CHEMISTRY STUDY MATERIALS FOR CLASS 12 GANESH KUMAR DATE: 30/06/2020

The p-Block Elements

Dioxygen (O₂)

Preparation: (i) By heating chlorates, nitrates and permanganates.

 $2\text{KClO}_3 \xrightarrow{\text{Heat}} 2\text{KCl} + 3\text{O}_2$

(ii) By the thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals.

$$2Ag_2O(s) \rightarrow 4Ag(s) + O_2(g); \qquad 2Pb_3O_4(s) \rightarrow 6PbO(s) + O_2(g)$$
$$2HgO(s) \rightarrow 2Hg(l) + O_2(g); \qquad 2PbO_2(s) \rightarrow 2PbO(s) + O_2(g)$$

(iii) By the decomposition of Hydrogen peroxide (H_2O_2) in presence of manganese dioxide.

$$2H_2O_2(aq) \rightarrow 2H_2O(1) + O_2(g)$$

(iv) On large scale it can be prepared from water or air. Electrolysis of water leads to the release of hydrogen at the cathode and oxygen n at the anode. It is also obtained by the fractional distillation of air. *Properties:*

Dioxygen directly reacts with metals and non-metals (except with some metals like Au, Pt etc and with some noble gases).

e.g.	$2Ca + O_2 \rightarrow 2CaO$	$P_4 + O_2 \longrightarrow P_4 O_{10}$
	$4 \operatorname{Al} + 3\operatorname{O}_2 \rightarrow 2\operatorname{Al}_2\operatorname{O}_3$	$C + O_2 \rightarrow CO_2$

Uses: 1) oxygen is used in oxyacetylene welding, in the manufacture of many metals, particularly steel.

- 2) Oxygen cylinders are widely used in hospitals, high altitude flying and in mountaineering.
- 3) Liquid O_2 is used in rocket fuels.

Oxides

Oxides are binary compounds of oxygen with other elements. There are two types of oxides – simple oxides (e.g., MgO, Al_2O_3) and mixed oxides (Pb_3O_4 , Fe_3O_4)

Simple oxides can be further classified on the basis of their acidic, basic or amphoteric character. An oxide that combines with water to give an acid is called acidic oxide (e.g., SO_2 , Cl_2O_7 , CO_2 , N_2O_5).

Generally, non-metal oxides are acidic but oxides of some metals in higher oxidation states also have acidic character (e.g., Mn_2O_7 , CrO_3 , V_2O_5 etc.).

The oxide which gives an alkali on dissolved in water is known as basic oxide (e.g., Na₂O, CaO, BaO). Generally, metallic oxides are basic in nature.

Some metallic oxides exhibit a dual behaviour. They show the characteristics of both acidic and basic oxides. Such oxides are known as amphoteric oxides. They react with acids as well as alkalies. E.g.: Al_2O_3 , Ga_2O_3 etc.

There are some oxides which are neither acidic nor basic. Such oxides are known as neutral oxides. Examples of neutral oxides are CO, NO and N₂O.

Ozone (O₃)

Ozone is an allotropic form of oxygen.

Preparation: When a slow dry stream of oxygen is passed through a silent electric discharge, oxygen is converted to ozone. The product is known as ozonised oxygen.

$$3 O_2(g) \rightarrow 2 O_3(g); \Delta H = +142 \text{ kJ/mol}$$

Since the formation of ozone from oxygen is an endothermic process, a silent electric discharge should be used, unless the ozone formed undergoes decomposition.

Properties: Pure ozone is a pale blue gas, dark blue liquid and violet-black solid. Ozone has a characteristic smell.

Ozone is thermodynamically unstable with respect to oxygen since its decomposition into oxygen results in the liberation of heat (Δ H is negative) and an increase in entropy (Δ S is positive). So the Gibbs energy change (Δ G) for this process is always negative

$$(\Delta G = \Delta H - T\Delta S).$$

Due to the ease with which it liberates nascent oxygen ($O_3 \rightarrow O_2 + O$), it acts as a powerful oxidising agent.

For e.g., it oxidises lead sulphide to lead sulphate $PbS(s) + 4O_3(g) \rightarrow PbSO_4(s) + 4O_2(g)$

Oxides of nitrogen (particularly nitric oxide) combine very rapidly with ozone and deplete it. Thus nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes, slowly depleting the concentration of the ozone layer in the upper atmosphere.

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

Estimation of ozone: When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer, iodine is liberated. The liberated iodine can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O_3 gas.

Structure: O₃ has an angular structure. It is a resonance hybrid of the following two forms:



Uses: It is used as a germicide, disinfectant and for sterilizing water. It is also used for bleaching oils, ivory, flour, starch, etc. It acts as an oxidising agent in the manufacture of potassium permanganate.

Allotropes of Sulphur

Sulphur forms a large number of allotropes. Among these **yellow rhombic** (α -sulphur) and **monoclinic** (β -sulphur) forms are the most important. The stable form at room temperature is rhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.

1. Rhombic sulphur (α -sulphur)- It is prepared by evaporating the solution of roll sulphur in CS₂. It is insoluble in water but readily soluble in CS₂.

2. Monoclinic sulphur (β -sulphur)-It is prepared by melting rhombic sulphur in a dish and cooling, till a crust is formed. Two holes are made in the crust and the remaining liquid is poured out. On removing the crust, colourless needle shaped crystals of β -sulphur are formed. It is stable above 369 K and transforms into α -sulphur below it. At 369 K both the forms are stable. This temperature is called transition temperature.

Both rhombic and monoclinic sulphur have S_8 molecules. The S_8 ring in both the forms is puckered and has a crown shape.



Sulphur Dioxide (SO₂)

Preparation: 1. Sulphur dioxide is formed when sulphur is burnt in air or oxygen:

 $S(s) + O_2(g) \rightarrow SO_2(g)$

2. In the laboratory it is obtained by treating a sulphite with dilute sulphuric acid.

$$\mathrm{SO}_{3}^{2^{-}}(aq) + 2\mathrm{H}^{+}(aq) \rightarrow \mathrm{H}_{2}\mathrm{O}(1) + \mathrm{SO}_{2}(g)$$

3. Industrially, it is produced by roasting of sulphide ores.

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

Properties: Sulphur dioxide is a colourless gas with pungent smell and is highly soluble in water.

With water, it forms a solution of sulphurous acid which is a dibasic acid and form two types of salts with alkalies – normal salt (sulphite) and acid salt (bisulphate or hydrogen sulphite).

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

With sodium hydroxide solution, it forms sodium sulphite, which then reacts with more sulphur dioxide to form sodium hydrogen sulphite.

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O \qquad \qquad Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$$

SO₂ is oxidised to sulphur trioxide by oxygen in the presence of vanadium pentoxide (V₂O₅) catalyst. $2SO_2 + O_2 \rightarrow 2SO_3$

Moist sulphur dioxide behaves as a reducing agent. It converts iron(III) ions to iron(II) ions and decolourises acidified potassium permanganate(VII) solution (This used as a test for SO₂).

$$2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

$$5 SO_2 + 2MnO_4^{-} + 2H_2O \longrightarrow 5 SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

Structure: SO₂ has an angular shape. It is a resonance hybrid of the following two canonical forms:



Uses: Sulphur dioxide is used (i) in refining petroleum and sugar (ii) in bleaching wool and silk and (iii) as an anti-chlor, disinfectant and preservative (iv) for the production of Sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite (v) Liquid SO_2 is used as a solvent to dissolve a number of organic and inorganic chemicals.
