UNIT 11 - GROUP 17

The Halogens

Group 17 consist of reactive non-metals which exist as diatomic molecules.

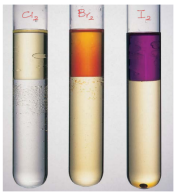
- They are volatile non-metals
- They exist as diatomic molecules that attract each other by van der Waals' forces (temporary and induced dipoles)
- Melting points increase down the group due to greater van der Waals' forces
- Decrease in reactivity down the group due to increasing atomic radius (outermost electron experiences less nuclear attraction)
- Reducing power increases down the group

Physical properties

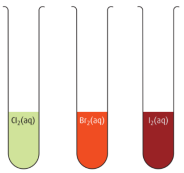
Element	Appearance	Boiling point/K	Electronegativity
Fluorine	Pale yellow gas	85	4.0
Chlorine	Yellow-green gas	238	3.0
Bromine	Dark red liquid	332	2.8
Iodine	Shiny dark grey solid	457	2.5

Colours of Solutions

Halogens in a non-polar organic solvent.



Chlorine solution is pale yellow-green, bromine solution is orange & iodine solution is red brown.



Hydrogen Halides

All the halogens can react with hydrogen, but the conditions vary due to the decreasing oxidising ability of the halogens. The reactivity with hydrogen decreases down the group due to the decreasing strength of the H-X bond, making the reaction less exothermic.

Halogen	Reaction condition	Equation	H_X Bond value
Chlorine	Explosive when exposed to UV light	$Cl_{2(g)} + H_{2(g)} \rightarrow 2HCl_{(g)}$	H–Cl 431 kJ/mol
Bromine	Slow reaction when heated	$Br_{2(g)} + H_{2(g)} \rightarrow 2HBr_{(g)}$	H–Br 366 kJ/mol
Iodine	Reversible reaction when heated	$I_{2(g)} + H_{2(g)} \rightleftharpoons 2HI_{(g)}$	H–I 299 kJ/mol

Hydrogen Halides are all colourless gases with the formula H-X. The bonds between hydrogen and the halogens are polar. Hydrogen chloride, hydrogen bromide and hydrogen iodide are similar in that they are very soluble in water to form acidic solutions.

Thermal Decomposition of H-X

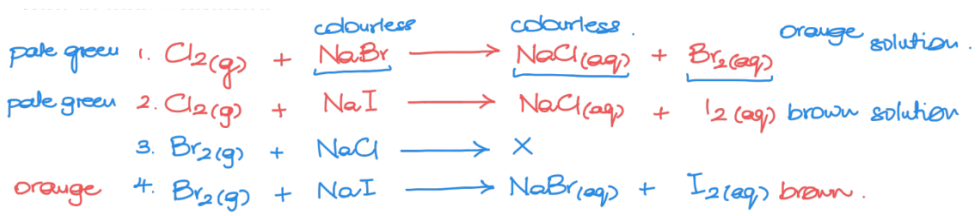
The bond energies decrease going down the group, making it easier to break the H-X bond. Hence, HI is less thermally stable than HCl.

Halogen	Reaction (if any)	Comment
chlorine	HCl(g)	no decomposition
bromine	$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$	some decomposition and gas appears slightly brown
iodine	$2HI(g) \rightarrow H_2(g) + I_2(g)$	almost complete decomposition and gas appears deep purple

Halides

Halide ions are ions of halogen elements in oxidation state -1.

A more reactive halogen oxidises the ions of a less reactive halogen. As halogens are oxidising agents, a more powerful oxidising agent displaces one that is less powerful.



Test for Halides

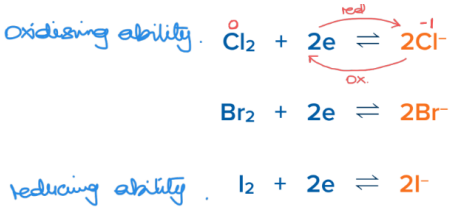
Using an acidified solution of silver nitrate.

Silver halides are insoluble. Adding silver nitrate to a solution of halides will produce a precipitate.

Halide ion	Reaction with $Ag^+(aq)$	Subsequent reaction with $NH_3(aq)$
Chloride	White precipitate is formed	Dissolves to form colourless solution
Bromide	Cream precipitate is formed	Only dissolves in concentrated ammonia
Iodide	Yellow precipitate is formed	Insoluble in ammonia

Redox Reactions

The forward reaction is the reduction of halogens, and the backward reaction is the oxidation of halides. Since oxidation power is based on the tendency to gain electrons, and reduction power is based on the tendency to lose electrons, a strong oxidising halogen has a weaker reducing halide.



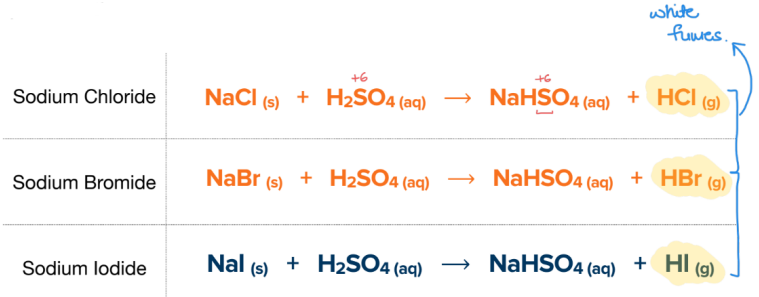
Reactions with Concentrated Sulfuric Acid

Adding concentrated sulfuric acid to a solid halide can be used as a test to distinguish between halides.

Down the group halides are strong reducing agents, they can further react to reduce sulphuric acid into many oxidation states.

Concentrated Sulfuric Acid with metal halides

When concentrated sulphuric acid is added to a solid metal halide, a hydrogen halide is produced.

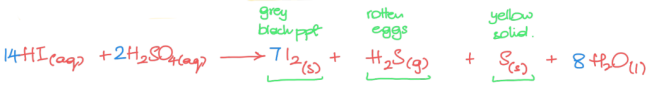


Concentrated Sulfuric Acid with H-X

Conc. sulfuric acid is a strong oxidising agent, but not strong enough to oxidise HCl.

However, with HBr, the principal products bromine and sulphur dioxide are produced.

HI is so easily oxidised that only a trace amount of it is found. The sulfuric acid is reduced not only to sulphur dioxide but further to sulphur and even to hydrogen sulphide.

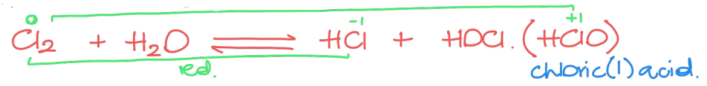


Halide	Observations	Product	Oxidation State of S	Reaction type
Chloride	White fumes	HCl	−1	Displacement of halide
Bromide	White fumes	HBr	−1	Displacement of halide
	Brown vapour	Br_2	0	Oxidation of halide
	Colourless gas	SO_2	+4	Reduction of acid
Iodide	White fumes	HI	−1	Displacement of halide
	Purple vapour	I_2	0	Oxidation of halide
	yellow solid	S_8	0	Reduction of sulfur
		H_2S	−2	

Disproportionation of Chlorine

When chlorine reacts with water and alkalis, chlorine oxoanions are formed.

Chlorine dissolves in water (reversible reaction) to form a mixture of weak chloric (I) acid and strong hydrochloric acid. A disproportionation reaction is one where an element can undergo both oxidation as well reduction in the same reaction. Bromine reacts in a similar way but to a much lesser extent. Iodine is almost insoluble in water and hardly reacts.



Chlorine with cold NaOH

When chlorine dissolves in NaOH at room temperature, it produces chlorate (I) and chloride ions:

Chlorine with hot NaOH

When chlorine is passed through hot conc. NaOH, it produces chloride ions and chlorate (V) :

Economic importance of Halogens

- Chlorine in water purification
- Manufacturing bleach (sodium chlorate (I), NaClO)
- Manufacturing PVC (poly chloroethene)
- Halogenated hydrocarbons
- CCl4 (tetrachloroethane) - dry cleaning solvent
- CFCs, aerosols
- Dettol