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1.4.3. Potassium Permanganate $KMnO_4$

i) Preparation -

a) $KMnO_4$ is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3. Dark green K_2MnO_4 disproportionates in a neutral or acidic solution to give $KMnO_4$.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O.$$
$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O.$$

b) Commercially, alkaline oxidative fusion of MnO_2 followed by electrolytic oxidation of manganate (VI).

$$MnO_2 \xrightarrow[\text{Oxidised with air or } KNO_3]{\text{Fused with KOH,}} \underset{\text{Manganate ion}}{MnO_4^{2-}} \xrightarrow[\text{oxidation in alkaline solution.}]{\text{Electrolytic}} \underset{\text{Permanganate ion}}{MnO_4^-}$$

c) In lab preparation, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

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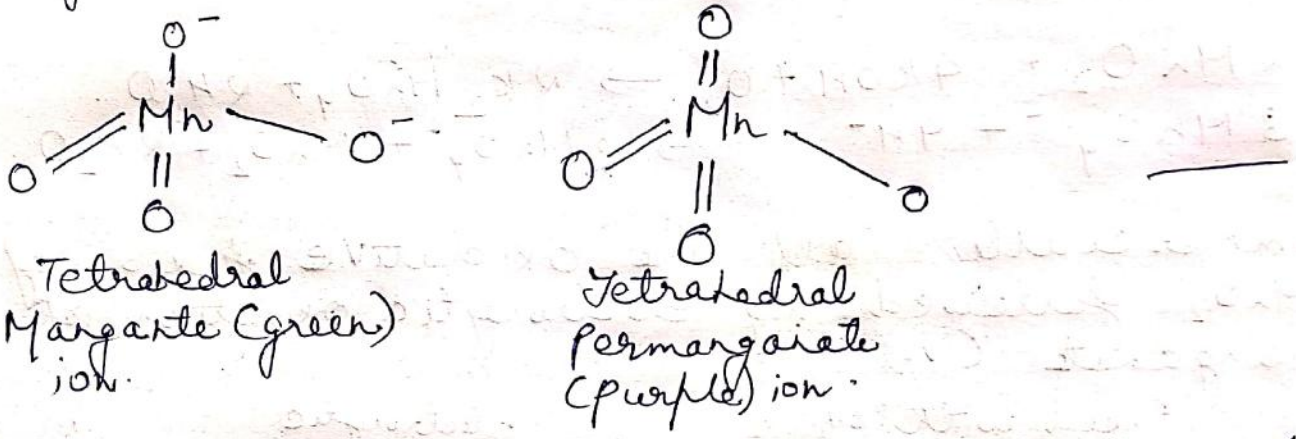
ii) Structure - a) The manganate and permanganate ions are tetrahedral; b) the green manganate is paramagnetic with one unpaired electron but the permanganate is diamagnetic. c) The π-bonding takes place by overlap of p-orbitals of oxygen with d-orbitals of manganese.

iii) Properties: a) $KMnO_4$ forms dark purple (almost black) crystals which are isostructural with those



iii) Properties - a) $KMnO_4$ forms dark purple (almost black) crystals which are isostructural with those $KClO_4$.

b) The salt is not very soluble in water (6.4g/100g of water at 298 K). But when heated it decomposes at 573 K.

$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2.$$

c) Its important properties are its intense colour and its weak temperature dependent paramagnetism due to Molecular Orbital theory.