Chemistry Study Materials for Class 12
(NCERT Based Notes of Chapter – 7)

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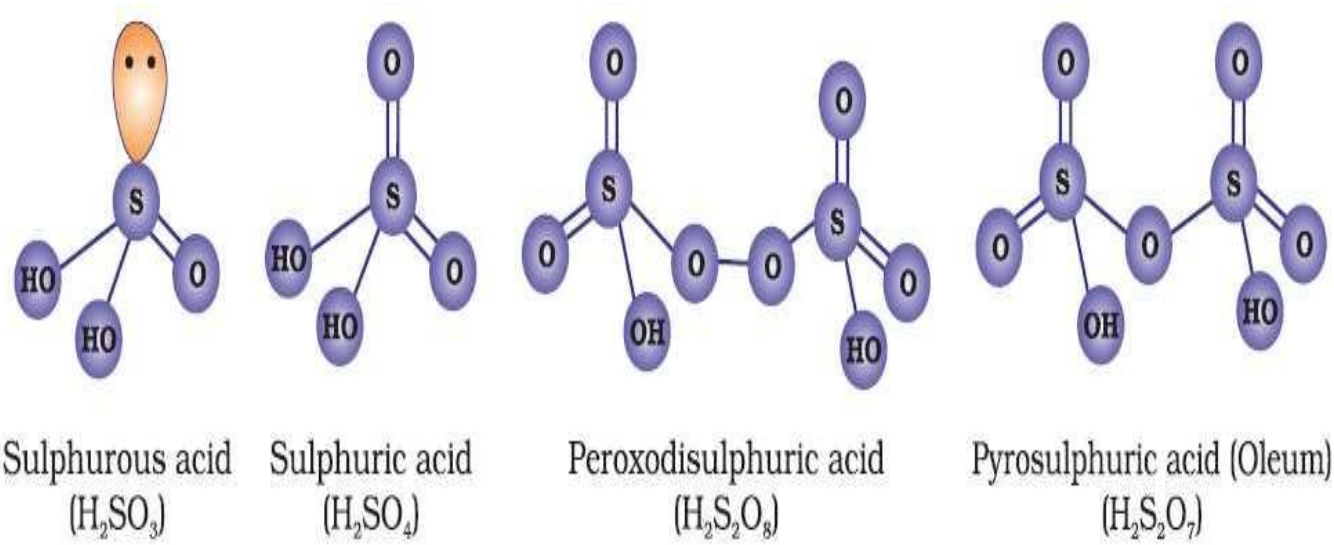
The p-Block Elements

Oxoacids of sulphur

Sulphur forms a large no. of oxoacids like Sulphurous acid (H_2SO_3), Dithionous acid ($H_2S_2O_4$), Sulphuric acid (H_2SO_4), Pyrosulphuric acid (Oleum, $H_2S_2O_7$), Peroxomonosulphuric acid (Caro's acid, H_2SO_5), Peroxodisulphuric acid (Marshell's acid, $H_2S_2O_8$) etc. structure of some oxoacids are:



Sulphuric Acid (H_2SO_4)

The most important oxoacid of sulphur is sulphuric acid which is also known as the '*King of Chemicals*'.

Manufacture:

Sulphuric acid is manufactured by the **Contact Process** which involves three steps:

(i) burning of sulphur or sulphide ores in air to generate SO_2.

$S(s) + O_2(g) \rightarrow SO_2(g)$ **Or,**

$4\ FeS_2(s) + 11\ O_2(g) \longrightarrow 2\ Fe_2O_3(s) + 8\ SO_2(g)$

(ii) conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5)

$$2SO_2 + O_2 \rightarrow 2SO_3$$

(iii) absorption of SO_3 in H_2SO_4 to give *Oleum* ($H_2S_2O_7$).

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

(iv) Dilution of oleum with water gives H_2SO_4 of the desired concentration.

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

Properties

Sulphuric acid is a colourless, dense, oily liquid. It dissolves in water with the evolution of a large quantity of heat. Hence, for diluting the acid, the concentrated acid must be added slowly into water with constant stirring.

Chemical properties: The chemical reactions of sulphuric acid are due to the following reasons:

(a) its low volatility

(b) strong acidic character

(c) strong affinity for water and

(d) its ability to act as an oxidising agent.

In aqueous solution, sulphuric acid ionises in two steps.

$$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-$$

$$HSO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + SO_4^{2-}$$

So it is dibasic and forms two series of salts: normal sulphates and acid sulphates.

Because of its low volatility sulphuric acid can be used for the manufacture of more volatile acids from their corresponding salts.

$2\ MX + H_2SO_4 \rightarrow 2\ HX + M_2SO_4$ (where X = F, Cl, NO_3 etc. and M is a metal)

Concentrated sulphuric acid is a strong dehydrating agent and drying agent. Many wet gases can be dried by passing them through sulphuric acid. Sulphuric acid removes water from organic compounds

e.g.: $C_{12}H_{22}O_{11} + H_2SO_4 \rightarrow 12C + 11H_2O$

Hot concentrated sulphuric acid is a moderately strong oxidising agent. It oxidises both metals and non- metals and the acid itself reduces to SO_2.

$$Cu + 2\ H_2SO_4(conc.) \rightarrow CuSO_4 + SO_2 + 2H_2O$$

$$S + 2H_2SO_4(conc.) \rightarrow 3SO_2 + 2H_2O$$

$$C + 2H_2SO_4(conc.) \rightarrow CO_2 + 2\ SO_2 + 2\ H_2O$$

Uses: The important uses of Sulphuric acid are:

1) In the manufacture of fertilizers 2) in petroleum refining 3) in the manufacture of pigments, paints and dyestuff intermediates 4) in detergent industry 5) in metallurgical applications 6) as electrolyte in storage batteries 7) in the manufacture of nitrocellulose products and 8) as a laboratory reagent.

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.

$2Al + 3Cl_2 \rightarrow 2AlCl_3$; $P_4 + 6Cl_2 \rightarrow 4PCl_3$

$2Na + Cl_2 \rightarrow 2NaCl$; $S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$

$2Fe + 3Cl_2 \rightarrow 2FeCl_3$;

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

$8NH_3 + 3Cl_2 \rightarrow 6NH_4Cl + N_2$; $NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$

(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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