The p-Block Elements

Group 17 Elements

Fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At) are the members of Group 17. They are collectively known as the halogens (means salt producers). They are highly reactive non-metallic elements. All these elements have seven electrons in their outermost shell (ns^2np^5) and so they do not readily lose their electron. So they have very high ionisation enthalpy.

Halogens have maximum negative electron gain enthalpy in the corresponding periods. This is due to the fact that the atoms of these elements have only one electron less than stable noble gas configurations. Electron gain enthalpy of these elements decreases down the group. However, the negative electron gain enthalpy of fluorine is less than that of chlorine. It is because, in fluorine the incoming electron goes to the 2p sub shell, but in Cl it enters in to the 3p sub shell. Due to the compactness of 2p sub shell compared to 3p sub shell, the electron – electron repulsion is greater in fluorine than in chlorine. So F does not easily gains electron.

Halogens have very high electronegativity. The electronegativity decreases down the group.

Fluorine is the most electronegative element in the periodic table.

All halogens have characteristic colour. For example, F_2 has yellow, Cl_2-greenish yellow, Br_2-red and I_2, violet colour. This is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level.

The bond dissociation enthalpy of F_2 is low. This is due to the relatively large electron-electron repulsion among the lone pairs in F_2 molecule.

All the halogens are highly reactive. They react with metals and non-metals to form halides. The reactivity of the halogens decreases down the group.

Halogens are strong oxidising agents since they readily accept electron. F_2 is the strongest oxidising halogen and it oxidises other halide ions in solution or in the solid phase.

Oxidation states

All the halogens exhibit –1 oxidation state. Chlorine, bromine and iodine also show + 1, + 3, + 5 and + 7 oxidation states in their oxides, oxy acids and in inter halogen compounds. Due to the absence of vacant d orbitals and the maximum electronegativity, fluorine exhibits only –1 oxidation state.

Anomalous behavior of fluorine

Due to the small size, highest electronegativity, low F-F bond dissociation enthalpy, and non availability of d orbitals in valence shell, fluorine shows properties different from other halogens.

Some of the anomalous properties of fluorine are:

1. Ionisation enthalpy, electronegativity, enthalpy of bond dissociation and electrode potentials are higher for fluorine than expected.
2. Ionic and covalent radii, m.p. and b.p. and electron gain enthalpy are quite lower than expected.
3. Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements).
4. F forms only one oxoacid while other halogens form a number of oxoacids.
5. Hydrogen fluoride is a liquid due to strong hydrogen bonding. While the hydrogen halides of other elements are gases.

Hydrides of halogens

Halogens react with hydrogen to give hydrogen halides which dissolve in water to form hydrohalic acids. The acidic strength of these acids varies in the order: HF < HCl < HBr < HI. The stability of these halides decreases down the group due to decrease in bond dissociation enthalpy from HF to HI.

Chlorine (Cl_2)

Preparation: It can be prepared by any one of the following methods:

(i) By heating manganese dioxide with concentrated hydrochloric acid.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

Conc. HCl can be replaced by a mixture of common salt and concentrated

$$H_2SO_4\ 4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$$

(ii) By the action of HCl on potassium permanganate.

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

Manufacture of chlorine

(i) **Deacon's process**: By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K. $4HCl + O_2 + CuCl_2 \rightarrow 2Cl_2 + 2H_2O$

(ii) **Electrolytic process**: Chlorine is obtained by the electrolysis of brine solution (concentrated NaCl solution). During electrolysis chlorine is liberated at the anode.

Properties: It is a greenish yellow gas with pungent and suffocating odour. It is soluble in water. It reacts with a number of metals and non-metals to form chlorides.

$$2Al + 3Cl_2 \rightarrow 2AlCl_3; \qquad P_4 + 6Cl_2 \rightarrow 4PCl_3$$
$$2Na + Cl_2 \rightarrow 2NaCl; \qquad S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$$
$$2Fe + 3Cl_2 \rightarrow 2FeCl_3\ ;$$

With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas with excess chlorine, nitrogen trichloride (explosive) is formed.

$$8NH_3 + 3Cl_2 \rightarrow 6NH_4Cl + N_2; \quad NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$$
(excess) (excess)

With cold and dilute alkalies chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate.

$$2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$$
(cold and dilute)

$$6\ NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$$
(hot and conc.)

With dry slaked lime it gives bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$$

Chlorine reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with unsaturated hydrocarbons.

$CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$

Methane Methyl chloride

$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$

Ethene 1,2-Dichloroethane

Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl. Hypochlorous acid (HOCl) so formed is unstable and dissociates to give nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

(i) It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.

$$2FeSO_4 + H_2SO_4 + Cl_2 \rightarrow Fe_2(SO_4)_3 + 2HCl$$

$$Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$$

$$SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$$

$$I_2 + 6H_2O + 5Cl_2 \rightarrow 2HIO_3 + 10HCl$$

(ii) It is a powerful bleaching agent; bleaching action is due to oxidation.

$$Cl_2 + H_2O \rightarrow 2HCl + [O]$$

Coloured substance + [O] → Colourless substance

It bleaches vegetable or organic matter in the presence of moisture. Its bleaching action is permanent.

Uses: It is used

(i) for bleaching wood pulp, bleaching cotton and textiles,

(ii) in the extraction of gold and platinum

(iii) in the manufacture of dyes, drugs and organic compounds such as CCl_4, $CHCl_3$, DDT, refrigerants, etc.

(iv) in sterilising drinking water and

(v) preparation of poisonous gases such as phosgene ($COCl_2$), tear gas (CCl_3NO_2), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

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