

Edexcel Chemistry IAL A-Level

Topic 8: Redox Chemistry and Groups 1, 2 and 7 Detailed Notes

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Topic 8A: Redox chemistry

Oxidation and Reduction

Oxidation is the loss of electrons. Reduction is the gain of electrons. This redox rule is remembered using the acronym **OILRIG** (oxidation is loss, reduction is gain).

Oxidation Number

Oxidation number gives the **oxidation state** of an element or ionic substance. Allocation of oxidation number to a species follows a number of rules:

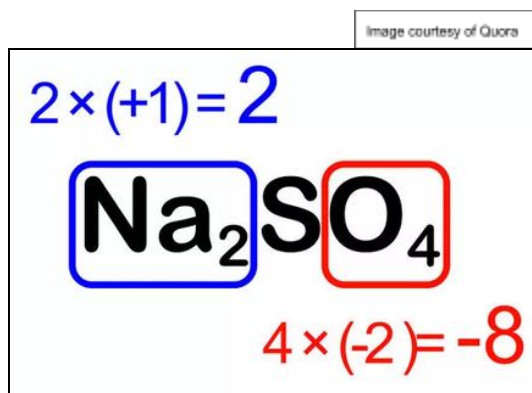
- The oxidation number of an **element is zero**.
- Oxidation numbers in a **neutral** compound add up to **zero**.
- Oxidation numbers in a charged compound add up to the **total charge**.
- **Hydrogen** has an oxidation number of **+1**.
- **Oxygen** has an oxidation number of **-2**.
- **Halogens** have an oxidation number of **-1**.
- **Group I** metals have an oxidation number of **+1**.
- **Group II** metals have an oxidation number of **+2**.

However, there are some **exceptions** to these rules:

- **Oxygen** has an oxidation number of **-1** in **peroxides**.
- **Hydrogen** has an oxidation number of **-1** in **metal hydrides**.

These rules can be used to work out the oxidation number of species or elements in a reaction.

Example:



This compound's total oxidation number is zero. Therefore, using the rules above, the oxidation number of sulfur can be found:





Known oxidation numbers: Na=+1, O=-2.

$$2 - 8 + x = 0$$

$$-6 + x = 0$$

$$x = 6$$

Example:

What is the oxidation state of oxygen in hydrogen peroxide, H_2O_2 ?

Hydrogen: +1, oxygen: -2 UNLESS in a peroxide

H_2O_2 is uncharged, therefore the sum of oxidations states must equal 0.

$$(2 \times +1) + (2 \times X) = 0$$

$$2 + 2X = 0$$

$$2X = -2$$

$$X = -1$$

Therefore, the oxidation state of oxygen in hydrogen peroxide is -1.

Roman numerals

Roman numerals can be used to give the oxidation number of an element that has a **variable oxidation state**, depending on the compound it's in.

Example:

Copper(II) sulphate - this tells you the oxidation number of copper is +2

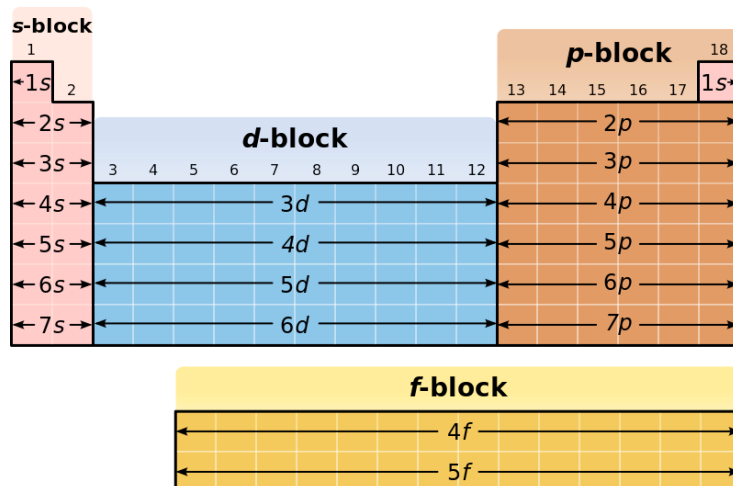
Iron(II) sulphate(VI) - this tells you the oxidation number of iron is +2 and the oxidation number of sulphur is +6

In the same way that oxidation numbers can be calculated from **formulas** of compounds, the formula of compounds may be deduced if the oxidation numbers of the elements (given by the **rules of oxidation states** and **roman numerals**) and the **overall charge** of the compound is known.

Oxidation state and the periodic table

Electrons are held in **orbitals**. Elements are arranged in the periodic table by **proton number** and also by their orbitals. These orbitals correspond with **blocks** on the Periodic Table. Each element in the block has **outer electrons in that orbital**.





Elements within the same **block** react in similar ways since their outermost electron is in the same type of **orbital**. This leads to some **patterns** in oxidation number in the periodic table:

- **s block elements** (groups 1 and 2 metals) generally **lose electrons**, so are **oxidised** and form species with **positive oxidation numbers**.
- **p block non-metals** generally **gain electrons**, so are **reduced** and form species with **negative oxidation states**.

Oxidising and Reducing Agents

An oxidising agent **accepts electrons** from the species that is being oxidised. Therefore it **gains electrons and is reduced**. This is seen as a **reduction** in oxidation number (gets more negative).

A reducing agent **donates electrons** to the species being reduced. Therefore it **loses electrons and is oxidised**. This is seen as an **increase** in oxidation number (gets more positive).

Redox Equations

Reactions in which oxidation and reduction occur **simultaneously** take place when one species loses electrons, which are then donated and gained by the other species. These reactions are known as **redox** reactions (**reduction - oxidation**). Being able to work out the oxidation number of atoms in a reaction enables you to work out if a redox reaction is a **disproportionation** reaction too.

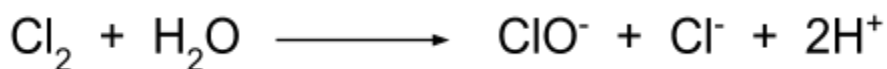




Disproportionation Reactions

In a **disproportionation reaction**, a species is both oxidised **and** reduced, seen as both an increase and a decrease in oxidation number for that species.

An example is seen when chlorine reacts with cold water to produce **chlorate(I) ions (ClO⁻)** and **chloride ions**. The oxidation state goes from zero (in Cl₂) to both **+1 (ClO⁻)** and **-1 (Cl⁻)**.



Half Equations

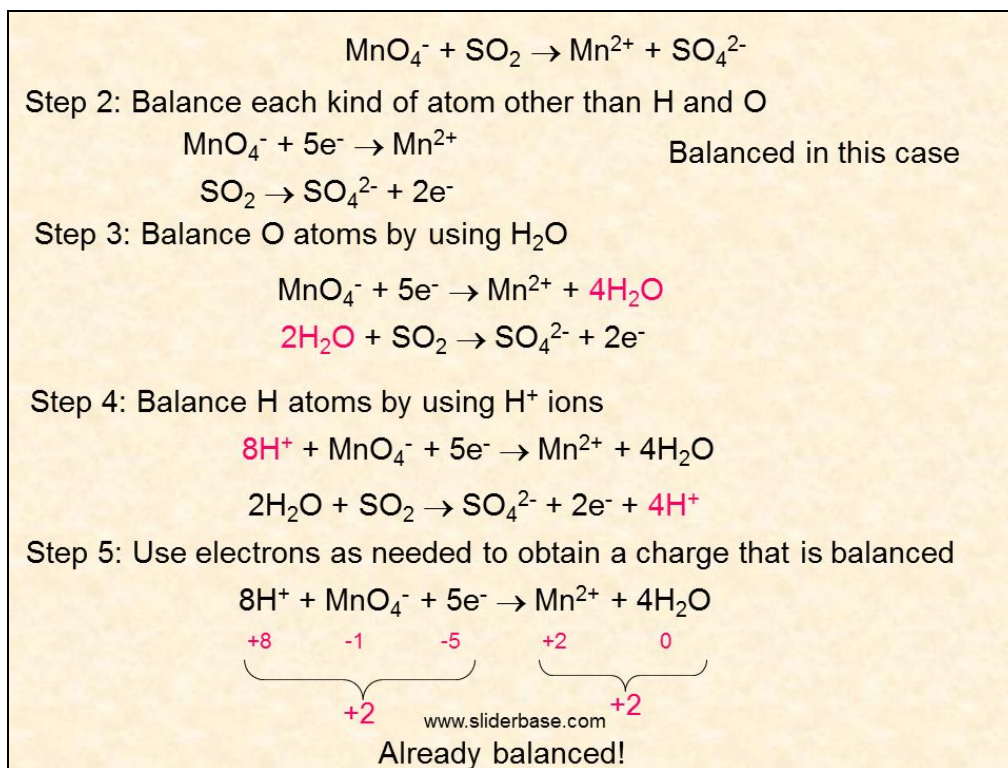
Half equations are used to show the **separate oxidation and reduction reactions** that occur in a redox reaction. They must be balanced in terms of the **species present and the charges** of the species on both sides of the equation.

In order to help write the equations, there is a useful method:

1. Balance all species, excluding **oxygen** and **hydrogen**.
2. Balance **oxygen** using **H₂O**.
3. Balance **hydrogen** using **H⁺ ions**.
4. Balance **charges** using **e⁻** (electrons).

Following this method ensures the half equations are **correctly balanced**.

Example:





Half equations can be **combined** in order to determine the **overall redox reaction**. In order to do this, the number of **electrons must be the same** for both half equations. This can be done by scaling up the number of moles. Once the half equations are combined, the electrons should be **cancelled out** on each side of the equation.

Example:

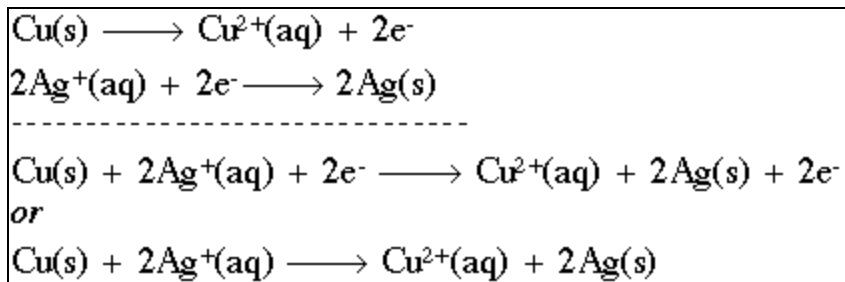


Image courtesy of Shodor

Topic 8B: The elements of Groups 1 and 2

Properties of the elements of Groups 1 and 2

When **Group 1** metals react, they lose an electron to **form 1+ ions**. This allows them to achieve a full outer shell.

When **Group 2** metals react, they lose two electrons to **form 2+ ions**. This allows them to achieve a full outer shell. The various **physical properties** of these elements follow trends down the group:

Atomic Radius

The atomic radius of Group 1 and Group 2 metals **increases** down the group due to additional electron shells.

Reactivity

Increased electron **shielding** and increased atomic radius down the group makes the outer electrons **easier to lose**. Therefore, reactivity of the Group 1 and Group 2 metals **increases** down the group.

Ionisation Energy





The first ionisation energy of Group 1 and Group 2 metals **decreases** down the group due to a greater atomic radius and increased amounts of shielding. This makes it easier for an electron to be removed.

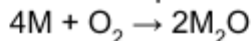
Reactions of Group 1 and Group 2 elements

Reactions with Oxygen

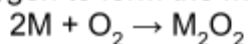
Group 1 metals react with oxygen to form **oxides**, and react in **excess oxygen** to also form a minor product of **metal peroxides**.

Group 1 metals, including potassium and the elements below potassium in the group, form **superoxide** compounds too. This is the major product for Rb, Cs and Fr.

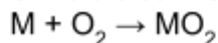
The general equation of Group 1 metals with oxygen is:



In excess oxygen to form the metal peroxide:

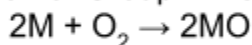


The most reactive metals can form superoxides:

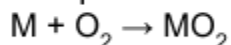


Group 2 metals also react with oxygen to form **oxides**. Once the reaction has been initiated it is **vigorous**. Only **strontium** and **barium** can react with excess oxygen and heat energy to form **peroxides**.

The general equation of Group 2 metals with oxygen is:



Strontium or barium may react with oxygen and form the peroxide:

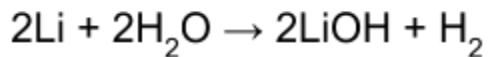


Reactions with Water

Group 1 alkali metals all react **vigorouslly** with cold water to form a **metal hydroxide** and **hydrogen gas**. As you move down the group, reactivity increases, so the reaction becomes more **violent**.

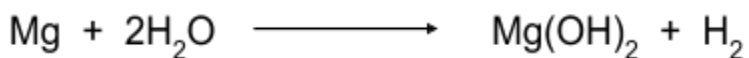
Example:





The Group 2 metals react with water in a redox reaction to produce a **metal hydroxide and hydrogen**. The metal hydroxide forms as an **alkaline solution**, hence why the Group 2 metals are known as the alkaline earth metals.

Example:



**Magnesium is oxidised from an oxidation state of 0 to +2.
(Oxidation is loss of e⁻)**

Magnesium reacts very slowly in this way with liquid water, however, the reaction can be much **faster with steam** as it provides the reaction with **extra energy**. When steam is used, the magnesium burns with a **bright white flame** to form hydrogen and magnesium oxide, a **white powder**.

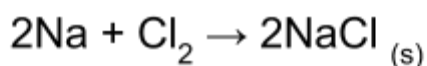
Example:



Reactions with Chlorine

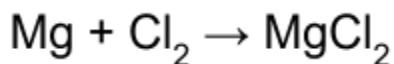
Group 1 metals all react with chlorine gas to form **metal chlorides**, which are all **white precipitates**. As with the Group 1 reactions with water, as you move down the group the reactions become **more vigorous** because the elements are **more reactive**.

Example:



Group 2 metals also react with chlorine to form **white precipitates** of **metal chlorides**, but the reaction **stoichiometry** is different.

Example:



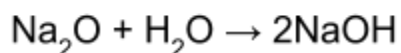


Reactions of Group 1 and Group 2 oxides and hydroxides

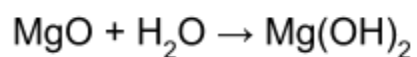
Reactions of Group 1 and 2 oxides with Water

Group 1 and Group 2 oxides react with water to form the **metal hydroxide** as the only product. This releases hydroxide ions, so the resulting solution is **alkaline**.

Example: Group 1



Example: Group 2

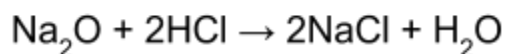


Reactions of Group 1 and 2 oxides and hydroxides with dilute acid

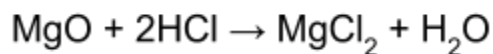
Group 1 and Group 2 oxides and hydroxides react with dilute acid to form **a salt** and **water**. This is a type of **neutralisation** reaction. The salt formed depends on the acid used:

- **Hydrochloric** acid forms **chloride** salts.
- **Sulfuric** acid forms **sulfate** salts.
- **Nitric** acid forms **nitrate** salts.

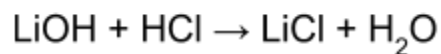
Example: Group 1 oxide



Example: Group 2 oxide

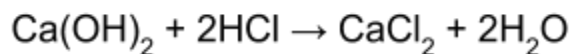


Example: Group 1 hydroxide





Example: Group 2 hydroxide



Solubility of Group 2 compounds

Solubility of Group 2 Hydroxides

The solubility of Group 2 hydroxides varies, allowing the compounds to have different uses. Solubility **increases down the group**, meaning magnesium hydroxide (Mg(OH)_2) is the least soluble and barium hydroxide (Ba(OH)_2) is the most soluble.

As a result, magnesium hydroxide is used in medicine as an **antacid** as it is alkaline and can neutralise acids. It is used in a similar way in agriculture to neutralise acidic soils.

Solubility of Group 2 Sulfates

Group 2 sulfates **decrease in solubility down the group**, meaning magnesium sulfate (MgSO_4) is the most soluble and barium sulfate (BaSO_4) is the least soluble.

The insolubility of **barium sulfate** means it is very useful in medicine as **barium meals**. Barium meals are a form of medical tracer that allow internal tissues and organs to be imaged. Barium sulfate is toxic if it enters the bloodstream, however because it is insoluble, it **cannot be absorbed** into the blood. Therefore, it is safe to use in this way.

Barium chloride is used as a **test for sulfate ions**. It reacts with sulfate ions to form barium sulfate, which is a white precipitate.

Example:



Thermal Decomposition

Thermal Decomposition of Group 2 metals

Group 2 carbonates and nitrates undergo **thermal decomposition** to produce solid metal oxides and a variety of gases. This is done by simply **heating** the substance in **aerobic** conditions (plenty of oxygen).





The Group 2 **carbonates** produce **carbon dioxide** along with the **metal oxide**, which forms as a white powder.

Example:



As you go down Group 2, **more heat** is required for this reaction as the ions increase in size and the carbonates increase in thermal stability.

The Group 2 **nitrates** produce **nitrogen dioxide and oxygen**, along with the white powdered **metal oxide**.

Example:

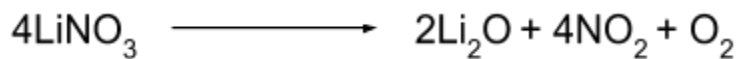


As you go down Group 2, **more heat** is required for this reaction as the ions increase in size and the nitrates increase in thermal stability.

Thermal Decomposition of Group 1 metals

Group 1 carbonates and nitrates also undergo **thermal decomposition** upon heating in **aerobic** conditions. In these reactions, **lithium** acts in a similar way to the Group 2 elements, with lithium nitrate producing lithium oxide, nitrogen dioxide and oxygen and lithium carbonate producing lithium oxide and carbon dioxide.

Example:



The rest of the Group 1 metals don't react in this same way as the reactions **rarely go to completion**. The remaining Group 1 nitrates produce a **metal nitrite and oxygen** whereas the remaining Group 1 carbonates simply **won't decompose** upon heating in a lab as they require **extremely high temperatures** to do so.

Example:





Explanation of the thermal stability trend

The elements of Group 1 and Group 2 form more **stable** carbonates and nitrates as you go down their groups, and so require more heat energy to undergo **thermal decomposition**. In Groups 1 and 2, as you go down the group, the ionic radius increases for the same overall charge. This means smaller ions have a **higher charge density**.

The smaller ions are able to **polarise** the negative carbonate and nitrate ions more and the more this negative ion is polarised, the less heat is required to separate the two ions. Therefore smaller ions form **less stable** carbonates and nitrates, and larger cations form more stable carbonates and nitrates.

Tests for Anions

Sulfate (SO_4^{2-})

Sulfate ions are tested for using **acidified BaCl_2** , which reacts to form a **white precipitate** of barium sulfate.

Example:



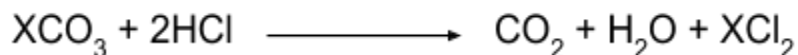
Hydroxide (OH^-)

Hydroxide ions indicate that the substance is alkaline. Therefore, they can be identified by using **damp red litmus paper** (which turns **blue**), or **universal indicator** (which turns **blue-purple**).

Carbonate (CO_3^{2-}) and Hydrogencarbonate (HCO_3^-)

When an acid such as HCl is added, a substance containing carbonate ions will **fizz** and **CO_2 gas** will be given off. This gas can be collected and bubbled through **limewater**, which will turn **cloudy**, identifying the gas as carbon dioxide.

Example:





Tests for Cations

Ammonium (NH_4^+)

If ammonium ions are present, adding NaOH and gently warming results in the formation of **ammonia gas**, which is **basic**. Therefore, the presence of ammonium ions can be tested by holding **damp red litmus paper** over a petri dish of the substance being tested. It will **turn blue** if ammonium ions are present.

Flame Tests

Group 1 and Group 2 metals can be identified within compounds, by the use of **flame tests**. Each metal has a unique flame **colour**.

Procedure:

1. Take a nichrome wire and clean it by placing it into a solution of concentrated hydrochloric acid and then into a blue bunsen burner flame.
2. Repeat this cleaning until there is no colour produced in the flame.
3. Dip the wire into the unknown metal compound and place it into the flame. Observe the flame colour produced.

The colours observed in the flame tests of Group 1 and Group 2 metal compounds:

Group 1	Colour
Lithium (Li^+)	Red
Sodium (Na^+)	Orange/Yellow
Potassium (K^+)	Lilac
Group 2	Colour
Magnesium (Mg^{2+})	No colour
Calcium (Ca^{2+})	Brick red
Strontium (Sr^{2+})	Crimson red
Barium (Ba^{2+})	Pale green

The formation of these colours in the flame test can be explained by **electron transitions**.

Electrons exist in orbitals and when energy (such as that supplied by a bunsen burner flame) is absorbed by the species, some **electrons** will be **promoted** to **orbitals** which have a **higher**





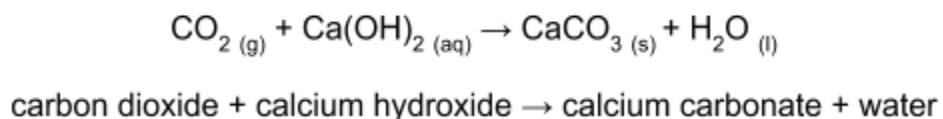
energy. The electrons will then drop back down to the original orbital they were in and during this process they **release energy**, some of which is in the form of **light**.

The colour produced depends on the **wavelength** of the light energy emitted. When some electrons drop back down to their original orbital, the energy emitted may not have a wavelength in the visible light part of the **electromagnetic spectrum**, which explains why not all atoms and ions produce a colour in the flame test.

Other chemical tests

Test for CO₂

If CO₂ gas is bubbled through **limewater** the solution will turn **cloudy**. This is because the carbon dioxide reacts with calcium hydroxide (limewater) to form **water and calcium carbonate** precipitate - which is white and therefore turns the water cloudy.



Test for O₂

The test for oxygen gas is very simple. Place a **glowing splint** (one that has just been extinguished) into a test tube containing the unknown gas. The splint will **relight** in oxygen.

Test for NO₂

Nitrogen dioxide is an **acidic gas**. Holding **blue litmus paper** in a test tube filled with this gas will cause it to **turn red**. This gas can also be recognised by its **reddish-brown colour**.

Acid-base Titrations

A titration is a practical method where a **standard solution** of known concentration is reacted with a solution of **unknown concentration**, in order to determine this property of the solution. There is a standard method to make up the standard solution, and carry out the titration.

Volumetric Solution - simple method

1. Weigh the sample bottle containing the solid on a (2 decimal place) balance.
2. Transfer the solid to a beaker and reweigh the sample bottle.
3. Record how much solid was added to the beaker.



- Add distilled water and stir with a glass rod until all the solid has dissolved.
- Transfer the mixture to a volumetric flask with washings.
- Use distilled water to make up the mixture to the 250 cm³ mark of the volumetric flask.
- Insert the stopper and invert the flask to mix.

Common errors in this method include **systematic errors** on the balance, **lost substance** in transfer processes and **overfilling** of the volumetric flask. These can be reduced using **washing** methods and by reading volumes from the **bottom of the meniscus**.

Titration - simple method

- Fill the burette with the standard solution of known concentration, ensuring the jet space in the burette is filled and doesn't contain air bubbles.
- Use a pipette filler and pipette to transfer 25 cm³ of the solution with unknown concentration into a conical flask.
- Add 2-3 drops of indicator.
- Record the initial burette reading.
- Titrate the contents of the conical flask by adding the solution from the burette until the indicator undergoes a definite, permanent colour change.
- Record the final burette reading and calculate the titre volume.
- Repeat until at least two concordant results are obtained (within 0.1cm³ of each other).

The equipment used in a titration all comes with their own **uncertainty values**. These values must be combined to find the overall uncertainty in the final answer.

The best way of reducing uncertainties in a titration is to **increase the titre volume needed** for the reaction. This can 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.

It is also important to carry out a **risk assessment** before undertaking any practical work. This should analyse **equipment, the lab environment** and the **chemicals** being used, and suggest methods for **reducing the risk** and what action should be taken if an accident occurs.

Indicators

There are two common indicators used in titrations:

Indicator	Colour in acidic solution	Colour in basic solution	pH range of colour change
Methyl orange	Red	Yellow	3-4
Phenolphthalein	Colourless	Pink	8-10





Solution concentrations

The concentration of a solution can be measured in mol dm^{-3} and g dm^{-3} which can be calculated using the following equations:

$$\text{Concentration (mol dm}^{-3}\text{)} =$$

$$\frac{\text{Number of moles (mol)}}{\text{Volume (dm}^3\text{)}}$$

$$\text{Concentration (g dm}^{-3}\text{)} =$$

$$\frac{\text{Mass (g)}}{\text{Volume (dm}^3\text{)}}$$

8C: Inorganic chemistry of Group 7 (limited to chlorine, bromine and iodine)

Trends in Halogen Properties

The Group 7 elements are **highly reactive non-metals**. In order to achieve a full outer shell, the halogens gain an electron and form a **1- ion**.

Atomic Radius

Atomic radius of Group 7 elements **increases down the group** due to additional electron shells.

Electronegativity

As you go down Group 7, **atomic radius and electron shielding increases**. This means electrons in the outer shells are less strongly attracted to the nucleus, and so are more easily removed. Therefore, electronegativity decreases down Group 7.

Melting and Boiling Point

The Group 7 elements are **simple covalent molecules**, held together with **van der waals** forces. The strength of these intermolecular forces increases as the relative atomic mass of the molecule increases. Therefore, the strength of the van der waals forces **increases down the group**. This means more energy is required to overcome them, resulting in higher melting and boiling points. This is why fluorine is a gas at room temperature, whereas iodine is a solid.

Reactivity

The Group 7 elements need to gain an electron in order to react. As atomic radius increases, this becomes harder as the positive attraction of the nucleus is weakened by additional **shielding**. Therefore, down Group 7 it is harder to attract an electron so **reactivity decreases**.





Physical properties

Halogen	Appearance at room temperature	Colour in aqueous solution	Colour in non-polar organic solution
Chlorine	Green gas	Pale green (almost colourless)	Pale green (almost colourless)
Bromine	Red-brown liquid	Orange/yellow	Red
Iodine	Grey-black solid	Brown	Violet

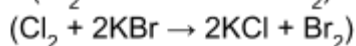
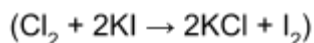
Oxidising Power of the Halogens

The halogens are good **oxidising agents** as they accept electrons from the species being oxidised and are reduced. This oxidising power **decreases down the group**, since their ability to attract electrons decreases due to shielding and a greater atomic radius.

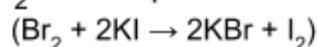
The relative oxidising strengths mean a halogen will **displace any halide beneath it** in the Periodic Table.

Example:

Cl_2 will displace Br^- and I^- ions.



Br_2 will displace I^- ions



I_2 won't displace any halide ions.

Halide ions

The negative ions of halogens are known as **halide ions**. Halide ions are **good reducing agents** as they donate electrons to the species being reduced and are themselves oxidised.

This reducing power **increases down the group**, as electrons are easier to lose from larger ions due to shielding and a larger atomic radius.





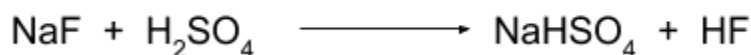
Reactions of Group 7 Elements and Ions

Redox reactions

The redox reactions between Group 1 and Group 2 halides and H_2SO_4 vary depending on the **reducing ability** of the halide:

Example:

1. Fluoride and Chloride ions



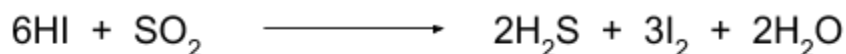
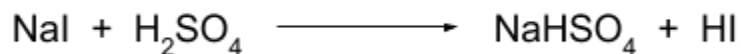
No further reactions take place since HF and HCl are not strong enough reducing agents to reduce H_2SO_4 . HF and HCl will both be observed as **misty fumes**.

2. Bromide ions



HBr will be observed as **misty fumes** from the first reaction. **Orange fumes** of Br_2 and **choking fumes** of SO_2 will be observed in the second reaction, where HBr reduces H_2SO_4 .

3. Iodide ions



HI will be observed as **misty fumes** from the first reaction. Similarly to above, HI then reduces H_2SO_4 to **solid iodine** and **choking fumes** of SO_2 . The HI will then further reduce the SO_2 to **toxic gas** H_2S (which smells of bad eggs).

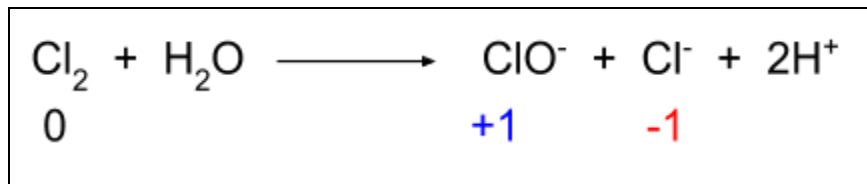


The **greater** the reducing power, the **further** the reaction will proceed as the halide is powerful enough to reduce more species. These reactions therefore represent the trend in reducing power in halide ions. Clearly, **reducing power increases** down Group 7.

Disproportionation Reactions

Chlorine reacts with cold water to produce **chlorate(I) ions (ClO⁻)** and **chloride ions** via a **disproportionation reaction**, as the chlorine is both oxidised and reduced. The oxidation state goes from zero to both **+1 and -1**.

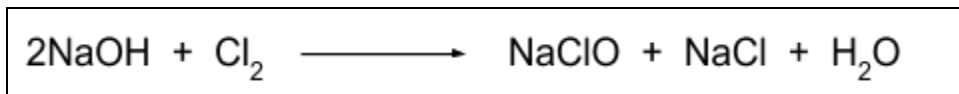
Example:



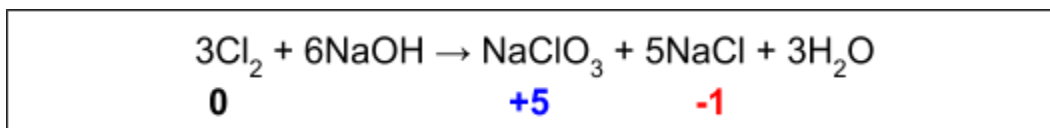
This reaction is used in **water treatment systems**, where chlorine is used in small quantities to kill bacteria. This poses some risks as chlorine can be **toxic**. However, the benefits of clean, treated water outweigh the risks.

A similar reaction of chlorine with cold dilute sodium hydroxide is used in bleach production. **Sodium chlorate(I)**, a key ingredient in the production of bleach, is produced via this disproportionation reaction.

Example:



If chlorine is reacted with **hot, concentrated alkali**, chlorine is disproportionated even further to form one species with an oxidation number of -1 and another with an oxidation number of +5.

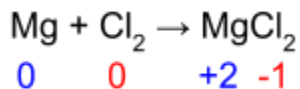


Oxidation reactions with Group 1 and Group 2 metals

Group 1 and Group 2 metals react with chlorine gas to form **metal chlorides**, which are all **white precipitates**. During these reactions **chlorine is reduced** and the **metal is oxidised**.

Example:





Precipitation Reactions of Halides

When combined with acidified silver nitrate, halide ions react to form different **coloured precipitates** depending on the ion present. The precipitates formed can be used to identify which halide is present in a solution. It may not always be clear to distinguish the colour of the precipitate so they can be tested further using **ammonia**.

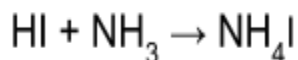
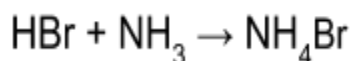
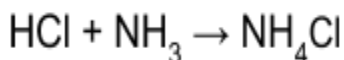
Example:

	Cl⁻	Br⁻	I⁻
+ AgNO₃	White precipitate (AgCl)	Cream precipitate (AgBr)	Yellow Precipitate (AgI)
+ dilute NH₃	Precipitate dissolves	No Change	No Change
+ conc. NH₃	Precipitate dissolves	Precipitate dissolves	No Change

Reactions of hydrogen halides

Hydrogen halides react with ammonia gas to form **ammonium salts**. The hydrogen halides (hydrogen chloride, hydrogen bromide and hydrogen iodide) are strong acids in solution and react with ammonia in an **acid-base reaction** to form a salt.

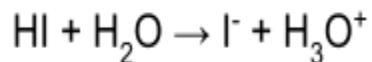
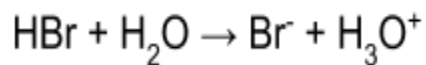
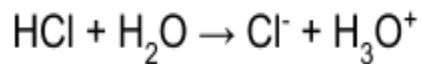
Example:



Hydrogen halides react with water to form **dilute acids**. In solution, these strong acids **dissociate** to release their halide ions and hydrogen ions. The hydrogen ions form a **hydroxonium ion** with water molecules in solution. The resulting solution is **acidic**.

Example:





Predictive chemistry

Using the **trends** in physical properties, chemical properties and reactions described for chlorine, bromine and iodine, **predictions** can be made for other halogens, including **fluorine** and **astatine**.

Example:

Use melting and boiling point trends in group 7 to predict the states of fluorine and astatine at room temperature.

Melting and boiling points increase as you go down the group since more intermolecular Van der Waals forces form with increasing Ar. Therefore, fluorine would be a gas at room temperature and astatine would be a solid at room temperature.

