9701 CHEMISTRY · TOPIC 11 · AS LEVEL

Group 17 — The Halogens

SHEET 1 OF 1
QUICK REVISION

01 · APPEARANCE AND VOLATILITY

Halogen	State	Colour
Cl_2	gas	pale green
Br_2	liquid	red-brown
I_2	solid	grey-black, purple vapour

All are diatomic. Boiling point **rises down the group**: more electrons per molecule means stronger London forces, so volatility falls.

02 · OXIDISING POWER

Decreases down the group. The atom gets larger and more shielded, so it attracts an electron less strongly and is reduced less readily.

Electronegativity and electron affinity both fall down the group, and E° values follow: F_2 +2.87, Cl_2 +1.36, Br_2 +1.07, I_2 +0.54 V.

03 · DISPLACEMENT REACTIONS

A halogen displaces the halide of any halogen **below** it.

Added to	Cl^-	Br^-	I^-
Cl_2	—	orange	brown
Br_2	none	—	brown
I_2	none	none	—

$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$. Shake with an organic solvent to confirm: Br_2 orange, I_2 violet in the hydrocarbon layer.

04 · HALIDE IONS AS REDUCING AGENTS

Reducing power increases down the group — the larger ion loses its outer electron more easily. This is the reverse of the halogens' oxidising trend.

Shown by the reaction with concentrated H_2SO_4, where the halide reduces the sulfur to progressively lower oxidation states.

05 · HALIDES WITH CONCENTRATED H_2SO_4

Halide	Products	Seen
Cl^-	HCl only	steamy fumes
Br^-	$HBr + Br_2 + SO_2$	red-brown fumes
I^-	$HI + I_2 + H_2S$	purple vapour, bad-egg smell

Sulfur is reduced from +6 to +4 (SO_2) by Br^- and as far as −2 (H_2S) by I^-, proving iodide is the strongest reducing agent.

06 · TESTING FOR HALIDE IONS

Acidify with dilute HNO_3 (removes carbonate), then add $AgNO_3$(aq):

Ion	Precipitate	In NH_3(aq)
Cl^-	white	dissolves in dilute
Br^-	cream	dissolves in concentrated
I^-	pale yellow	insoluble

$Ag^+ + X^- \rightarrow AgX(s)$. Solubility in ammonia falls down the group, which is what separates the three.

07 · CHLORINE WITH WATER

$Cl_2 + H_2O \rightleftharpoons HCl + HClO$

Chlorine **disproportionates**: 0 → −1 and +1. HClO is the bactericide used to treat water; the risk of chlorine's toxicity is judged against the far larger benefit of killing waterborne pathogens.

08 · CHLORINE WITH ALKALI

Cold dilute NaOH
$Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$
0 → −1 and +1 · the bleach reaction

Hot concentrated NaOH
$3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$
0 → −1 and +5

09 · HYDROGEN HALIDES

All are colourless gases that fume in moist air and dissolve to give acidic solutions.

Thermal stability decreases down the group — the H–X bond gets longer and weaker, so HI decomposes to iodine and hydrogen on gentle heating while HCl does not.

10 · WORKED EXAMPLE — IDENTIFY THE HALIDE

A solution gives a cream precipitate with acidified $AgNO_3$ that dissolves only in concentrated ammonia. Warmed with concentrated H_2SO_4 it gives red-brown fumes and a choking gas.

Cream + concentrated NH_3 → **Br^-**
Red-brown fumes = Br_2, choking gas = SO_2
$2Br^- + 2H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O + SO_4^{2-}$

11 · USES

Chlorine — water treatment, bleach, PVC and solvents. Bromine — flame retardants and silver bromide in photography. Iodine — antiseptic and dietary supplement.

Chlorofluorocarbons were once used as refrigerants and propellants but are now banned because their chlorine radicals catalyse ozone depletion.

12 · EQUATIONS TO KNOW

$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$
$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$
$Br_2 + 2I^- \rightarrow 2Br^- + I_2$

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

$Cl_2 + H_2O \rightleftharpoons HCl + HClO$
$Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$
$3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

13 · WORKED EXAMPLE — DISPLACEMENT

Chlorine water is shaken with aqueous potassium iodide and a little hexane. Describe and explain what is seen.

The aqueous layer turns brown as iodine forms; the hexane layer above turns violet because iodine is more soluble in the non-polar solvent.

$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$
Chlorine is the stronger oxidising agent, so it takes electrons from iodide.

TRENDS IN ONE LINE

Down Group 17: radius ↑, electronegativity ↓, boiling point ↑, oxidising power of X_2 ↓, reducing power of X^- ↑, stability of HX ↓.

Two ideas do all the explaining: increasing atomic size with more shielding, and increasing numbers of electrons for London forces.

MARKS LOST HERE

— Reversing the two trends: X_2 gets **less** oxidising down the group while X^- gets **more** reducing.

— Acidifying the halide test with HCl, which adds chloride of its own.

— Missing the change in oxidation numbers when asked to prove disproportionation.

— Explaining boiling points by "stronger covalent bonds"; it is London forces between molecules.