Group 17 elements

Fluorine (F_2) - pale yellow colour gas

Chlorine (Cl_2) - pale green colour gas

Bromine (Br_2)- red-brown fuming liquid

Iodine (I_2) - violet-black solid with lustrous effect

Astatine (At)- radioactive metal

(Fluorine to Iodine: non metals)

Group trends

Halogens are reactive and can only be found naturally as compounds.

Fluorine is the most electronegative element and exhibits -1 and 0 oxidation states.

The halogens other than fluorine form stable compounds corresponding to nearly all values of the oxidation numbers from -1 to +7. However, compounds of bromine with the oxidation state of +7 are unstable.

Due to the smaller atomic radius, fluorine can stabilize higher oxidation states of other elements.

Eg: MnF_4, CuF_2

Oxidizing ability of halogens decreases down the group. Fluorine is a powerful oxidizing agent. The reactivity of halogens decreases down the group. This can be explained by using the displacement reactions of halogens.

$Cl_2(aq) + 2NaBr(aq) \longrightarrow 2NaCl(aq) + Br_2(aq)$

$Br_2(aq) + 2NaI(aq) \longrightarrow 2NaBr(aq) + I_2(aq)$:

The bond energy of F_2 (155 kJ mol-1) is less than that of Cl_2 (240 kJ mol-1) due to repulsion between the non-bonded electron pairs of fluorine atoms (due to its smaller size). This is a reason for the high reactivity of fluorine gas. Down the Group 17 bond energies show a gradual decrease (Cl_2 = 240 kJ mol-1, Br_2 = 190 kJ mol-1 and I_2 = 149 kJ mol-1).

Bond energies decrease in the order; $Cl_2<Br_2<F_2<I_2$

Properties of Group 17 elements

	F	Cl	Br	I	**At
Ground state electronic configuration	$[He]2s^2 2p^5$	$[Ne]3s^2 3p^5$	$[Ar]3d^{10} 4s^2 4p^5$	$[Kr]4d^{10} 5s^2 5p^5$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^5$
van der Waals radius/ pm	135	180	195	215	-
Ionic radius X^-/ pm	133	181	196	220	-
Covalent radius/pm	71	99	114	133	-
Melting point/ °C	-220	-101	-7.2	114	-
Boiling point/ °C	-188	-34.7	55.8	184	-
Pauling electronegativity	4.0	3.2	3.0	2.7	-
Electron gain enthalpy/ kJ mol^{-1} $X(g) + e \longrightarrow X^-(g)$	-328	-349	-325	-295	-

***Not relevant to the current G. C. E. (A/L) Chemistry Syllabus*

Simple compounds of Group 17

1. Hydrogen halides

Hydrogen halides are acidic in water. HF has the ability to produce extensive hydrogen bonding; however, HF is a gas (boiling point 20 °C) at room temperature and under atmospheric pressure.

Q: compare boiling points of hydrogen halides and give reason.

Acidic nature of hydrogen halides in aqueous solutions

For HF; $HF(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$, partial dissociation(weak acid)

For other hydrogen halides (HCl, HBr and HI);

$HX(g) + H_2O(l) \longrightarrow H_3O^+(aq) + X^-(aq)$, complete dissociation(strong acid)

HF is a weak acid whereas the other hydrogen halides are strong acids in the aqueous medium. HF has the high bond energy (strongest covalent bond), which makes it difficult to dissociate in water to produce H^+ ions readily. The acidic strength of hydrogen halides increases down the Group 17. This can be explained using the same fact mentioned above. Some selected properties of Group 17 hydrogen halides are shown in below table.

	HF	HCl	HBr	HI
Melting point/ °C	-84	-114	-89	-51
Boiling point / °C	20	-85	-67	-35
Bond length/ pm	92	127	141	161
Bond dissociation energy/ kJ mol^{-1}	570	432	366	298

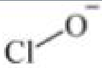
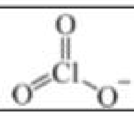
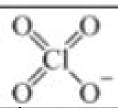
2. Silver halides

Silver halides can be used to identify the halides (chloride, bromide, and iodide) using the colour of the precipitate. Few selected properties are shown below.

Silver halide	Colour	Solubility in ammonia
AgCl	White	Dissolves in dil. aqueous ammonia
AgBr	Pale yellow	Dissolves in conc. aqueous ammonia
AgI	Yellow	Insoluble in both dil. and conc. aqueous ammonia

3. Oxides and Oxo acids of chlorine

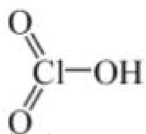
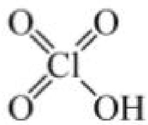
Chlorine forms several oxides and oxoanions with variable oxidation states. Some oxoanions are strong oxidizing agents. Selected oxides of chlorine are shown below.

Oxidation state	Formula of oxide	Formula of oxoanion	Structure of oxoanion
+1	Cl_2O	ClO^-	
+3		ClO_2^-	
+5		ClO_3^-	
+6	ClO_3 and Cl_2O_6		
+7	Cl_2O_7	ClO_4^-	

Chlorine forms four types of oxoacids. The acidic strength increases with the increasing oxidation number of the chlorine atom. Oxidizing power of oxoacids of chlorine changed as follows.

$HClO > HClO_2 > HClO_3 > HClO_4$

The oxidation state of chlorine in $HClO$, $HClO_2$, $HClO_3$, $HClO_4$, respectively are +1, +3, +5 and +7. The higher the oxidation state the stronger the acid will be. Therefore the variation of acidic strength is $HClO < HClO_2 < HClO_3 < HClO_4$.

	$HClO$	$HClO_2$	$HClO_3$	$HClO_4$
Oxidation state	+1	+3	+5	+7
Structure				

4. Halides

Most covalent halides react vigorously with water. But CCl4 does not hydrolyze (organic compound). Most fluorides and some other halides are inert.

Chlorides of group 14 and 15 elements react with less water as follows.

$SiCl_4(l) + 2H_2O(l) \longrightarrow 4HCl(aq) + SiO_2(s)$

$PCl_5(l) + H_2O(l) \longrightarrow POCl_3(aq) + 2HCl(aq)$

Chlorides of group 14 and 15 elements react excess water as follows.

$SiCl_4(l) + 3H_2O(l) \longrightarrow 4HCl(aq) + H_2SiO_3(aq)$

$NCl_3(l) + 3H_2O(l) \longrightarrow NH_3(aq) + 3HOCl(aq)$

$PCl_3(l) + 3H_2O(l) \longrightarrow H_3PO_3(aq) + 3HCl(aq)$

$PCl_5(l) + 4H_2O(l) \longrightarrow H_3PO_4(aq) + 5HCl(aq)$

$AsCl_3(s) + 3H_2O(l) \longrightarrow H_3AsO_3(aq) + 3HCl(aq)$

$SbCl_3(aq) + H_2O(l) \longrightarrow SbOCl(s) + 2HCl(aq)$

$BiCl_3(aq) + H_2O(l) \longrightarrow BiOCl(s) + 2HCl(aq)$