Edexcel International AS Chemistry

Your notes

Group 7

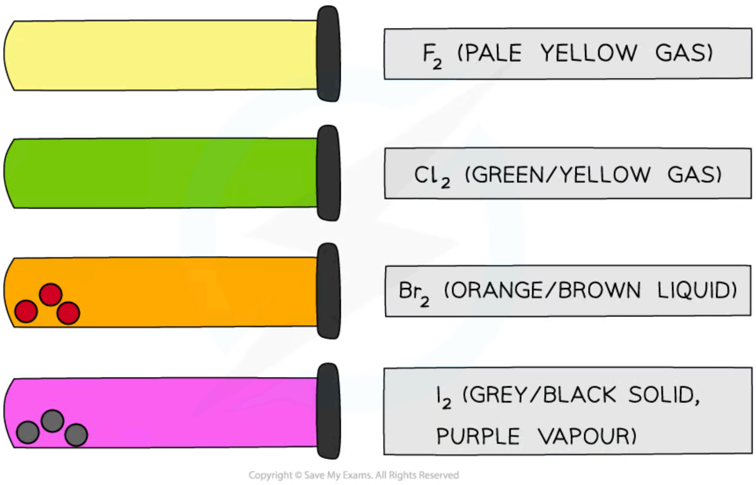
Contents

Trends of the Group 7 Elements

- The Group 7 elements are called **halogens**
- The halogens have uses in water purification and as bleaching agents (chlorine), as flame-retardants and fire extinguishers (bromine) and as antiseptic and disinfectant agents (iodine)

Colours

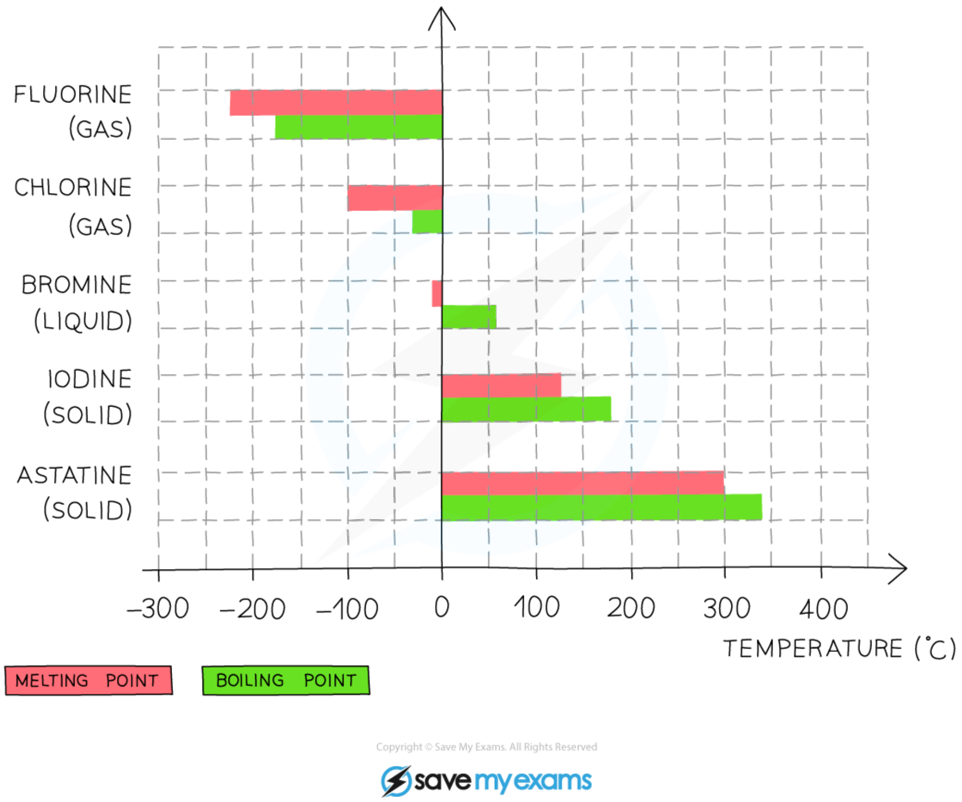
- All halogens have distinct **colours** which get **darker** going down the group



The colours of the Group 7 elements get darker going down the group

Volatility

- **Volatility** refers to how easily a substance can evaporate
  - A volatile substance will have a low boiling point



The melting and boiling points of the Group 7 elements increase going down the group which indicates that the elements become less volatile

- Going down the group, the **boiling point** of the elements increases which means that the **volatility** of the halogens decreases
  - This means that fluorine is the most volatile and iodine the least volatile

Trend in melting and boiling points

- Halogens are non-metals and are **diatomic molecules** at room temperature
  - This means that they exist as molecules which are made up of two similar atoms, such as F_2
- The halogens are **simple molecular structures** with **weak** London dispersion forces between the diatomic molecules caused by instantaneous dipole-induced dipole forces

Your notes

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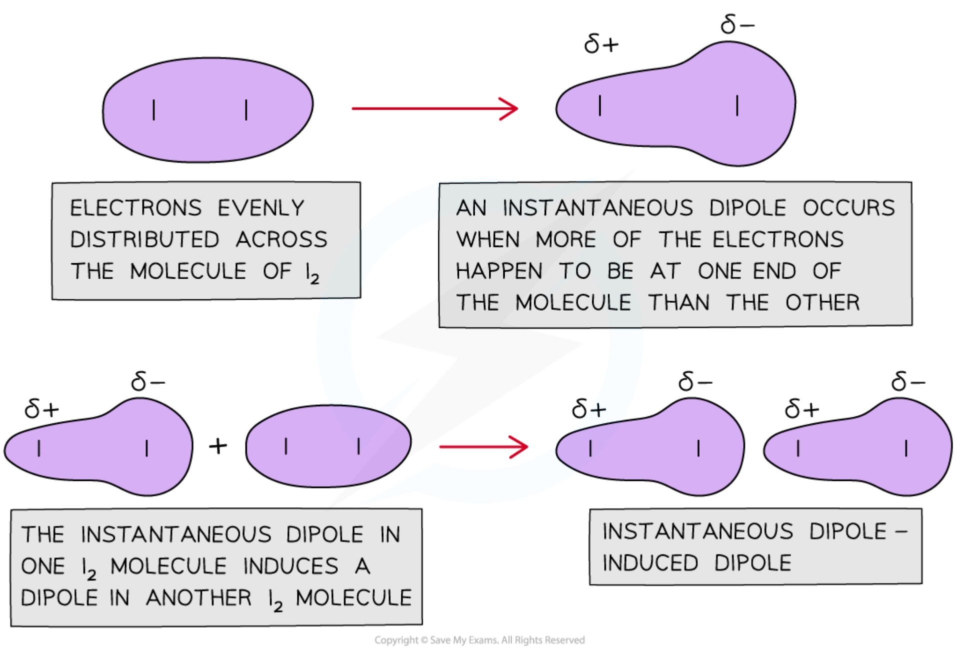
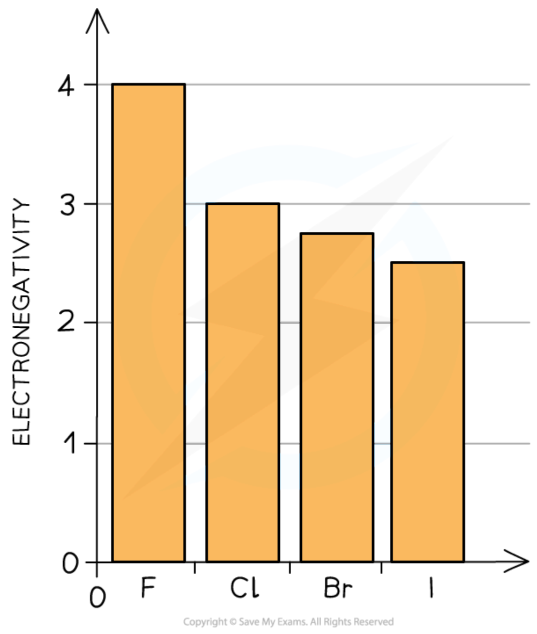


The diagram shows that a sudden imbalance of electrons in a nonpolar molecule can cause an instantaneous dipole. When this molecule gets close to another non-polar molecule it can induce a dipole as the cloud of electrons repel the electrons in the neighbouring molecule to the other side

- The more **electrons** there are in a molecule, the greater the instantaneous dipole-induced dipole forces
- Therefore, the **larger** the molecule the **stronger** the London dispersion forces between molecules
- This is why as you go down the group, it gets more difficult to separate the molecules and the **melting** and **boiling points** increase
- As it gets more difficult to separate the molecules, the **volatility** of the halogens **decreases** going down the group

Trend in electronegativity

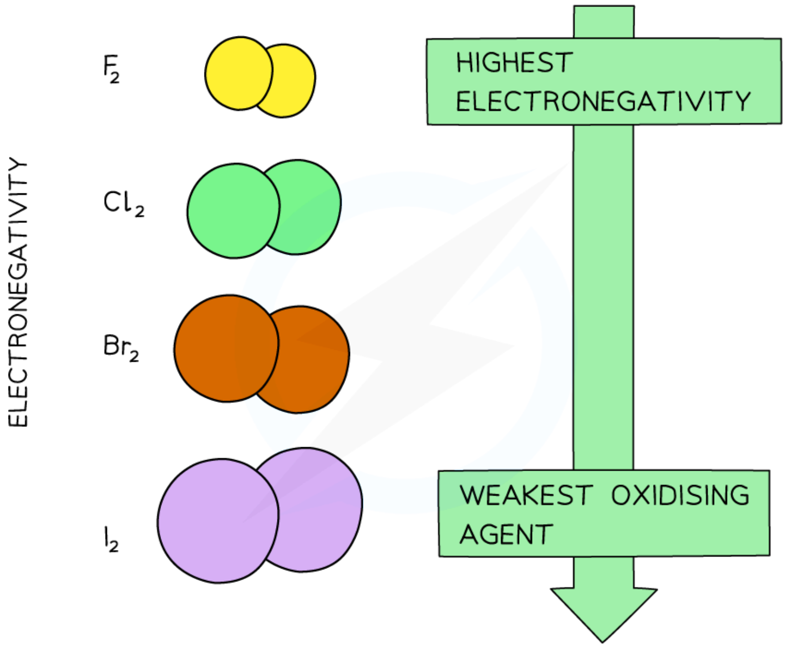
- The electronegativity of of the halogens decreases down the group



The electronegativity of the halogens decreases going down the group

- The **electronegativity** of an atom refers to how strongly it attracts electrons towards itself in a covalent bond
- The decrease in electronegativity is linked to the size of the halogens
- Going down the group, the atomic radii of the elements increase which means that the outer shells get further away from the nucleus
- An 'incoming' electron will therefore experience more **shielding** from the attraction of the positive nuclear charge
- The halogens' ability to accept an electron (their **oxidising power**) therefore decreases going down the group

Your notes



With increasing atomic size of the halogens (going down the group) their electronegativity, and therefore oxidising power, decreases

Reactivity

- When a halogen atom reacts it will usually gain an electron, to form a **1–** ion ($X + e^- \rightarrow X^-$)
- The oxidation number has decreased from 0 to -1, therefore reduction has occurred
- Therefore halogens will act as oxidising agents
- Down Group 7 we have seen that the atoms become larger so the outer electrons are further away and are therefore more shielded from the positive nucleus
- Larger halogen atoms such as iodine will find it more difficult to attract incoming electrons needed to form the 1– ion
- Therefore the reactivity decreases down Group 7

Reaction with hydrogen

- To demonstrate the decrease in the reactivity we can look a the reaction with hydrogen gas
- The table outlines the trend in the reactivity of the halogens with hydrogen gas
- As we can see the reaction becomes less vigorous down the group

Reaction between Halogen & Hydrogen Gas

Your notes

Equation for Reaction	Description of Reaction
$H_2(g) + F_2(g) \longrightarrow 2HF(g)$	Reacts explosively even in cool, dark conditions
$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$	Reacts explosively in sunlight
$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$	Reacts slowly on heating
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	Forms an equilibrium mixture on heating

Your notes

Halogen Displacement

- The reactivity of halogens is also shown by their **displacement reactions** with other halide ions in solutions
  - A **more reactive** halogen can displace a **less reactive** halogen from a halide solution of the less reactive halogen
  - Eg. The addition of chlorine water to a solution of bromine water:

Cl_2 (aq) + 2NaBr (aq) → 2NaCl (aq) + Br_2 (aq)

  - The chlorine has displaced the bromine from solution as it is more reactive which can be summarised in the following ionic equation by removing the sodium spectator ions:

Cl_2 (aq) + $2Br^-$ (aq) → $2Cl^-$ (aq) + Br_2 (aq)

  - Chlorine can also displace iodine from a solution of iodide ions:

Cl_2 (aq) + $2I^-$ (aq) → $2Cl^-$ (aq) + I_2 (aq)

- We can see these are both redox reactions by taking a look at changes in the oxidation number of each element in the reaction
  - Br and I both change from = -1 → 0 so the bromine and iodine have been oxidised in their respective reactions
  - Cl = 0 → -1 so the chlorine has been reduced in both reactions
  - No change in oxidation number for the sodium

Chlorine with Bromides & Iodides

- If you add chlorine solution to colourless potassium bromide or potassium iodide solution a displacement reaction occurs:
  - The solution becomes **yellow**-**orange** as bromine is formed
  - The solution becomes **brown** as iodine is formed
- If an **organic solvent** is added, such as cyclohexane, the following observations are seen:
  - The organic layer will appear **yellow-orange** as bromine is formed
  - The organic layer will appear **purple** as iodine is formed
  - The organic solvent is useful as the the halogens are more soluble in this layer which helps observe the colour changes more easily
- Chlorine is **above** bromine and iodine in Group 7 so it is more reactive
- Chlorine will **displace** bromine or iodine from an aqueous solution of the metal halide:

$$Cl_2\,(aq) + 2KBr\,(aq) \rightarrow 2KCl\,(aq) + Br_2\,(aq)$$

chlorine + potassium bromide → potassium chloride + bromine

$$Cl_2\,(aq) + 2KI\,(aq) \rightarrow 2KCl\,(aq) + I_2\,(aq)$$

chlorine + potassium iodide → potassium chloride + iodine

Your notes

Bromine with Iodides

- Bromine is above iodine in Group 7 so it is **more** reactive
- Bromine will displace iodine from an aqueous solution of the metal iodide

bromine + potassium iodide → potassium bromide + iodine

$$Br_2\,(aq) + 2KI\,(aq) \rightarrow 2KBr\,(aq) + I_2\,(aq)$$

- The reaction will turn **brown** as iodine is formed
- If an organic solvent is added the organic layer will appear **purple** as iodine is formed
- We can show that this is a redox reaction by looking at the changes in oxidation numbers:
  - I = -1 → 0 so the iodine has been oxidised
  - Br = 0 → -1 so the bromine has been reduced
  - No change in oxidation number for the potassium
- Rather than writing the full equation, we can also write the ionic equation by removing the potassium spectator ion

$$Br_2\,(aq) + 2I^-\,(aq) \rightarrow 2Br^-\,(aq) + I_2\,(aq)$$

Redox Reactions of the Halogens

Reactions with Group 1 & 2 metals

- The halogens react with some metals to form **ionic compounds** which are **metal halide salts**
- In all reactions where halogens are reacting with metals, the metals are being oxidised
- Reaction of sodium and chlorine
  - $2Na\ (s) + Cl_2\ (g) \rightarrow 2NaCl\ (s)$
  - Na is being oxidised, the oxidation number is changing from 0 to +1
- Calcium is a group 2 metal:
  - $Ca\ (s) + Br_2\ (l) \rightarrow CaBr_2\ (s)$
  - Ca is being oxidised, the oxidation number is changing from 0 to +2
- Therefore the halogens are acting as oxidising agents

Reactions with Iron(II)

- Chlorine and bromine can oxidise iron(II) to iron(III)

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

$$Br_2\ (g) + 2Fe^{2+}\ (aq) \rightarrow 2Br^-\ (aq) + 2Fe^{3+}\ (aq)$$

- However, iodine is not a strong enough oxidising agent to oxidise iron(II) to iron(III)
- Iodine is actually oxidised from iodide ions to iodine by iron(III)

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

Disproportionation reaction

- A **disproportionation reaction** is a reaction in which the same species is both oxidised and reduced
- The reaction of **chlorine** with **dilute alkali** is an example of a disproportionation reaction
- In these reactions, the chlorine gets oxidised and reduced at the same time
- Different reactions take place at different **temperatures** of the dilute alkali

Chlorine in cold alkali (15 °C)

- The reaction that takes place is:

$$Cl_2(aq) + 2NaOH\ (aq) \longrightarrow NaCl\ (aq) + NaClO\ (aq) + H_2O(l)$$

- The ionic equation is:

$$\underset{0}{Cl_2(aq)} + 2OH^-(aq) \longrightarrow \underset{-1}{Cl^-(aq)} + \underset{+1}{ClO^-(aq)} + H_2O(aq)$$

REDUCTION

OXIDATION

- The ionic equation shows that the chlorine gets both oxidised and reduced
- Chlorine gets oxidised as there is an increase in ox. no. from 0 to +1 in $ClO^-(aq)$
  - The half-equation for the oxidation reaction is:

$$\underset{0}{\tfrac{1}{2}Cl_2} + 2OH^-(aq) \longrightarrow \underset{+1}{ClO^-(aq)} + H_2O + e^-$$

- Chlorine gets reduced as there is a decrease in ox. no. from 0 to -1 in $Cl^-(aq)$
  - The half-equation for the reduction reaction is:

$$\underset{0}{\tfrac{1}{2}Cl_2} + e^- \longrightarrow \underset{-1}{Cl^-}$$

Chlorine in hot alkali (70 °C)

- The reaction that takes place is:

$$3Cl_2(aq) + 6NaOH(aq) \longrightarrow 5NaCl(aq) + NaClO_3(aq) + 3H_2O(l)$$

- The ionic equation is:

$$\underset{0}{Cl_2(aq)} + 6OH^-(aq) \longrightarrow \underset{-1}{5Cl^-(aq)} + \underset{+5}{ClO_3^-(aq)} + H_2O(l)$$

REDUCTION

OXIDATION

- The ionic equation shows that the chlorine gets both oxidised and reduced

- Chlorine gets oxidised as there is an increase in ox. no. from 0 to +5 in ClO_3^-(aq)
  - The half-equation for the oxidation reaction is:

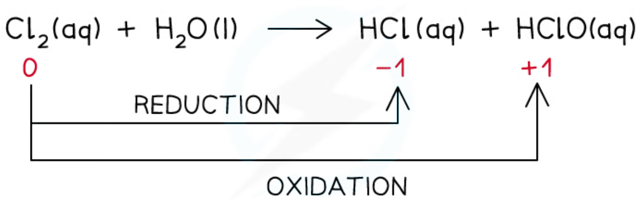
$$\underset{0}{\tfrac{1}{2}Cl_2} + 6OH^- \longrightarrow \underset{+5}{ClO_3^-} + 3H_2O + e^-$$

- Chlorine gets reduced as there is a decrease in ox. no. from 0 to -1 in Cl^-(aq)
  - The half-equation for the reduction reaction is:

$$\underset{0}{2\tfrac{1}{2}Cl_2} + e^- \longrightarrow \underset{-1}{5Cl^-}$$

Drinking water

- Chlorine can be used to clean water and make it drinkable
- The reaction of chlorine in water is a **disproportionation reaction** in which the chlorine gets both **oxidised** and **reduced**



The disproportionation reaction of chlorine with water in which chlorine gets reduced to HCl and oxidised to HClO

- Chloric(I) acid (HClO) **sterilises** water by killing **bacteria**
- Chloric acid can further dissociate in water to form ClO^-(aq):

$$\mathbf{HClO\ (aq) \rightarrow H^+\ (aq) + ClO^-\ (aq)}$$

- ClO^-(aq) also acts as a **sterilising agent** cleaning the water

Other Reactions of the Halogens

Concentrated sulfuric acid

- Chloride, bromide and iodide ions react with concentrated sulfuric acid to produce **toxic gases**
- These reactions should therefore be carried out in a fume cupboard
- The general reaction of the halide ions with concentrated sulfuric acid is:

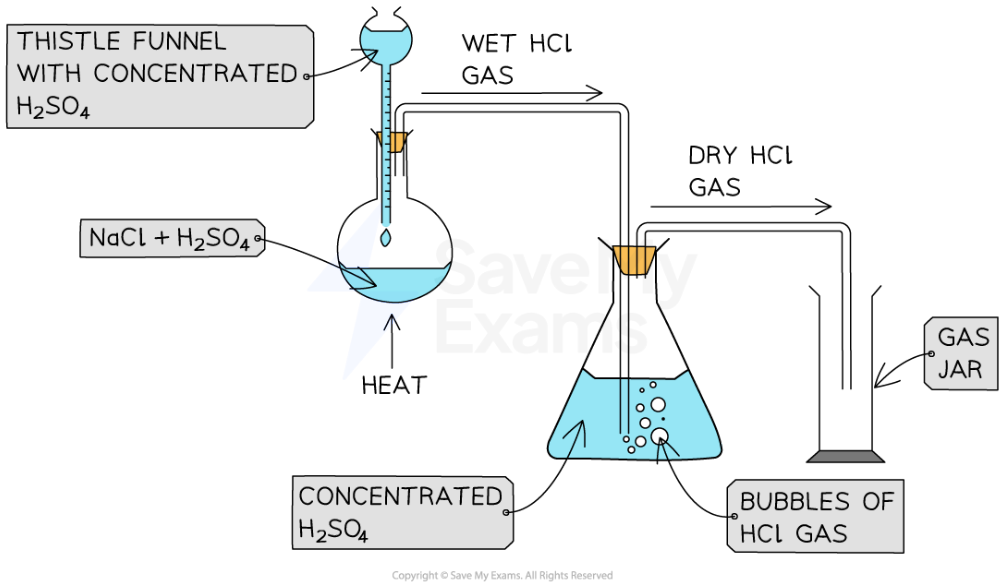
$$H_2SO_4(l) + X^-(aq) \rightarrow HX(g) + HSO_4^-(aq)$$

(general equation)

Where **X^-** is the halide ion

Reaction of chloride ions with concentrated sulfuric acid

- Concentrated sulfuric acid is dropwise added to sodium chloride crystals to produce **hydrogen chloride gas**



Apparatus set up for the reaction of sodium chloride with concentrated sulfuric acid

- The reaction that takes place is:

$$H_2SO_4\,(l) + NaCl\,(s) \rightarrow HCl\,(g) + NaHSO_4\,(s)$$

- The HCl gas produces is seen as **misty fumes**

Reaction of bromide ions with concentrated sulfuric acid

- The **thermal stability** of the hydrogen halides decreases down the group
- The reaction of sodium bromide and concentrated sulfuric acid is:

$$H_2SO_4\ (l) + NaBr\ (s) \rightarrow HBr\ (g) + NaHSO_4\ (s)$$

- The concentrated sulfuric acid **oxidises** HBr which decomposes into **bromine** and **hydrogen gas** and sulfuric acid itself is **reduced** to **sulfur dioxide gas**:

$$2HBr\ (g) + H_2SO_4\ (l) \rightarrow Br_2\ (g) + SO_2\ (g) + 2H_2O\ (l)$$

- The bromine is seen as a **reddish-brown gas**

Reaction of iodide ions with concentrated sulfuric acid

- The reaction of sodium iodide and concentrated sulfuric acid is:

$$H_2SO_4\ (l) + NaI\ (s) \rightarrow HI\ (g) + NaHSO_4\ (s)$$

- **Hydrogen iodide** decomposes the **easiest**
- Sulfuric acid oxidises the hydrogen iodide to several extents:
- The concentrated sulfuric acid **oxidises** HI and is itself **reduced** to **sulfur dioxide gas**:

$$2HI\ (g) + H_2SO_4\ (l) \rightarrow I_2\ (g) + SO_2\ (g) + 2H_2O\ (l)$$

- Iodine is seen as a violet/purple vapour
- The concentrated sulfuric acid **oxidises** HI and is itself **reduced** to **sulfur**:

$$6HI\ (g) + H_2SO_4\ (l) \rightarrow 3I_2\ (g) + S\ (s) + 4H_2O\ (l)$$

- Sulfur is seen as a **yellow solid**
- The concentrated sulfuric acid **oxidises** HI and is itself **reduced** to **hydrogen sulfide**:

$$8HI\ (g) + H_2SO_4\ (l) \rightarrow 4I_2\ (g) + H_2S\ (s) + 4H_2O\ (l)$$

- Hydrogen sulfide has a **strong smell of bad eggs**

Further redox reaction involving sulfur dioxide

- HI is such a strong reducing agent that it can reduce sulfur dioxide, SO_2, further to hydrogen sulfide, H_2S

$$SO_2\ (g) + 6HI\ (g) \rightarrow H_2S\ (g) + 3I_2\ (s) + 2H_2O\ (l)$$

- Sulfur is reduced from +4 in SO_2 to –2 in H_2S, a gain of 6 electrons:
  - This demonstrates reduction
- The iodide ion is oxidised to iodine (I_2), seen as purple vapour
- The bad egg smell of H_2S confirms the presence of this gas
- This final step highlights the maximum reducing power of iodide ions, not seen with Cl^- or Br^-

Halide ion Reactions with Concentrated Sulfuric Acid Table

Your notes

Halide ion	Reaction with conc H_2SO_4	Observations
Cl^- (aq)	H_2SO_4 (l) + NaCl (s) → HCl (g) + $NaHSO_4$ (s)	Misty fumes of HCl gas
Br^- (aq)	H_2SO_4 (l) + NaBr (s) → HBr (g) + $NaHSO_4$ (s) H_2SO_4 (l) + 2HBr (g) → Br_2 (g) + SO_2 (g) + $2H_2O$ (l)	Misty fumes of HBr gas Choking gas of SO_2 and reddish brown gas of Br_2
I^- (aq)	H_2SO_4 (l) + NaI (s) → HI (g) + $NaHSO_4$ (s) H_2SO_4 (l) + 2HI (g) → I_2 (s) + SO_2 (g) + $2H_2O$ (l) H_2SO_4 (l) + 6HI (g) → $3I_2$ (s) + S (s) + $4H_2O$ (l) H_2SO_4 (l) + 8HI (g) → $4I_2$ (s) + H_2S (g) + $4H_2O$ (l)	Misty fumes of HI gas Choking gas of SO_2 and purple vapour of I_2 Yellow solid of S (s) Strong, bad egg smell of H_2S (g)

Explaining the Trend in Reducing Ability of Halide Ions

- As you go down Group 7, the halide ions get bigger (Cl^- → Br^- → I^-)
- So, the attraction between the outer electrons and the nucleus gets weaker
- This makes it easier for the larger halide ions to lose electrons
- When they lose electrons, they reduce other substances,
- So the reducing power increases down the group:
  - $Cl^- < Br^- < I^-$

Silver ions & ammonia

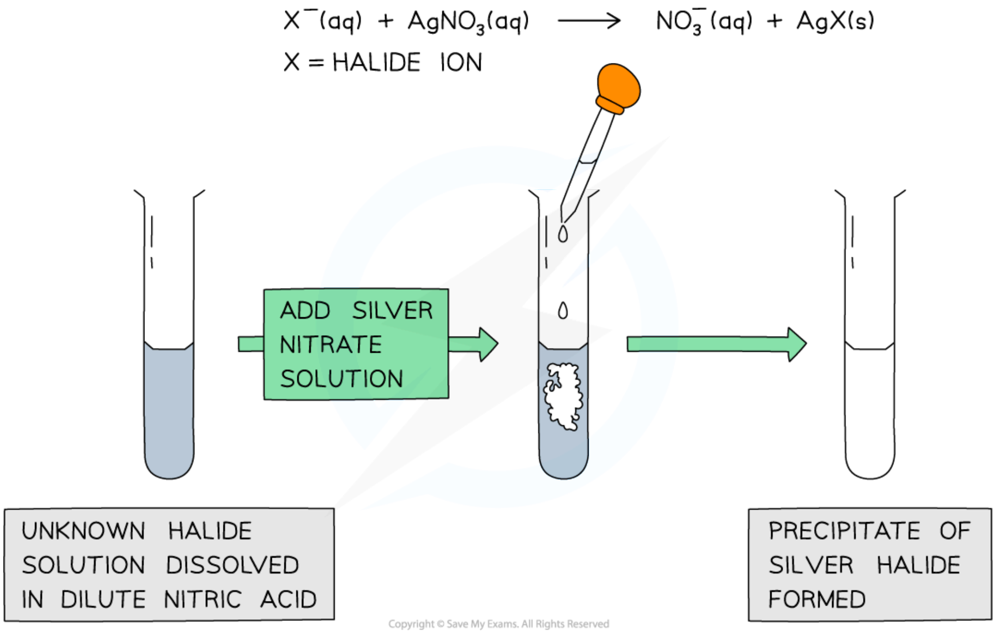
- Halide ions can be identified in an **unknown solution** by dissolving the solution in **nitric acid** and then adding a **silver nitrate solution** followed by **ammonia** solution
- The halide ions will react with the silver nitrate solution as follows:

$$\mathbf{AgNO_3\,(aq) + X^-\,(aq) \rightarrow AgX\,(s) + NO_3^-\,(aq)}$$

$$\mathbf{Ag^+\,(aq) + X^-\,(aq) \rightarrow AgX\,(s)}$$

- $\mathbf{X^-}$ is the halide ion in both equations
- If the unknown solution contains halide ions, then a **precipitate** of the **silver halide** will be formed (AgX)

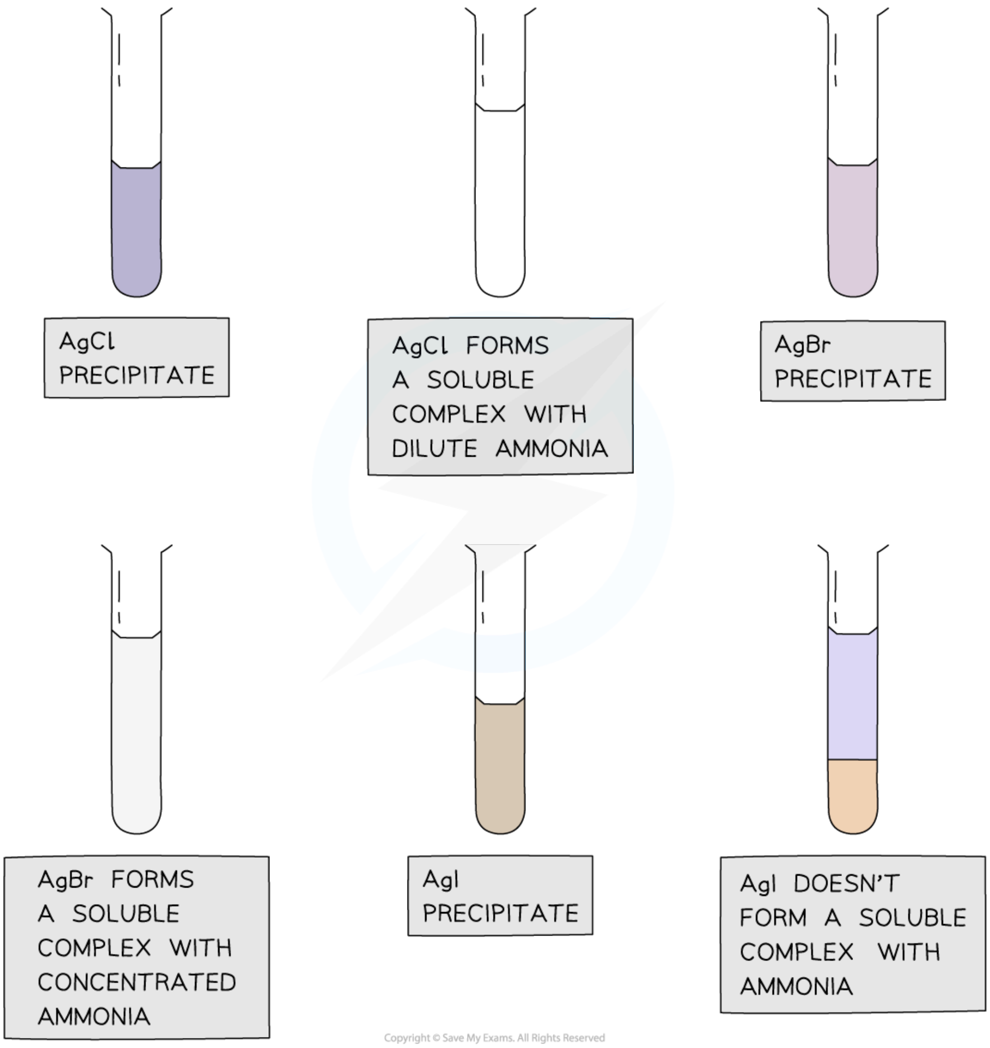
Your notes



A silver halide precipitate is formed upon addition of silver nitrate solution to halide ion solution

- **Dilute** followed by **concentrated ammonia** is added to the silver halide solution to identify the halide ion
- If the precipitate dissolves in **dilute** ammonia the unknown halide is **chloride**
- If the precipitate does not dissolve in dilute but in **concentrated** ammonia the unknown halide is **bromide**
- If the precipitate does not dissolve in **dilute** nor **concentrated** ammonia the unknown halide is iodide

Your notes



Silver chloride and silver bromide precipitates dissolve on addition of ammonia solution whereas silver iodide doesn't

Reaction of Halide Ions with Silver Nitrate & Ammonia Solutions Table

Halide ion	Colour of Silver Halide Solution	Effect of adding dil. NH_3	Effect of adding conc. NH_3
Cl^- (aq)	White	Dissolves	Dissolves
Br^- (aq)	Cream	Insoluble	Dissolves
I^- (aq)	Pale yellow	Insoluble	Insoluble

Reactions with hydrogen halides

- When a halogen reacts with hydrogen a hydrogen halide is produced, for example:
    - **Cl_2 (g) + H_2 (g) → 2HCl (g)**
- These hydrogen halides react with ammonia gas to form **ammonium halides**
    - **NH_3 (g) + HCl (g) → NH_4Cl (s)**
- Hydrogen halides will also react with water
- For example, hydrogen chloride also dissolves in water to form **hydrochloric acid**
    - **HCl (g) → H^+ (aq) + Cl^- (aq)**

Fluorine & Astatine

Fluorides and Astatides

- If you are asked to predict reactions of fluorides and astatides that you are not familiar with you can use the information about Group 7 to help
- There are, however, exceptions to some of the reactions
    - For example, silver fluoride is soluble, so we can not used acidified silver nitrate to test for the presence of fluoride ions
        - Ag^+ (aq) + F^- (aq) → AgF (aq)

Worked Example

Write an equation to show the formation of an acid when hydrogen astatide is added to water.

Answer:

- Based on the reaction of hydrogen iodide with water:
    - HI (g) + H_2O (g) → H_3O^+ (aq) + I^- (aq)
    - So, hydrogen astatide must be:
        - **HAt (g) + H_2O (g) → H_3O^+ (aq) + At^- (aq)**

Your notes