GROUP 17 : INORGANIC CHEMISTRY
↳ Halogens

- Also known as p-block elements

Fluorine	F	9	$1s^2 2s^2 2p^5$
Chlorine	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Bromine	Br	35	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
Iodine	I	53	$[Kr]\ 4d^{10} 5s^2 5p^5$
Astatine	At	85	Radioactive

Element	Color	State at RTP	B.P/°C	Solubility in water	Solubility in organic
F_2	Pale yellow	Gas	-188	Soluble	–
Cl_2	Yellow Green	Gas	-35	Moderately soluble	Yellowish solution
Br_2	Dark Red	Liquid	58	Slightly soluble	Orange-brown Solution
I_2	Black	Solid	183	Insoluble	Violet-purple Solution
Astatine	Black	Solid	–	–	–

Note: Aqueous Iodine is actually iodine dissolved in KI(aq) and not in water.

$I_2(s) + KI(aq) \longrightarrow KI_3(aq)$ → aqueous iodine
red-brown solution

PHYSICAL PROPERTIES

1. Atomic Radius
   - Increases down the group
   - as there are more complete shells of electrons

2. 1st Ionisation Energy
   - Decreases down the group
   - Down the group, the outer electrons experience a greater shielding effect

3. Boiling points
   - Increasing down the group
     ↳more polarisable electrons, stronger ID-ID forces of attraction and hence more energy required to overcome them
   - Volatility decreases

CHEMICAL PROPERTIES / REACTIONS

1. Oxidising power
   - All halogens are oxidising agents so they themselves get reduced by gaining an electron

$$X_2 + 2e^- \longrightarrow 2X^- \quad \text{where X is a halogen}$$

strongest oxidising agent because of its smaller radius and higher charge density ← $F_2 + 2e^- \longrightarrow 2F^-$ → weakest reducing agent

$Cl_2 + 2e^- \longrightarrow 2Cl^-$

oxidising power decreases ↓

$Br_2 + 2e^- \longrightarrow 2Br^-$

Weakest oxidising agent because of it's larger radius and lower charge density ← $I_2 + 2e^- \longrightarrow 2I^-$ → Strongest Reducing agent

- The oxidising power decreases down the group as the atomic radius increases, the element gains an electron less readily as the charge density decreases

F +9 → Smaller radius ↳ higher charge density ↳ attracts e^- more readily

I +53 → bigger radius ↳ lesser charge density ↳ attracts e^- less readily

Comparing the strengths of the oxidising agent

- Cl_2 and Br_2 can oxidise $Na_2S_2O_3$, sodium thiosulfate, to Na_2SO_4, sodium sulfate easily
- But I_2 oxidizes $Na_2S_2O_3$ to $Na_2S_4O_6$ (sodium tetrathionate)

Gonna compare oxidation no.'s in these two oxidation rxns.

with Br_2/Cl_2 → $\overset{0}{4Cl_2} + \overset{+2}{S_2O_3} + 5H_2O \xrightarrow{\text{oxidation}} \overset{+6}{2SO_4^{2-}} + 10H^+ + \overset{-1}{8Cl^-}$

- Oxid. state of S changes from +2 to +6 with Cl_2/ Br_2

with I_2 → $\overset{0}{I_2} + 2\overset{+2}{S_2O_3} \xrightarrow{\text{oxidation}} \overset{+2.5}{S_4O_6} + 2\overset{-1}{I^-}$

- Oxid. state of S changes from +2 to +2.5 with I_2

- Cl_2 is a stronger oxidising agent than I_2, because it oxidised $Na_2S_2O_3$ to a greater extent. The oxidation state of S changed by +4.
- I_2 is a weaker O.A than Cl_2 because it oxidised $Na_2S_2O_3$ to a lesser extent The oxidation state of S changed by +0.5.

REACTIONS OF HALOGENS WITH HYDROGEN GAS

- All halogens react with H_2 gas to form hydrides HX

$$X_2 + H_2 \longrightarrow 2HX$$

$F_2(g) + H_2(g) \longrightarrow 2HF(g)$ explodes with H_2 / very rapid

$Cl_2^{(g)} + H_2^{(g)} \longrightarrow 2HCl(g)$ rapid rxn / explodes in sunlight

$Br_2^{(l)} + H_2^{(g)} \longrightarrow 2HBr(g)$ slow rxn, heat at 200°C, Pt catalyst

$I_2^{(s)} + H_2^{(g)} \rightleftharpoons 2HI(g)$ no rxn unless heated strongly

HF, HCl, HBr, HI → all are white vapours / fumes

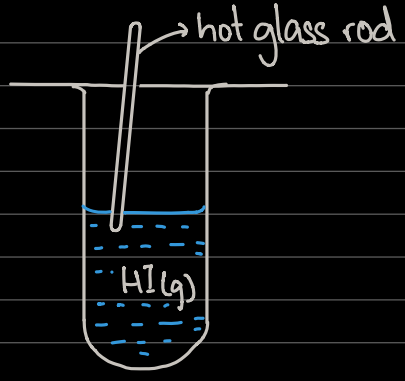
Thermal stability of the hydrides:

- As the size of the halogen increases down the group, the H–X bond gets weaker / longer

$HF \xrightarrow{\text{heat}}$ No rxn
$HC \xrightarrow{\text{heat}}$ No rxn
} → Stable to heat

$2HBr \xrightarrow{\text{heat}} H_2(g) + Br_2(g)$
red-brown vapour that condenses to red-brown liquid

$2HI \rightleftharpoons H_2(g) + I_2(g)$
purple vapour that solidifies to a black solid



- The hot glass rod provides sufficient energy to break the H-I bond.

$$2HI \underset{\text{rod}}{\overset{\text{hot glass}}{\rightleftharpoons}} H_2 + I_2$$

purple vapor or black solid

DISPLACEMENT REACTIONS

- A more reactive halogen will displace a less reactive halogen from it's compound
- Each halide ion can be oxidised by the halogen above it in the group

	$Cl_2(g)$	$Br_2(l)$	$I_2(s)$
NaCl	No Rxn	No Rxn	No Rxn
NaBr	$Cl_2 + 2NaBr \rightarrow 2NaCl + Br_2$ Yellow-green color fades Red-brown vapor/liquid seen	No Rxn	No Rxn
NaI	$Cl_2 + 2NaI \rightarrow 2NaCl + I_2$ Yellow-green color of $Cl_2(g)$ fades — Purple vapors of I_2	$Br_2 + 2NaI \rightarrow 2NaBr + I_2$ Purple vapor or black solid Red-brown color of Br_2 disappears	No Rxn

TESTS FOR THE HALIDE IONS

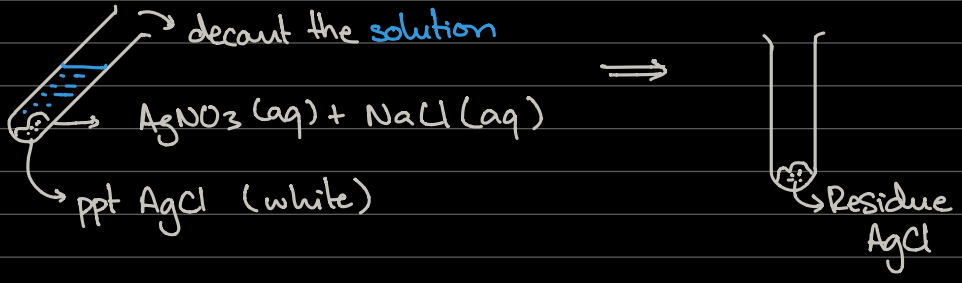
Steps:
1. to the unknown halide, add acidified $AgNO_3(aq)$
2. to the same reaction (test tube), add excess $NH_3(aq)$

CHLORINE

STEP 1:

- the silver halide ppts out

$$NaCl(aq) + AgNO_3(aq) \longrightarrow NaNO_3(aq) + \underbrace{AgCl(s)}_{\text{white ppt}}$$ → what reacts (or does not react) with NH_3 aq.

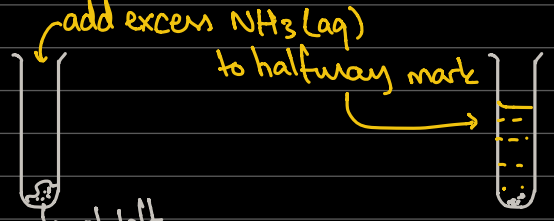


STEP 2:

diammine silver (I) chloride

$AgCl(s) + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$

(fully dissolves in; excess NH_3; $[Ag(NH_3)_2]^+$ soluble) → one compound



If the white ppt dissolves → the salt is a chloride

BROMINE

STEP 1:

Remember, all nitrates = soluble

$NaBr(aq) + AgNO_3(aq) \longrightarrow NaNO_3(aq) + AgBr(s)$

$AgBr(s)$: cream-colored ppt

Ionic: $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$

STEP 2:

$AgBr(s) + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]^+ + Br^-(aq)$

(only partially dissolves in excess NH_3)

$[Ag(NH_3)_2]^+$: only partially soluble

IODINE

STEP 1:

$NaI(aq) + AgNO_3(aq) \longrightarrow NaNO_3(aq) + AgI(s)$

$AgI(s)$: pale yellow ppt

STEP 2:

$AgI(s) + NH_3(aq) \longrightarrow$ No Rxn

(not soluble in NH_3)

Hence insoluble

SUMMARY OF TESTS

	$AgNO_3(aq)$	dilute $NH_3(aq)$	conc. $NH_3(aq)$
NaCl	AgCl white	Soluble	Soluble
NaBr	AgBr cream	Partially Soluble	Soluble
NaI	AgI pale yellow	Insoluble	Insoluble

REACTIONS WITH CONC H_2SO_4

Cl $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl(g)$ → white fumes

could have written Na_2SO_4 but this is preferred

Br $NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr(g)$ → white fumes

$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$

- Br_2: red-brown gas evolves
- SO_2: colourless acidic oxide, RA
  - can be tested using a strip of filter paper dipped in $KMnO_4$

- Concentrated H_2SO_4 behaves as an oxidising agent, as it has been reduced from H_2SO_4 to SO_2
- Bromide ions are reducing agents, as Br^- has been oxidised to Br_2

I $NaI + H_2SO_4 \longrightarrow NaHSO_4 + HI(g)$ white fumes

$8HI + H_2SO_4 \longrightarrow 4I_2 + H_2S(g) + 4H_2O$ (conc.)

- $4I_2$: purple vapour
- $H_2S(g)$: pungent odour

- The iodide ion is a better reducing agent than the bromide ion because it was able to reduce sulfur from +6 to −2 (overall change of −8)
  - Bromide ion was only able to cause an overall change of −2 (+6 to +4)
- Conc. H_2SO_4 is not strong enough to oxidise HCl to Cl or HF to F, so we don't talk about those rxns.

REACTION OF Cl_2 WITH NaOH(aq) OR OTHER ALKALIS

1. cold, dilute NaOH (aq) (15°C)

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

Cl_2 has been both oxidised and reduced

"Disproportionation": when the same species is both oxidised and reduced

2. hot, concentrated NaOH (aq) at 70°C

$$3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$

sodium chlorate(V)

- Also disproportionation

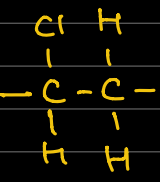
USES OF HALOGENS

FLUORINE

- Used to manufacture CFCs (chlorofluorocarbons)
- Used to manufacture polymers (ie. PTFE – Teflon)

CHLORINE

- Used to manufacture polymers (ie. PVC - Polyvinyl chloride)



- Used to make bleach (NaClO)
- Used in the manufacture of HCl acid
- Used as a disinfectant in the purification of water:

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

↳ disinfectant hypochlorous acid

- Used to make organic solvents (ie. CH_2Cl_2, CCl_4, $CHCl_3$)

BROMINE

- AgBr is used in photography (film)
- Used to make dyes and pharmaceutical compounds
- Used to make flame retardants (ie CH_2BrCl)

IODINE

- Mild antiseptic
- AgI is used to develop photographic film