [2]

- (ii) Explain why the two reactions produce different gaseous products. [3]

- (iii) Describe how ammonia gas can be used to show that hydrogen chloride has been given off in the reaction between sodium chloride and concentrated sulfuric acid. [2]

- (b) Hydrogen halides react with water.

- (i) Write an equation for the reaction between hydrogen bromide and water. [1]

- (ii) Explain the effect that the solution formed has on methyl orange indicator. [3]

- (c) Describe how you would show that an aqueous solution contains both chloride and iodide ions. [4]

(Total for Question 10 = 15 marks)

- 11** Radium (Ra) and astatine (At) are radioactive elements in Groups 2 and 7 respectively in the Periodic Table.

- (a) Predict the appearance at room temperature of

(i) radium [1]

(ii) astatine. [2]

- (b) Predict the reactivity of astatine compared to that of iodine. Justify your answer. [3]

- (c) Write an equation for the reaction of astatine with hydrogen. State symbols are not required. [1]

- (d) Write an equation for the reaction between radium and chlorine. State symbols are not required. [1]

- (e) The product of the reaction between radium and water, and the pH of the resulting solution, are most likely to be:

A radium oxide and 1

B radium oxide and 14

C radium hydroxide and 1

D radium hydroxide and 12

[1]

(Total for Question 11 = 9 marks)

- 12** This question is about some compounds of the elements in Group 2 of the Periodic Table.

- (a) Water was slowly added to a solid lump of calcium oxide. The lump got very hot and broke apart to form another white solid.

Excess water was added to this white solid and the mixture was filtered to produce a colourless solution. The solution turned milky when carbon dioxide was bubbled through it.

- (i) State why the lump of calcium oxide got very hot when water was added. [1]

- (ii) Name the colourless solution formed when an excess of water was added to the white solid, and predict its pH. [2]

- (iii) Write an equation for the reaction between this colourless solution and carbon dioxide. Include state symbols. [2]

- (b) Calcium oxide can be formed in several ways.

One way is to heat calcium in oxygen. Another way is to heat calcium nitrate.

- (i) Write an equation for each method of forming calcium oxide. State symbols are not required. [2]

- (ii) Explain the trend in decomposition temperatures of the Group 2 nitrates. [4]

(Total for Question 11 = 11 marks)