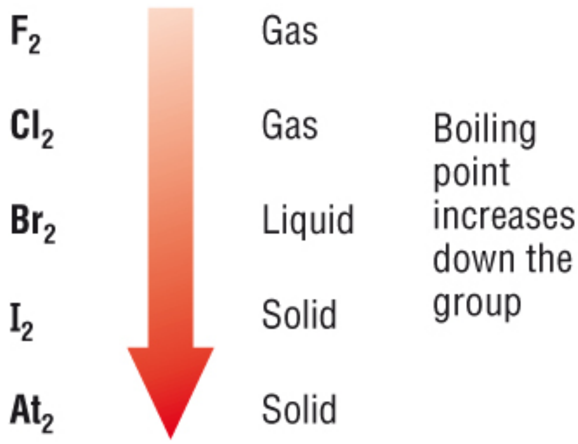
2.3 Group 7 – The Halogens

Physical properties of the Halogens:

- The melting and boiling point of the halogens increases with atomic number due to increased van der Waals (from increased number of electrons).
- This can be seen by their physical states at room temperature.
- Iodine sublimes to a purple vapour.



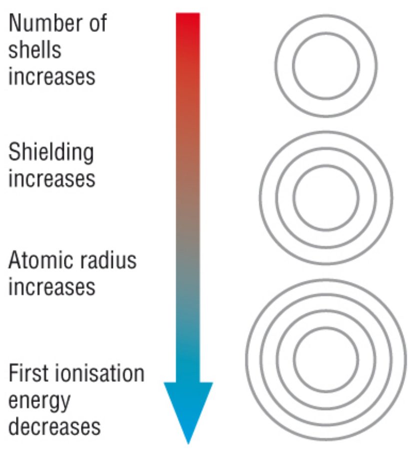
Atomic radius – Increases down the Group:

- **Shells:** **More** electron shells
- **Shielding:** **More** shielding (more inner shells)

Ionic radius – Larger than atomic radius**:**

- **1e added to shell:** **More electrons being attracted by same number of protons**

First ionisation - Decreases down the Group:



- **Shells:** **More** electron shells
- **Shielding:** **More** shielding (more inner shells)
- **No. Protons:** Number of protons **increases** but is **outweighed** by shells and shielding
- **Attraction:** Therefore attraction is **less**
- **Energy:** **Energy** required to remove an electron **decreases**

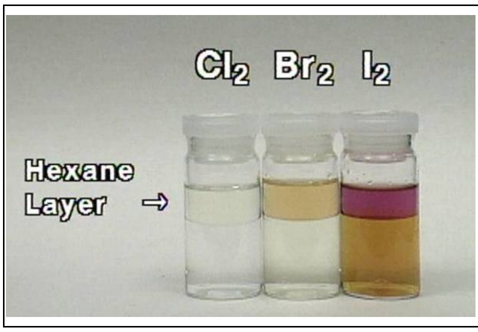
Reactivity – Decreases down the Group:

- All **gain 1 electrons forming a 1- ion** when they react.
- **More shells**
- **More shielding**
- **Increase in number of protons is outweighed by shells and shielding**
- **Attraction to capture an electrons decreases down the Group**
- **Reactivity decreases** as you go **down the group**

Trend in electronegativity decreases down the Group:
- Down the group there are more shells which outweigh the increase in number of protons.
- This reduces the halogen's ability to attract bonding pairs of electrons towards itself

<u>Appearance and solubility of the Halogens</u>

- The halogens are sparingly soluble in water – VDW vs H bonding.
- As you go down the group they become less soluble (as VDW increases).
- They are however soluble in non - polar solvents such as cyclohexane – VDW vs VDW.
- The colours when dissolved in water and a non - polar solvent are shown below:



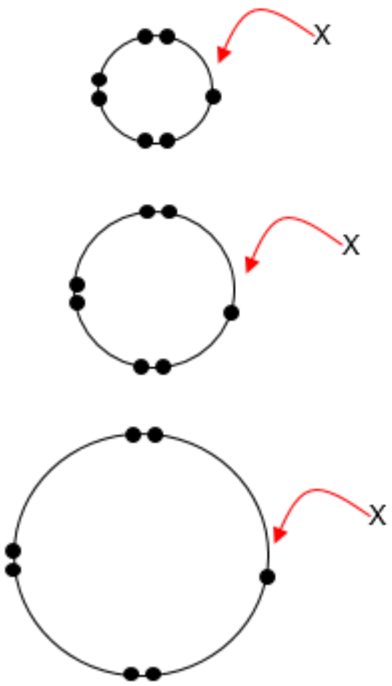
Halogen	In water	In cyclohexane
Cl_2	Pale green	Pale Green
Br_2	Orange	Orange
I_2	Brown	Violet

Halogens as oxidising agents:

$$\frac{1}{2}Cl_2 \quad + \quad e^- \quad \rightarrow \quad Cl^-$$

- **Gain of electrons** is **Reduction**
- This means that whatever they react with must **lose electrons** and be **Oxidised**
- This makes the **Halogens** good **Oxidising agents**
- **Reactivity decreases** as you go **down the Group**.
- This means they **gain their electrons less readily**.
- This means as you go **down Group 7**, their **oxidising power decreases**.

Explanation:



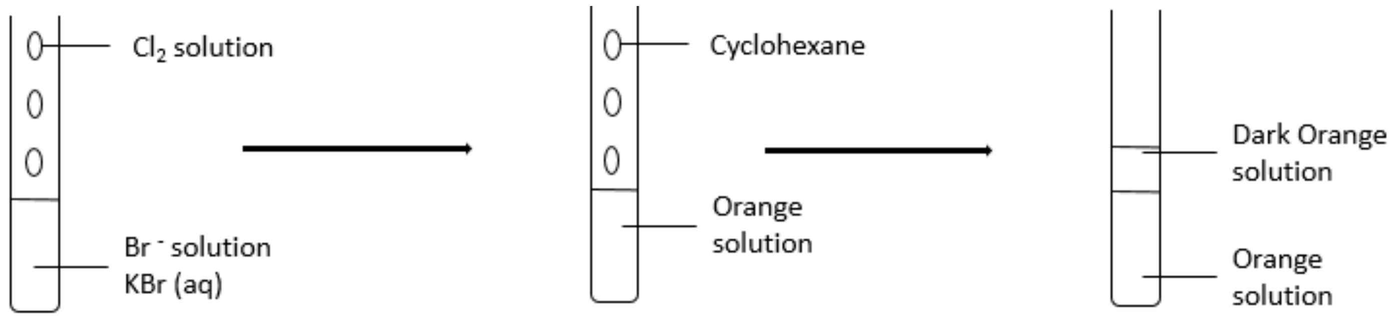
- All **gain 1 electrons forming a 1- ion** when they react.
- **More shells**
- **More shielding**
- **Increase in number of protons is outweighed by shells and shielding**
- **Attraction to capture an electrons decreases down the Group**
- **Reactivity decreases** as you go **down the group**
- **The power of the Oxidising agent decreases** as you go **down the group**

Displacement reactions of the halogens:

- Redox reactions show the Halogens ability to form ions reduces as you go down the Group.
- By competing the Halogens (Cl_2, Br_2, and I_2) with the Halides (Cl^-, Br^-, and I^-)
- Each Halogen is mixed with each of the Halides.
- The more reactive Halogen will oxidise and displace the Halide of a less reactive Halogen.
- Halogens are coloured in solution and in a hydrocarbon solvent such as cyclohexane.
- This can indicate whether a redox reaction has occurred:

	$Cl^-_{(aq)}$	$Br^-_{(aq)}$	$I^-_{(aq)}$
$Cl_{2(aq)}$ **Add cyclohexane**		**Orange** **Dark orange**	**Brown** **Purple**
$Br_{2(aq)}$ **Add cyclohexane**	**No reaction** Stays orange / dark orange		**Brown** **Purple**
$I_{2(aq)}$ **Add cyclohexane**	**No reaction** Stays brown / purple	**No reaction** Stays Brown / purple	

Interpretation:



1) Chlorine and Potassium bromide:
Full equation and colours:

$$Cl_{2(aq)} + 2KBr_{(aq)} \rightarrow 2KCl_{(aq)} + Br_{2(aq)}$$

Pale green (Cl_2); **Orange** / **Orange (in cyclohexane)** (Br_2)

Ionic equation:

$$Cl_{2(aq)} + 2Br^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + Br_{2(aq)}$$

Half equations:

$$Cl_{2(aq)} + 2e^- \rightarrow 2Cl^-_{(aq)}$$

$$2Br^-_{(aq)} \rightarrow 2e^- + Br_{2(aq)}$$

Explanation:

Chlorine is further up the Group than Bromine so is a stronger oxidising agent, so accepts electrons more readily than bromine

2) Chlorine and Potassium iodide:
Full equation and colours:

$$Cl_{2(aq)} + 2KI_{(aq)} \rightarrow 2KCl_{(aq)} + I_{2(aq)}$$

Pale green (Cl_2); **Brown** / **Purple (in cyclohexane)** (I_2)

Ionic equation:

$$Cl_{2(aq)} + 2I^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + I_{2(aq)}$$

Half equations:

$$Cl_{2(aq)} + 2e^- \rightarrow 2Cl^-_{(aq)}$$

$$2I^-_{(aq)} \rightarrow 2e^- + I_{2(aq)}$$

Explanation:

Chlorine is further up the Group than Iodine so is a stronger oxidising agent, so accepts electrons more readily than Iodine

3) Chlorine and Potassium iodide:
Full equation and colours:

$Br_{2(aq)}$	+	$2KI_{(aq)}$	→	$2KBr_{(aq)}$	+	$I_{2(aq)}$
Orange						**Brown**
						Purple (in cyclohexane)

Ionic equation:

$$Br_{2(aq)} + 2I^{-}_{(aq)} \rightarrow 2Br^{-}_{(aq)} + I_{2(aq)}$$

Half equations:

$$Br_{2(aq)} + 2e^{-} \rightarrow 2Br^{-}_{(aq)}$$

$$2I^{-}_{(aq)} \rightarrow 2e^{-} + I_{2(aq)}$$

Explanation:

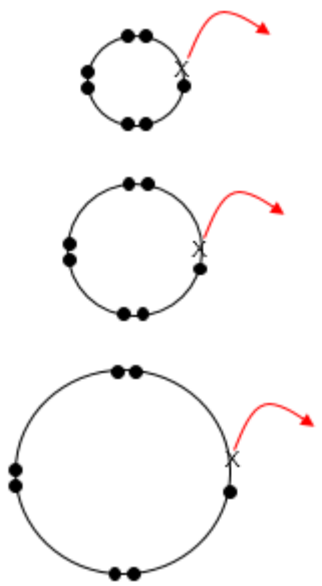
Bromine is further up the Group than Iodine so is a stronger oxidising agent, so accepts electrons more readily than Iodine

Halides as reducing agents:

$$I^-_{(aq)} \rightarrow e^- + \tfrac{1}{2}I_{2(aq)}$$

- **Loss of electrons is Oxidation**
- This means that whatever they react with must **gain electrons** and be **Reduced**
- This makes the **Halides** good **Reducing agents**
- As you go down the Group, **electrons are lost more readily**.
- This means as you go **down Group 7**, their **reducing power increases**.

Explanation:



- All **lose 1 electrons forming a halogen** when they react.
- **More shells**
- **More shielding**
- **Increase in number of protons is outweighed by shells and shielding**
- **Attraction to decreases down the Group**
- **Reactivity increases down the group**
- **The power of the Reducing agent increases** as you go **down the group**

Reactions of the Halides, X^- with concentrated sulphuric acid, H_2SO_4

Reduction products of Sulphuric acid, H_2SO_4:

Name	Sulphuric acid	Sulphur dioxide	Sulphur	Hydrogen sulphate
Formula	H_2SO_4	SO_2	S	H_2S
Oxidation number	+6	+4	0	-2
Test for sulphur product	White fumes with NH_3 gas / Damp blue litmus paper terns red	Dichromate paper turns orange → green	Yellow solid	Lead ethanoate paper turns black
As the power of the Reducing agent increases H_2SO_4 becomes more reduced - Therefore the halide must be oxidised to the halogen				
How far	F^- and Cl^-			
		Br^- and I^-		
				I^-

The Experiment: Reactions of the Halide ions, X^- with Sulphuric acid, H_2SO_4

- Add 0.1g of the solid halide (eg KCl) to a test tube.
- Add 10 drops of concentrated sulphuric acid, H_2SO_4 and warm if necessary.

Observations:

Solid halide	*Observations*	*Further observations*
KCl	White fumes	No further reaction
KBr	White fumes	Brown fumes (Br_2) and SO_2
KI	White fumes	Purple fumes (I_2), SO_2, S and H_2S

Equations:

1) With KCl / Cl^- / Chloride ion

$$\underset{-1}{NaCl} + \underset{+6}{H_2SO_4} \rightarrow \underset{+6}{NaHSO_4} + \underset{\text{White fumes}}{\underset{-1}{HCl}}$$

Cl^- cannot reduce H_2SO_4, it is not a strong enough reducing agent

2) With KBr / Br^- / Bromide ion

$$\underset{-1}{NaBr} + \underset{+6}{H_2SO_4} \rightarrow \underset{+6}{NaHSO_4} + \underset{\text{White fumes}}{\underset{-1}{HBr}}$$

Br^- can reduce H_2SO_4 to SO_2 but no further as it is a stronger reducing agent:

Half equations: Construct and balance using electrons:

$$2Br^- \rightarrow \underset{\text{Brown fumes}}{Br_2} + 2e^-$$

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

Overall:

$$2HBr + H_2SO_4 \rightarrow \underset{\text{Brown fumes}}{Br_2} + SO_2 + 2H_2O$$

3) **With KI / I^- / Iodide ion**

NaI	+	H_2SO_4	→	$NaHSO_4$	+	HI
-1		+6		+6		-1
						White fumes

I^- can reduce H_2SO_4 to SO_2 / S / H_2S as it is the strongest reducing agent

This happens in 3 simultaneous reactions:

a) **To make SO_2:**

Half equations: Construct and balance using electrons:

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

Purple fumes

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

Overall:

$$2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$$

Purple fumes

b) **To make S:**

Half equations: Construct and balance using electrons:

$$2I^- \rightarrow I_2 + 2e^- \quad \times 3$$

Purple fumes

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

Overall:

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

Purple fumes

c) **To make H_2S:**

Half equations: Construct and balance using electrons:

$$2I^- \rightarrow I_2 + 2e^- \quad \times 4$$

Purple fumes

$$H_2SO_4 + 8H^+ + 8e^- \rightarrow H_2S + 4H_2O$$

Overall:

$$8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$$

Purple fumes

Summary of the reduction reactions of the Halides:

1) **All Halides do the following – H_2SO_4 is not reduced:**

NaX	+	H_2SO_4	$\rightarrow$	$NaHSO_4$	+	HX
-1		+6		+6		-1
						White fumes

2) **The HX – Bromide and Iodide will reduce H_2SO_4 to SO_2**

2HX	+	H_2SO_4	$\rightarrow$	X_2	+	SO_2	+	$2H_2O$
-1		+6		0		+4		
				Brown / purple fumes				

3) **The HX –Iodide will also reduce H_2SO_4 to H_2S (and S)**

6HX	+	H_2SO_4	$\rightarrow$	$3X_2$	+	S	+	$4H_2O$
-1		+6		0		0		
				Purple fumes				

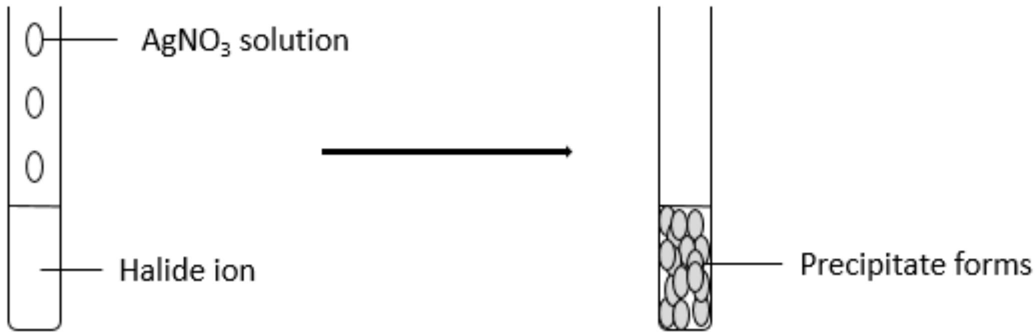
8HX	+	H_2SO_4	$\rightarrow$	$4X_2$	+	H_2S	+	$4H_2O$
-1		+6		0		-2		
				Purple fumes				

Summary of Oxidation / Reduction of the Halogens and the Halides

Halogens		Halides	
F_2	Oxidising strength increases up Group: Electrons are gained more readily	F^-	Reducing strength increases down Group: Electrons are lost more readily
Cl_2		Cl^-	
Br_2		Br^-	
I_2		I^-	

Testing for Halide ions – (Part of Required Practical 4)

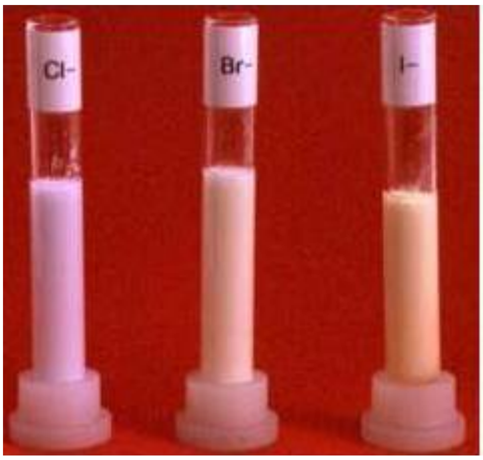
- Dissolve a small amount of Halide compound in water
- Add **nitric acid** to **remove any other ions** that may interfere with the test such as carbonates.
- Add a few drops of silver nitrate, **$AgNO_3$**.
- The silver ions, Ag^+ combines with the Halide ions, X^- to **form a silver halide precipitate**
- The silver halide precipitates are coloured depending upon the halide present:



- **Sometimes it is difficult to judge the exact colour.**
- **Ammonia can be added** as the different silver halides as they have different solubility's in ammonia**.**
- **The solubility of the precipitates decreases down the group.**

Results:

Halide ion	***Observations***	***With Ammonia***	***Solubility of the precipitate***
Cl^-	White precipitate	Dissolves in dilute NH_3 solution	Most soluble
Br^-	Cream precipitate	Dissolves in concentrated NH_3 solution	
I^-	Yellow precipitate	Insoluble	Least soluble



Equations:

1) **Potassium Chloride + Silver nitrate**

Full:

$KCl_{(aq)} + AgNO_{3(aq)} \rightarrow KNO_{3(aq)} + AgCl_{(s)}$

White Precipitate
Soluble in dilute NH_3

Ionic:

$Cl^-_{(aq)} + Ag^+_{(aq)} \rightarrow AgCl_{(s)}$

2) **Potassium Bromide + Silver nitrate**

Full:

$KBr_{(aq)} + AgNO_{3(aq)} \rightarrow KNO_{3(aq)} + AgBr_{(s)}$

Cream Precipitate
Soluble in conc NH_3

Ionic:

$Br^-_{(aq)} + Ag^+_{(aq)} \rightarrow AgBr_{(s)}$

3) **Potassium Iodide + Silver nitrate**

Full:

$KI_{(aq)} + AgNO_{3(aq)} \rightarrow KNO_{3(aq)} + AgI_{(s)}$

Cream Precipitate
Insoluble in conc NH_3

Ionic:

$I^-_{(aq)} + Ag^+_{(aq)} \rightarrow AgI_{(s)}$

Generally:

$X^-_{(aq)} + Ag^+_{(aq)} \rightarrow AgX_{(s)}$

Disproportionation reactions – Uses of chlorine and Chlorate (I)

Disproportionation

Disproportionation:
Is a REDOX reaction where the same element has been both Oxidised and Reduced

1) Chlorine and cold NaOH – Bleach:

$$\underset{0}{Cl_{2(aq)}} + 2NaOH_{(aq)} \rightarrow \underset{-1}{NaCl_{(aq)}} + \underset{+1}{NaClO_{(aq)}} + H_2O_{(l)}$$

- The Cl has been oxidised and reduced in this reaction.
- Sodium chlorate (I) is used in bleach.
- Uses – bleaching paper / textiles / cleaning toilets

2) Chlorine and drinking water:

$$\underset{0}{Cl_{2(aq)}} + H_2O_{(l)} \rightarrow \underset{-1}{HCl_{(aq)}} + \underset{+1}{HClO_{(aq)}}$$

Or dissociated:

$$Cl_{2(aq)} + H_2O_{(l)} \rightarrow 2H^+_{(aq)} + Cl^-_{(aq)} + ClO^-_{(aq)}$$

- In this reaction, the Cl has been oxidised and reduced too.
- The chlorate (I) ion kills bacteria.
- Chlorine reacts with organic compounds from plant decomposition to form chlorinated compounds – carcinogenic.
- Chlorine is toxic.
- Risk and Benefit must be assessed when making decisions on this scale.

Further reactions - In sunlight HClO decomposes further:

$$HClO_{(aq)} \rightarrow HCl_{(aq)} + \tfrac{1}{2}O_{2(aq)}$$

Or dissociated:

$$HClO_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)} + \tfrac{1}{2}O_{2(aq)}$$

- Combining these 2 reactions gives:

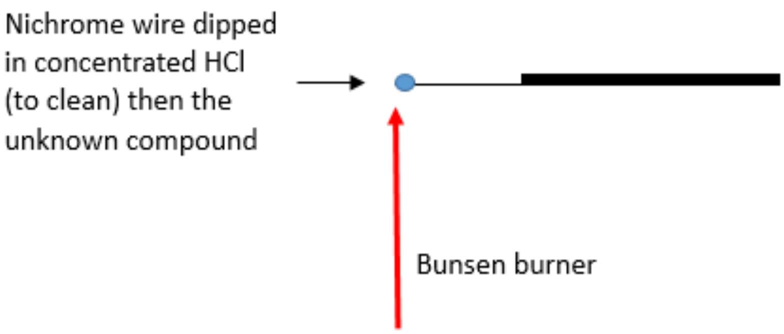
$$Cl_{2(aq)} + H_2O_{(l)} \rightarrow 2HCl_{(aq)} + \tfrac{1}{2}O_{2(aq)}$$

- This means that the reaction between chlorine and water **in sunlight** produces hydrochloric acid and oxygen:

Required Practical 4 – Test for ions

Positive ions:

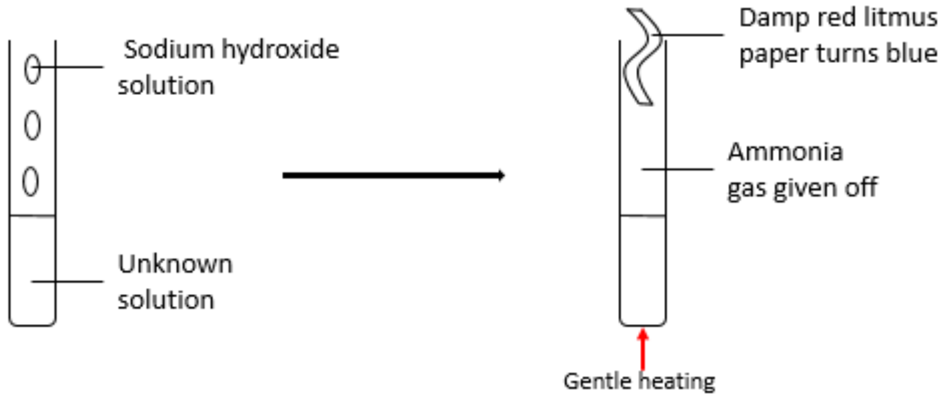
1) Test for Group 2 metal ions, M^{2+} - Flame tests



Metal ion	*Flame colour*
Calcium, Ca^{2+}	**Brick red**
Strontium, Sr^{2+}	**Red**
Barium, Ba^{2+}	**Pale green**

2) Test for ammonium ions, NH_4^+:

$$NH_4^+{}_{(aq)} \quad + \quad OH^-{}_{(aq)} \quad \rightarrow \quad NH_{3(g)} \quad + \quad H_2O_{(l)}$$

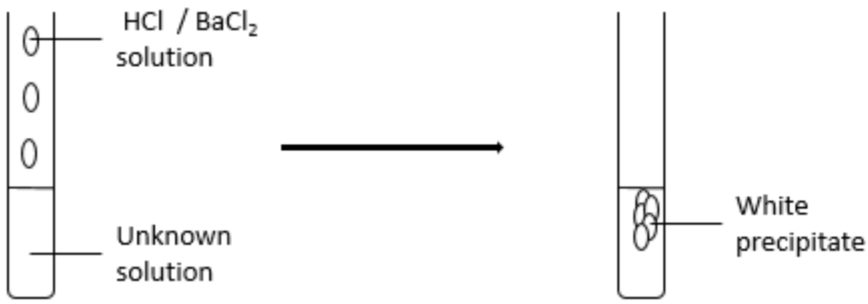


- With sodium hydroxide and heat, ammonia gas is given off.
- Litmus paper must be damp for ammonia gas to dissolve in.
- **Turns Blue**

Negative ions:

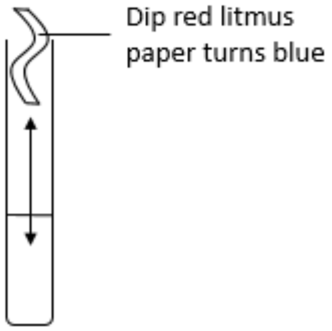
3) Test for sulphate ions, SO_4^{2-}

$$Ba^{2+}{}_{(aq)} \quad + \quad SO_4^{2-}{}_{(aq)} \quad \rightarrow \quad BaSO_{4(s)}$$



- Add **HCl** first – This removes any sulphites or carbonates that may also give a white precipitate.
- Add **$BaCl_2$** solution: **White precipitate of $BaSO_4$** will form.

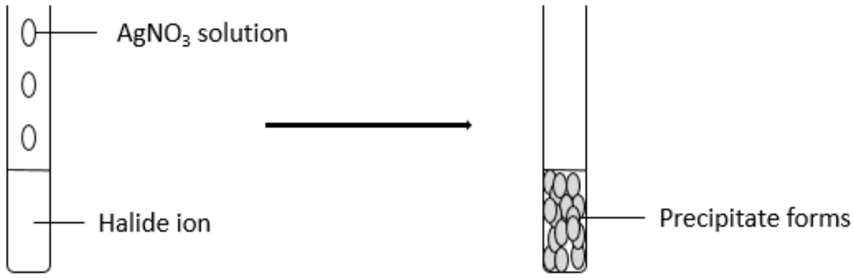
4) Test for hydroxide ions, OH^-



- Dip red litmus paper onto the solution.
- If it turns blue, hydroxide, OH^- are present.

5) Testing for Halide ions, X^-

$$X^-_{(aq)} \quad + \quad Ag^+_{(aq)} \quad \rightarrow \quad AgX_{(s)}$$



- Add **nitric acid** to **remove any other ions** that may interfere with the test.
- Add silver nitrate, $\mathbf{AgNO_3}$.
- The silver ions, Ag^+ combines with the Halide ions, X^- to **form a silver halide precipitate**

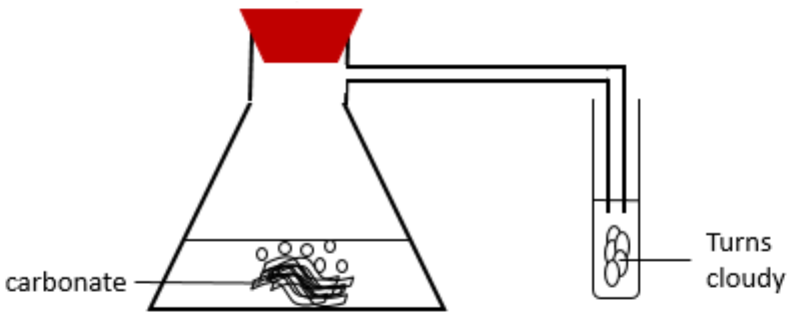
- **Ammonia can be added** as the different silver halides as they have different solubility's in ammonia**.**

Results:

Halide ion	*Observations*	*With Ammonia*	*Solubility of the precipitate*
Cl^-	White precipitate	Dissolves in dilute NH_3 solution	Most soluble
Br^-	Cream precipitate	Dissolves in concentrated NH_3 solution	
I^-	Yellow precipitate	Insoluble	Least soluble

6) Testing for carbonate ions, CO_3^{2-}

$$CO_3^{2-}{}_{(aq)} \quad + \quad 2H^+_{(aq)} \quad \rightarrow \quad CO_{2(g)} \quad + \quad H_2O_{(l)}$$



- Add **hydrochloric acid**.
- It will fizz if carbonate present, $\mathbf{CO_3^{2-}}$.
- $\mathbf{CO_2}$ gas is made.
- $\mathbf{CO_2}$ will turn **limewater cloudy**.