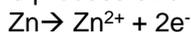


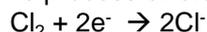
8A. Redox

oxidation is the process **of electron loss**:



It involves an increase in oxidation number

reduction is the process **of electron gain**:



It involves a decrease in oxidation number

Rules for assigning oxidation numbers

1. All uncombined elements have an oxidation number of zero
2. The oxidation numbers of the elements in a compound add up to zero
3. The oxidation number of a monoatomic ion is equal to the ionic charge
4. In a polyatomic ion (CO_3^{2-}) the sum of the individual oxidation numbers of the elements adds up to the charge on the ion
5. Several elements have invariable oxidation numbers in their common compounds.

eg. Zn, Cl_2 , O_2 , Ar all have oxidation numbers of zero

In NaCl Na = +1 Cl = -1
Sum = +1 -1 = 0

e.g. Zn^{2+} = +2 Cl⁻ = -1

e.g. in CO_3^{2-} C = +4 and O = -2
sum = +4 + (3 x -2) = -2

Group 1 metals = +1

Group 2 metals = +2

Al = +3

H = +1 (except in metal hydrides where it is -1 eg NaH)

F = -1

Cl, Br, I = -1 except in compounds with oxygen and fluorine

O = -2 except in peroxides (H_2O_2) where it is -1 and in compounds with fluorine.

We use these rules to identify the oxidation numbers of elements that have variable oxidation numbers.

What is the oxidation number of Fe in FeCl_3

Using rule 5, Cl has an O.N. of -1

Using rule 2, the O.N. of the elements must add up to 0

Fe must have an O.N. of +3

in order to cancel out 3 x -1 = -3 of the Cl's

Note the oxidation number of Cl in CaCl_2 = -1 and not -2 because there are two Cl's
Always work out the oxidation for one atom of the element

Naming using oxidation number

If an element can have various oxidation numbers then the oxidation number of that element in a compound can be given by writing the number in roman numerals

FeCl_2 : Iron (II) chloride

FeCl_3 : Iron (III) chloride

MnO_2 : Manganese (IV) Oxide

In IUPAC convention the various forms of sulfur, nitrogen and chlorine compounds where oxygen is combined are all called sulfates, nitrates and chlorates with relevant oxidation number given in roman numerals. If asked to name these compounds remember to add the oxidation number.

NaClO : sodium chlorate(I)

NaClO_3 : sodium chlorate(V)

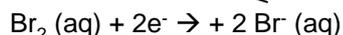
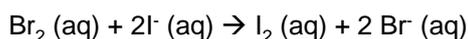
K_2SO_4 : potassium sulfate(VI)

K_2SO_3 : potassium sulfate(IV)

NaNO_3 : sodium nitrate (V)

NaNO_2 : sodium nitrate (III)

Redox equations and half equations

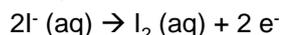


Br has reduced as it has gained electrons

A reduction half equation only shows the parts of a chemical equation involved in reduction
The electrons are on the left

The oxidising agent is Bromine water. It is an **electron acceptor**

An oxidising agent (or oxidant) is the species that causes another element to oxidise. It is itself reduced in the reaction



I has oxidised as it has lost electrons

An oxidation half equation only shows the parts of a chemical equation involved in oxidation
The electrons are on the right

The reducing agent is the iodide ion. It is an **electron donor**

A reducing agent (or reductant) is the species that causes another element reduce. It is itself oxidised in the reaction.

reducing agents are electron donors

oxidising agents are electron acceptors

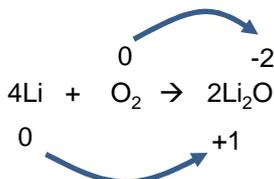
When naming oxidising and reducing agents always refer to full name of substance and not just name of element

Redox Reactions

metals generally form ions by losing electrons with an increase in oxidation number to form positive ions:
 $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

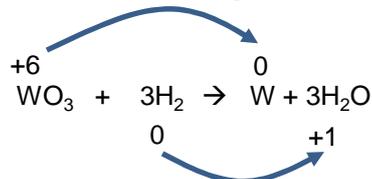
non-metals generally react by gaining electrons with a decrease in oxidation number to form negative ions
 $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$

Oxygen is reducing because its oxidation number is decreasing from 0 to -2



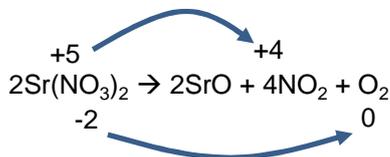
Lithium is oxidising because its oxidation number is increasing from 0 to +1

Tungsten is reducing because its oxidation number is decreasing from +6 to 0



Hydrogen is oxidising because its oxidation number is increasing from 0 to +1

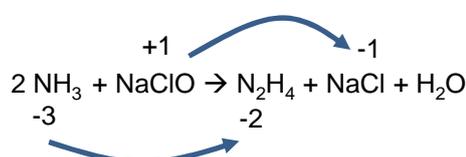
Nitrogen is reducing because its oxidation number is decreasing from +5 to +4



Oxygen is oxidising because its oxidation number is increasing from -2 to 0

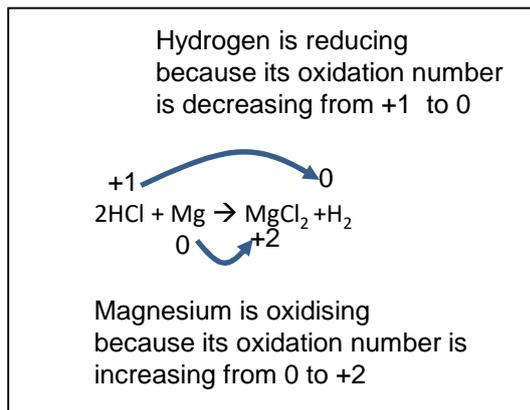
Note that not all the oxygen atoms are changing oxidation number in this reaction

Chlorine is reducing because its oxidation number is decreasing from +1 to -1

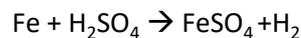


Nitrogen is oxidising because its oxidation number is increasing from -3 to -2

Redox Reactions of Metals and acid



Be able to write equations for reactions of metals with hydrochloric acid and sulphuric acid



Observations: These reaction will effervesce because H_2 gas is evolved and the metal will dissolve

Disproportionation

Disproportionation is the name for a reaction where an element in a single species simultaneously oxidises and reduces.



Chlorine is both simultaneously reducing and oxidising changing its oxidation number from 0 to -1 and 0 to +1

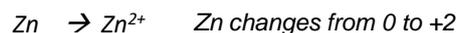


Copper(I) ions (+1) when reacting with sulphuric acid will disproportionate to Cu^{2+} (+2) and Cu (0) metal

Balancing Redox equations

Writing half equations

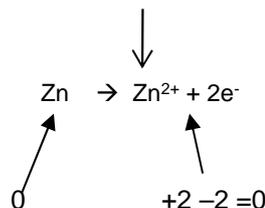
1. Work out oxidation numbers for element being oxidised/ reduced



2. Add electrons equal to the change in oxidation number

For reduction add e's to reactants

For oxidation add e's to products



3. check to see that the sum of the charges on the reactant side equals the sum of the charges on the product side

More complex Half equations

If the substance that is being oxidised or reduced contains a varying amount of O (eg $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$) then the half equations are balanced by adding H^+ , OH^- ions and H_2O .

In acidic conditions use H^+ and H_2O

Example: Write the half equation for the change $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$

1. Balance the change in O.N. with electrons

*Mn changes from +7 to +2
Add 5 electrons to reactants*



2. Add H_2O in products to balance O's in MnO_4^-



3. Add H^+ in reactants to balance H's in H_2O



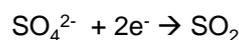
4. check to see that the sum of the charges on the reactant side equals the sum of the charges on the product side



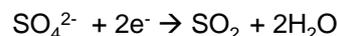
Example: Write the half equation for the change $\text{SO}_4^{2-} \rightarrow \text{SO}_2$

1. Balance the change in O.N. with electrons

*S changes from +6 to +4
Add 2 electrons to reactants*



2. Add H_2O in products to balance O's in SO_4^{2-}



3. Add H^+ in reactants to balance H's in H_2O



4. check to see that the sum of the charges on the reactant side equals the sum of the charges on the product side

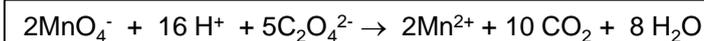
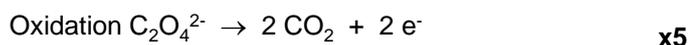
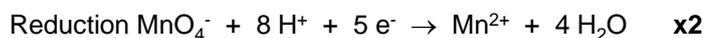


Combining half equations

To make a full redox equation combine a reduction half equation with a oxidation half equation

To combine two half equations there must be equal numbers of electrons in the two half equations so that the electrons cancel out

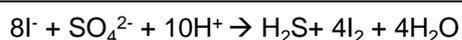
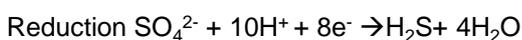
Example 1



Multiply the half equations to get equal electrons

Add half equations together and cancel electrons

Example 2



Multiply the half equations to get equal electrons

Add half equations together and cancel electrons

8B: Group 1+2

Atomic radius

Atomic **radius increases** down the groups.
As one goes down the groups, the atoms have **more shells of electrons** making the atom bigger.

Melting points

Down the group the melting **points decrease**. The **metallic bonding** weakens as the **atomic size increases**. The distance between the positive ions and delocalized electrons increases. Therefore the electrostatic attractive forces between the **positive ions** and the **delocalized electrons** weaken.

1st ionisation energy

The outermost electrons are held more weakly because they are **successively further from the nucleus** in additional shells.

In addition, the outer shell electrons become **more shielded** from the attraction of the nucleus by the repulsive force of inner shell electrons

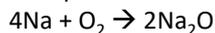
Group 2 reactions

Reactivity of group 1 and 2 metals **increases** down the group

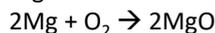
The reactivity increases down the group as the atomic radii increase there is more shielding. The nuclear attraction decreases and it is easier to remove (outer) electrons and so cations form more easily

Reactions with oxygen.

Group 1 and 2 metals will burn in oxygen.



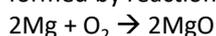
Mg burns with a bright white flame.



The oxides of group 1 and 2 are usually white solids with high melting points due to their ionic bonding.

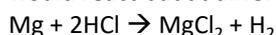
Mg will also react slowly with oxygen without a flame.

Mg ribbon will often have a thin layer of magnesium oxide on it formed by reaction with oxygen.



This needs to be cleaned off by emery paper before doing reactions with Mg ribbon.

If testing for reaction rates with Mg and acid, an un-cleaned Mg ribbon would give a false result because both the Mg and MgO would react but at different rates.



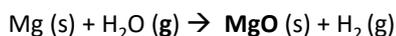
Reactions with chlorine

The group 1 and 2 metals will react with chlorine

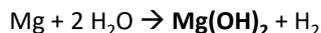


Reactions with water.

Magnesium burns in **steam** to produce **magnesium oxide** and hydrogen. The Mg would burn with a bright white flame.

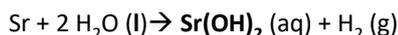
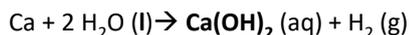


Mg will also react with warm water, giving a different **magnesium hydroxide** product.

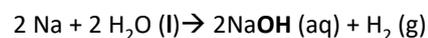


This is a much slower reaction than the reaction with steam and there is no flame.

The other group 2 metals will react with **cold water** with increasing vigour down the group to form **hydroxides**.



Group 1 metals also react with **cold water** with increasing vigour down the group to form **hydroxides**.



The hydroxides produced make the water alkaline

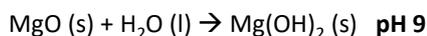
One would observe:

- fizzing, (more vigorous down group)
- the metal dissolving, (faster down group)
- the solution heating up (more down group)
- and with calcium a white precipitate appearing (less precipitate forms down group)

Reactions of the Oxides of Group 1 & 2 elements with water

Group 1 and 2 ionic oxides react with water to form hydroxides

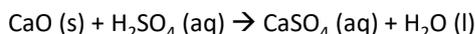
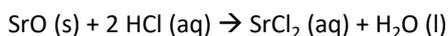
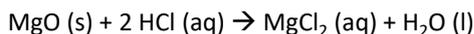
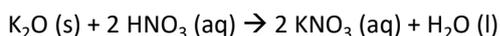
The ionic oxides are basic as the oxide ions accept protons to become hydroxide ions in this reaction (acting as a bronsted lowry base)



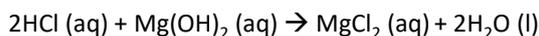
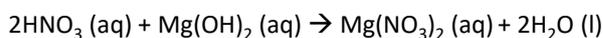
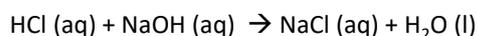
$\text{Mg}(\text{OH})_2$ is only slightly soluble in water so fewer free OH^- ions are produced and so lower pH



Reactions of the Oxides of Group 1& 2 with Acids



Reactions of the hydroxides of Group 1& 2 with Acids



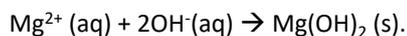
Solubility of Group 2 hydroxides

Group II hydroxides become **more soluble** down the group.

All Group II hydroxides when not soluble appear as white precipitates.

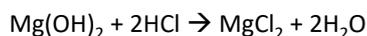
Magnesium hydroxide is classed as insoluble in water.

Simplest Ionic Equation for formation of $\text{Mg}(\text{OH})_2 (\text{s})$



A suspension of magnesium hydroxide in water will appear slightly alkaline (pH 9) so some hydroxide ions must therefore have been produced by a very slight dissolving.

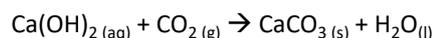
Magnesium hydroxide is used in medicine (in suspension as milk of magnesia) to neutralise excess acid in the stomach and to treat constipation.



It is safe to use because it so weakly alkaline. It is preferable to using calcium carbonate because it will not produce carbon dioxide gas.

Calcium hydroxide is reasonably soluble in water. It is used in agriculture to neutralise acidic soils.

An aqueous solution of calcium hydroxide is called lime water and can be used a test for carbon dioxide. The limewater turns cloudy as white calcium carbonate is produced.



Barium hydroxide would easily dissolve in water. The hydroxide ions present would make the solution strongly alkaline.

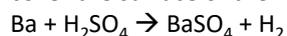


Solubility of Group 2 Sulfates

Group II sulfates become **less soluble** down the group.

BaSO_4 is the least soluble.

If barium metal is reacted with sulfuric acid it will only react slowly as the insoluble barium sulfate produced will cover the surface of the metal and act as a barrier to further attack.



The same effect will happen to a lesser extent with metals going up the group as the solubility increases.

The same effect does not happen with other acids like hydrochloric or nitric as they form soluble group 2 salts.

Thermal decomposition of Group 1 & 2 carbonates

Group 2 carbonates decompose on heating to produce group 2 oxides and carbon dioxide gas.



Group 2 carbonates are more thermally stable as you go down the group. As the cations get bigger they have less of a polarising effect and distort the carbonate ion less. The C-O bond is weakened less so it less easily breaks down

Group 1 carbonates do not decompose with the exception of Lithium. As they only have +1 charges they don't have a big enough charge density to polarise the carbonate ion. Lithium is the exception because its ion is small enough to have a polarising effect

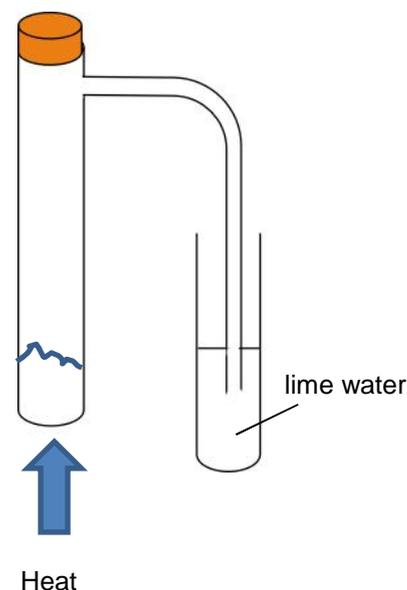


There are a number of experiments that can be done to investigate the ease of decomposition.

One is to heat a known mass of carbonate in a side arm boiling tube and pass the gas produced through lime water. Time for the first permanent cloudiness to appear in the limewater. Repeat for different carbonates using the same moles of carbonate/same volume of limewater/same Bunsen flame and height of tube above flame.

Thermal decomposition is defined as the use of heat to break down a reactant into more than one product

The ease of thermal decomposition **decreases** down the group



Thermal decomposition of Group 1 & 2 Nitrates

Group 2 nitrates decompose on heating to produce group 2 oxides, oxygen and nitrogen dioxide gas.

You would observe brown gas evolving (NO_2) and the white nitrate solid is seen to melt to a colourless solution and then re-solidify



The ease of thermal decomposition **decreases** down the group

The explanation for change in thermal stability is the same as for carbonates. Magnesium nitrate decomposes the easiest because the Mg^{2+} ion is smallest and has the greater charge density. It causes more polarisation of the nitrate anion and weakens the N-O bond

Group 1 nitrate do not decompose in the same way as group 2 with the exception of Lithium nitrate. They decompose to give a Nitrate (III) salt and oxygen.



Sodium Nitrate(V) Sodium Nitrate(III)

Lithium nitrate decomposes in the same way as group 2 nitrates



Flame tests

Method

Use a **nichrome wire** (nichrome is an unreactive metal and will not give out any flame colour)
Clean the wire by dipping in **concentrated hydrochloric acid** and then heating in Bunsen flame
If the sample is not powdered then grind it up.
Dip wire in solid and put in Bunsen flame and observe flame

Lithium : Scarlet red

Sodium : Yellow

Potassium : lilac

Rubidium : red

Caesium: blue

Magnesium: no flame colour (energy emitted of a wavelength outside visible spectrum)

Calcium: brick red

Strontium: red

Barium: apple green

Explanation for occurrence of flame

In a flame test the heat causes the electron to move to a higher energy level.

The electron is unstable at the higher energy level and so drops back down. As it drops **back down from the higher to a lower energy level**, energy is emitted in the form of visible light energy with the wavelength of the observed light

Testing for Negative ions (anions)

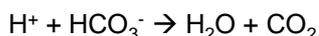
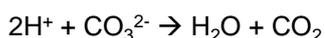
Testing for Presence of a carbonate CO_3^{2-} and hydrogencarbonates HCO_3^-

Add any dilute acid and observe effervescence.

Bubble gas through limewater to test for CO_2 – will turn limewater cloudy

Fizzing due to CO_2 would be observed if a carbonate or a

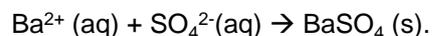
hydrogencarbonate was present



Testing for Presence of a sulfate

Acidified BaCl_2 solution is used as a reagent to test for sulfate ions

If **Barium Chloride** is added to a solution that contains sulfate ions a **white precipitate** forms



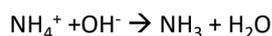
Other anions should give a negative result which is no precipitate forming

The acid is needed to react with carbonate impurities that are often found in salts which would form a white Barium carbonate precipitate and so give a false result

Sulfuric acid cannot be used to acidify the mixture because it contains sulfate ions which would form a precipitate

Testing for positive ions (cations)

Test for ammonium ion NH_4^+ , by reaction with warm $\text{NaOH}(\text{aq})$ forming NH_3



Ammonia gas can be identified by its pungent smell or by turning red litmus paper blue

Titration

The method for carrying out the titration

- rinse equipment** (burette with acid, pipette with alkali, conical flask with distilled water)
- pipette 25 cm³ of alkali into conical flask**
- touch surface of alkali with pipette** (to ensure correct amount is added)
- adds acid solution from burette**
- make sure the jet space** in the burette **is filled** with acid
- add a few drops of indicator** and refer to colour change at end point
- phenolphthalein [pink (alkali) to colourless (acid): end point pink colour just disappears] [use if NaOH is used]
- methyl orange [yellow (alkali) to red (acid): end point orange] [use if HCl is used]
- use a white tile underneath the flask to help observe the colour change
- add acid to alkali whilst **swirling the mixture** and **add acid dropwise at end point**
- note burette reading** before and after addition of acid
- repeats titration** until **at least 2 concordant results** are obtained- two readings within 0.1 of each other

There will be a small amount of the liquid left in the pipette when it has been emptied. Do not force this out. The pipette is calibrated to allow for it.

If the jet space in the burette is not filled properly prior to commencing the titration it will lead to errors if it then fills during the titration, leading to a larger than expected titre reading.

Working out average titre results

Only make an average of the concordant titre results

Recording results

- Results should be clearly recorded in a table
- Result should be recorded in full (i.e. both initial and final readings)
- Record titre volumes to 2dp (0.05 cm³)**

Testing batches

In quality control it will be necessary to do titrations/testing on several samples as the amount/concentration of the chemical being tested may vary between samples.

Safety precautions

Acids and alkalis are corrosive (at low concentrations acids are irritants)

Wear eye protection and gloves

If spilled immediately wash affected parts after spillage

If substance is unknown treat it as potentially toxic and wear gloves.

A conical flask is used in preference to a beaker because it is easier to swirl the mixture in a conical flask without spilling the contents.

Distilled water can be added to the conical flask during a titration to wash the sides of the flask so that all the acid on the side is washed into the reaction mixture to react with the alkali. It does not affect the titration reading as water does not react with the reagents or change the number of moles of acid added.

Only distilled water should be used to wash out conical flasks between titrations because it does not add and extra moles of reagents

If 2 or 3 values are within 0.10cm³ and therefore concordant or close then we can say results are accurate and reproducible and the titration technique is good/ consistent

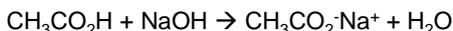
Titrating mixtures

If titrating a mixture to work out the concentration of an active ingredient it is necessary to consider if the mixture contains other substances that have acid base properties.

If they don't have acid base properties we can titrate with confidence.

More complicated titration calculations- taking samples

Example 26: A 25.0cm³ sample of vinegar was diluted in a 250cm³ volumetric flask. This was then put in a burette and 23.10cm³ of the diluted vinegar neutralised 25.0 cm³ of 0.100 M NaOH. What is the concentration of the vinegar in gdm⁻³ ?



Step 1: work out amount, in mol, of sodium hydroxide
 amount = conc x vol
 = 0.10 x 0.025
 = 0.00250 mol

Step 2: use balanced equation to give moles of CH₃CO₂H
 1 moles NaOH : 1 moles CH₃CO₂H
 So 0.00250 NaOH : 0.00250 moles CH₃CO₂H

Step 3 work out concentration of diluted CH₃CO₂H in 23.1 (and 250 cm³) in mol dm⁻³

conc = amount/Volume
 = 0.00250 / 0.0231
 = 0.108 mol dm⁻³

Step 4 work out concentration of original concentrated CH₃CO₂H in 25cm³ in mol dm⁻³

conc = 0.108 x 10 = 1.08 mol dm⁻³

Step 5 work out concentration of CH₃CO₂H in original concentrated 25 cm³ in gdm⁻³

conc in gdm⁻³ = conc in mol dm⁻³ x Mr
 = 1.08 x 60 = 64.8 g dm⁻³

Example 27. An unknown metal carbonate reacts with hydrochloric acid according to the following equation.
 $\text{M}_2\text{CO}_3(\text{aq}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{MCl}(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
 A 3.96 g sample of M₂CO₃ was dissolved in distilled water to make 250 cm³ of solution. A 25.0 cm³ portion of this solution required 32.8 cm³ of 0.175 mol dm⁻³ hydrochloric acid for complete reaction. Calculate the Mr of M₂CO₃ and identify the metal M

1. Calculate the number of moles of HCl used

amount = conc x vol
 = 0.175 x 0.0328
 = 0.00574 mol

2. Work out number of moles of M₂CO₃ in 25.0 cm³ put in conical flask

use balanced equation to give moles of M₂CO₃
 2 mol HCl : 1 mol M₂CO₃
 So 0.00574 NaOH : 0.00287 moles M₂CO₃

3. Calculate the number of moles M₂CO₃ acid in original 250 cm³ of solution

Moles in 250cm³ = 0.00287 x 10
 = 0.0287

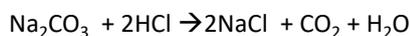
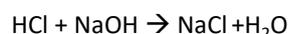
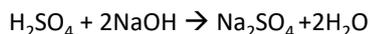
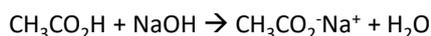
4. work out the Mr of M₂CO₃

Mr = mass / amount
 = 3.96 / 0.0287 = 138.0

5. Work out Ar of M = $\frac{138-12-16 \times 3}{2}$

Ar of M = 39 M = potassium

Common Titration Equations



Example 28

950 mg of impure calcium carbonate tablet was crushed. 50.0 cm³ of 1.00 mol dm⁻³ hydrochloric acid, an excess, was then added. After the tablet had reacted, the mixture was transferred to a volumetric flask. The volume was made up to exactly 100 cm³ with distilled water. 10.0 cm³ of this solution was titrated with 11.1cm³ of 0.300 mol dm⁻³ sodium hydroxide solution.

What is the percentage of CaCO₃ by mass in the tablet?

1. Calculate the number of moles of sodium hydroxide used

amount = conc x vol
 = 0.30 x 0.0111
 = 0.00333 mol

2. Work out number of moles of hydrochloric acid left in 10.0 cm³

use balanced equation to give moles of HCl
 1 mol NaOH : 1 mol HCl
 So 0.00333 NaOH : 0.00333 moles HCl

3. Calculate the number of moles of hydrochloric acid left in 100 cm³ of solution

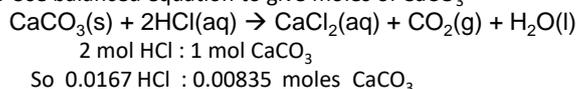
Moles in 100cm³ = 0.00333 x 10
 = 0.0333

4. Calculate the number of moles of HCl that reacted with the indigestion tablet.

In original HCl 50.0 cm³ of 1.00 mol dm⁻³ there is 0.05 moles

moles of HCl that reacted with the indigestion tablet. = 0.05 - 0.0333 = 0.0167

5 Use balanced equation to give moles of CaCO₃



6. work out the mass of CaCO₃ in original tablet

mass = amount x Mr
 = 0.00835 x 100 = 0.835 g

percentage of CaCO₃ by mass in the tablet = $\frac{0.835}{0.950} \times 100 = 87.9\%$

Uncertainty

Readings and Measurements

Readings

the values found from a single judgement when using a piece of equipment

Measurements

the values taken as the difference between the judgements of two values (e.g. using a burette in a titration)

The uncertainty of a reading (one judgement) is at least ± 0.5 of the smallest scale reading.
The uncertainty of a measurement (two judgements) is at least ± 1 of the smallest scale reading.

Calculating Apparatus Uncertainties

Each type of apparatus has a sensitivity uncertainty

- balance ± 0.001 g
- volumetric flask ± 0.1 cm³
- 25 cm³ pipette ± 0.1 cm³
- burette ± 0.05 cm³

Calculate the percentage error for each piece of equipment used by

$$\% \text{ uncertainty} = \pm \frac{\text{uncertainty}}{\text{Measurement made on apparatus}} \times 100$$

e.g. for pipette

$$\% \text{ uncertainty} = 0.05 / 25 \times 100$$

To calculate the maximum percentage apparatus uncertainty in the final result add all the individual equipment uncertainties together.

To decrease the apparatus uncertainties you can either decrease the sensitivity uncertainty by using apparatus with a greater resolution (finer scale divisions) or you can increase the size of the measurement made.

Uncertainty of a measurement using a burette.

If the burette used in the titration had an uncertainty for each reading of ± 0.05 cm³ then during a titration two readings would be taken so the uncertainty on the titre volume would be ± 0.10 cm³.

Reducing uncertainties in a titration

Replacing measuring cylinders with pipettes or burettes which have lower apparatus uncertainty will lower the error

To reduce the uncertainty in a burette reading it is necessary to make the titre a larger volume. This could be done by: increasing the volume and concentration of the substance in the conical flask or by decreasing the concentration of the substance in the burette.

If looking at a series of measurements in an investigation the experiments with the smallest readings will have the highest experimental uncertainties.

Reducing uncertainties in measuring mass

Using a more accurate balance or a larger mass will reduce the uncertainty in weighing a solid
Weighing sample before and after addition and then calculating difference will ensure a more accurate measurement of the mass added.

Calculating the percentage difference between the actual value and the calculated value

If we calculated an Mr of 203 and the real value is 214, then the calculation is as follows:

Calculate difference $214 - 203 = 11$

$$\% = 11 / 214 \times 100$$
$$= 5.41\%$$

If the %uncertainty due to the apparatus $<$ percentage difference between the actual value and the calculated value then there is a discrepancy in the result due to other errors.

If the %uncertainty due to the apparatus $>$ percentage difference between the actual value and the calculated value then there is no discrepancy and all errors in the results can be explained by the sensitivity of the equipment.

8C Halogens

Fluorine (F₂): very pale yellow gas. It is highly reactive
Chlorine : (Cl₂) greenish, reactive gas, poisonous in high concentrations
Bromine (Br₂) : red liquid, that gives off dense brown/orange poisonous fumes
Iodine (I₂) : shiny grey solid sublimes to purple gas.

Trend in melting point and boiling point

Increase down the group

As the molecules become larger they have more electrons and so have larger London forces between the molecules. As the intermolecular forces get larger more energy has to be put into break the forces. This increases the melting and boiling points

Trend in electronegativity

Electronegativity is the relative tendency of an atom in a molecule to attract electrons in a covalent bond to itself.

As one goes down the group the electronegativity of the elements decreases.

As one goes down the group the atomic radii increases due to the increasing number of shells. The nucleus is therefore less able to attract the bonding pair of electrons

The reactivity of the halogens decreases down the group as the atoms get bigger with more shielding so they less easily attract and accept electrons. They therefore form -1 ions less easily down the group

1. The oxidation reactions of halide ions by halogens.

A halogen that is a strong oxidising agent will displace a halogen that has a lower oxidising power from one of its compounds

The oxidising strength decreases down the group. Oxidising agents are electron acceptors.

Chlorine will displace both bromide and iodide ions; bromine will displace iodide ions

know these observations !

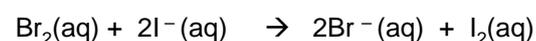
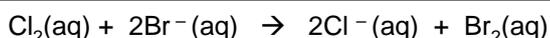
	Chlorine (aq)	Bromine (aq)	Iodine (aq)
potassium chloride (aq)	<i>Very pale green solution, no reaction</i>	<i>Yellow solution, no reaction</i>	<i>Brown solution, no reaction</i>
potassium bromide (aq)	Yellow solution, Cl has displaced Br	<i>Yellow solution, no reaction</i>	<i>Brown solution, no reaction</i>
potassium iodide (aq)	Brown solution, Cl has displaced I	Brown Solution, Br has displaced I	Brown Solution, no reaction

The colour of the solution in the test tube shows which free halogen is present in solution. Chlorine = very pale green solution (often colourless), Bromine = **yellow solution** Iodine = **brown solution** (sometimes black solid present)

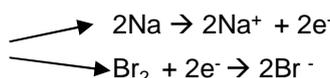
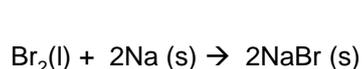
Observations if an organic solvent is added

	Chlorine (aq)	Bromine (aq)	Iodine (aq)
potassium chloride (aq)	colourless, no reaction	yellow, no reaction	purple, no reaction
potassium bromide (aq)	yellow, Cl has displaced Br	yellow, no reaction	purple, no reaction
potassium iodide (aq)	purple, Cl has displaced I	purple, Br has displaced I	purple, no reaction

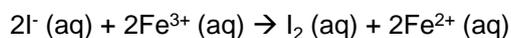
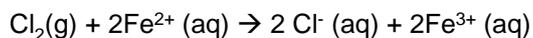
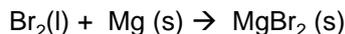
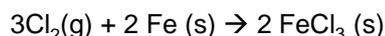
The colour of the organic solvent layer in the test tube shows which free halogen is present in solution. Chlorine = colourless Bromine = **yellow** Iodine = **purple**



The oxidation reactions of metals and metal ion by halogens.



In all reactions where halogens are reacting with metals, the metals are being oxidised



Chlorine and Bromine can oxidise Fe^{2+} to Fe^{3+} . Iodine is not strong enough oxidising agent to do this reaction. The reaction is reversed for Iodine

The disproportionation reactions of chlorine and chlorate(I).

Disproportionation is the name for a reaction where an element simultaneously oxidises and reduces.

Chlorine is both simultaneously reducing and oxidising changing its oxidation number from 0 to -1 and 0 to +1

Chlorine with water:



If some universal indicator is added to the solution it will first turn red due to the acidity of both reaction products. It will then turn colourless as the HClO bleaches the colour.

The pale greenish colour of these solutions is due to the Cl_2

Chlorine is used in water treatment to kill bacteria. It has been used to treat drinking water and the water in swimming pools. The benefits to health of water treatment by chlorine outweigh its toxic effects.

Reaction of halogens with cold dilute NaOH solution:

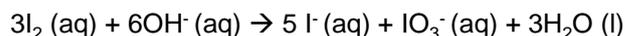
Cl_2 , Br_2 , and I_2 in aqueous solutions will react with cold sodium hydroxide. The colour of the halogen solution will fade to colourless



The mixture of NaCl and NaClO is used as Bleach and to disinfect/ kill bacteria

Reaction of halogens with hot dilute NaOH solution:

With hot alkali disproportionation also occurs but the halogen that is oxidised goes to a higher oxidation state.



In IUPAC convention the various forms of sulfur and chlorine compounds where oxygen is combined are all called sulfates and chlorates with relevant oxidation number given in roman numerals. If asked to name these compounds remember to add the oxidation number.

NaClO: sodium chlorate(I)

NaClO₃: sodium chlorate(V)

K₂SO₄ potassium sulfate(VI)

K₂SO₃ potassium sulfate(IV)

The reaction of halide salts with concentrated sulfuric acid.

The Halides show increasing power as reducing agents as one goes down the group. This can be clearly demonstrated in the various reactions of the solid halides with concentrated sulfuric acid.

Know the equations and observations of these reactions very well.

Explanation of differing reducing power of halides

A reducing agent donates electrons.

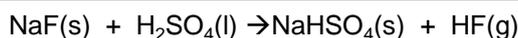
The reducing power of the halides increases down group 7

They have a greater tendency to donate electrons.

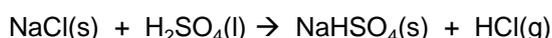
This is because as the ions get bigger it is easier for the outer electrons to be given away as the pull from the nucleus on them becomes smaller.

Fluoride and Chloride

The H_2SO_4 is not strong enough an oxidising reagent to oxidise the chloride and fluoride ions. No redox reactions occur. Only acid-base reactions occur.



Observations: White steamy fumes of HF are evolved.

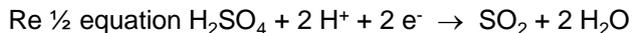
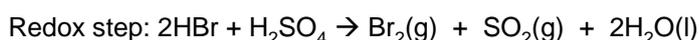


Observations: White steamy fumes of HCl are evolved.

These are acid-base reactions and not redox reactions. H_2SO_4 plays the role of an acid (proton donor).

Bromide

Br- ions are stronger reducing agents than **Cl-** and **F-** and after the initial acid-base reaction reduce the Sulfur in H_2SO_4 from +6 to +4 in SO_2



Observations: White steamy fumes of HBr are evolved.

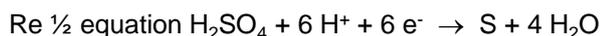
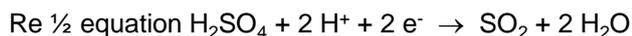
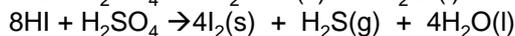
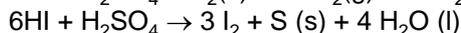
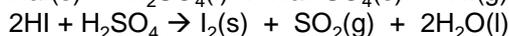
Red fumes of Bromine are also evolved and a colourless, acidic gas **SO_2**

Reduction product = sulfur dioxide

Note the H_2SO_4 plays the role of acid in the first step producing HBr and then acts as an oxidising agent in the second redox step.

Iodide

I- ions are the strongest halide reducing agents. They can reduce the Sulfur from +6 in H_2SO_4 to +4 in SO_2 , to 0 in S and -2 in H_2S .



Observations:

White **steamy fumes** of HI are evolved.

Black solid and **purple fumes** of Iodine are also evolved

A **colourless**, acidic **gas** SO_2

A **yellow solid** of Sulfur

H_2S (Hydrogen Sulfide), a **gas** with a **bad egg smell**,

Reduction products = sulfur dioxide, sulfur and hydrogen sulfide

Note the H_2SO_4 plays the role of acid in the first step producing HI and then acts as an oxidising agent in the three redox steps

Often in exam questions these redox reactions are worked out after first making the half-equations

The reactions of halide ions with silver nitrate.

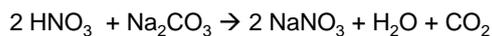
This reaction is used as a test to identify which halide ion is present. The test solution is made acidic with **nitric acid**, and then **Silver nitrate solution** is added dropwise.

Fluorides produce no precipitate
Chlorides produce a **white precipitate**
 $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$
Bromides produce a **cream precipitate**
 $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$
Iodides produce a **pale yellow precipitate**
 $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$

Effect Of ammonia on Silver Halides

The silver halide precipitates can be treated with ammonia solution to help differentiate between them if the colours look similar:

The role of nitric acid is to react with any carbonates present to prevent formation of the precipitate Ag_2CO_3 . This would mask the desired observations



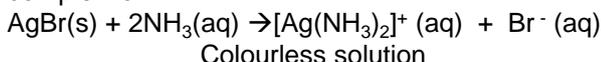
Effect Of Light on Silver Halides

The precipitates (except AgI) darken in sunlight forming silver. This reaction is used in photography to form the dark bits on photographic film

Silver chloride dissolves in **dilute ammonia** to form a complex ion



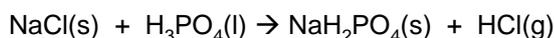
Silver bromide dissolves in **concentrated ammonia** to form a complex ion



Silver iodide does not react with ammonia – it is too insoluble.

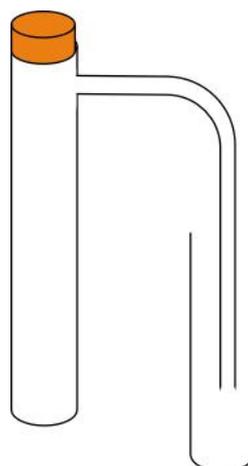
Producing hydrogen halides

Hydrogen halides are made by the reaction of solid sodium halide salts with phosphoric acid



Observations: White steamy fumes of the Hydrogen Halides are evolved.

The Steamy fumes of HCl are produced when the HCl meets the air because it dissolves in the moisture in the air



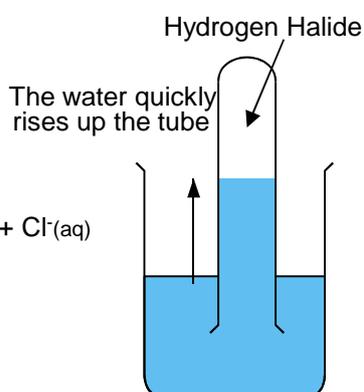
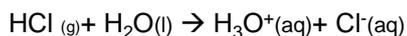
This is the apparatus used to make the hydrogen halide using phosphoric acid.

Notice the downward delivery which is used because the hydrogen halides are more dense than air

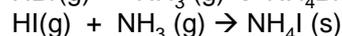
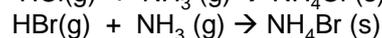
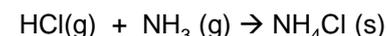
Phosphoric acid is not an oxidising agent and so does not oxidise HBr and HI. Phosphoric acid is more suitable for producing hydrogen halides than the ones with concentrated sulfuric acid to make HCl, HBr, and HI because there are no extra redox reactions taking place and no other products.

Solubility in water :

The hydrogen halides are all soluble in water. They dissolve to form acidic solutions.



All the hydrogen halides react readily with ammonia to give the **white smoke** of the ammonium halide



This can be used as a test for the presence of hydrogen halides