POTASSIUM PERMANGANATE ($KMnO_4$) :

Preparation

This is the most important and well known salt of permanganic acid and is prepared from the pyrolusite ore. It is prepared by fusing pyrolusite ore either with KOH or K_2CO_3 in presence of atmospheric oxygen or any other oxidising agent such as KNO_3. The fused mass turns green with the formation of potassium manganate, K_2MnO_4.

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$
$$2MnO_2 + 2K_2CO_3 + O_2 \longrightarrow 2K_2MnO_4 + 2CO_2$$

The fused mass is extracted with water and the solution is now treated with a current of chlorine or ozone or carbon dioxide to convert manganate into permanganate.

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$
$$2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$$
$$3K_2MnO_4 + 2CO_2 \longrightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3$$

$$MnO_4^{2-}\text{ (green)} \longrightarrow MnO_4^{-}\text{ (purple)} + e^-$$

Recording

Continue..

- **Properties**

(a) Physical :

It is purple coloured crystalline compound. It is moderately soluble in water at room temperature.

(b) Chemical :

(i) Effect of heating

When heated alone or with an alkali, it decomposes evolving oxygen.

$$2KMnO_4 \xrightarrow{750K} K_2MnO_4 + MnO_2 + O_2$$

$$2K_2MnO_4 \xrightarrow[\text{Heat}]{\text{Red}} 2K_2MnO_3 + O_2$$

$$4KMnO_4 + 4KOH \xrightarrow{\Delta} 4K_2MnO_4 + 2H_2O + O_2$$

or

$$4MnO_4^- + 4OH^- \xrightarrow{\Delta} 4MnO_4^{2-} + O_2 + 2H_2O.$$

MnO_4^{2-} in dilute alkaline, water and acidic solutions is unstable and disproportionates to give MnO_4^- and MnO_2 .

$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2\downarrow + 2H_2O$$
$$3MnO_4^{2-} + 2H_2O \longrightarrow 2MnO_4^- + MnO_2\downarrow + 4OH^-$$

Continue..

On treatment with concentrated H_2SO_4 ($KMnO_4$ is taken in excess), it forms manganese heptoxide via permanganyl sulphate which decomposes explosively on heating.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow 2KHSO_4 + (MnO_3)_2SO_4 + 2H_2O$$
$$(MnO_3)_2SO_4 + H_2O \longrightarrow Mn_2O_7 + H_2SO_4$$
$$Mn_2O_7 \longrightarrow 2MnO_2 + \frac{3}{2}O_2$$
$$KMnO_4 + 3H_2SO_4 \text{ (conc.)} \longrightarrow K^+ + MnO_3^+ \text{ (green)} + 3HSO_4^- + H_3O^+.$$

Potassium permanganate is a powerful oxidising agent.
Potassium permanganate acts as an oxidising agent in alkaline, neutral or acidic solutions.

In alkaline & neutral medium :

In strongly alkaline medium $KMnO_4$ is reduced to manganate.

$$2KMnO_4 + 2KOH \text{ (conc.)} \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

or

$$e^- + MnO_4^- \longrightarrow MnO_4^{2-}$$

However if solution is dilute then K_2MnO_4 is converted in to MnO_2 which appears as a brownish precipitate.

$$2K_2MnO_4 + 2H_2O \longrightarrow 2MnO_2 + 4KOH + 2[O]$$

or

$$2e^- + 2H_2O + MnO_4^{2-} \longrightarrow MnO_2 + 4OH^-$$

Continue..

(a) It oxidises ethene to glycol.

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + H_2O + [O] \longrightarrow \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

In alkaline medium $KMnO_4$ solution is also known as Bayer's reagent (1% alkaline $KMnO_4$ solution).

(b) It oxidises iodide into iodate.

$$3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^- \times [2]$$
$$6OH^- + I^- \longrightarrow IO_3^- + 3H_2O + 6e^-$$

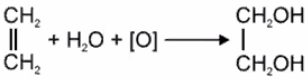
$$2MnO_4^- + I^- + H_2O \longrightarrow 2MnO_2 + IO_3^- + 2OH^-$$

(c) H_2S is oxidised into sulphur :

$$2MnO_4^- + 3H_2S \longrightarrow 2MnO_2 + 2OH^- + 2H_2O + 3S$$

Continue..

(a) It oxidises ethene to glycol.



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(c) H_2S is oxidised into sulphur :

$$2MnO_4^- + 3H_2S \longrightarrow 2MnO_2 + 2OH^- + 2H_2O + 3S$$

Continue..

In acidic medium (in presence of dilute H_2SO_4) :

Manganous sulphate is formed. The solution becomes colourless.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

or $$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

This medium is used in quantitative (volumetric) estimations. The equivalent mass of $KMnO_4$ in acidic medium is $= \frac{\text{Molecular mass}}{5}$.

SO_2 is oxidised to H_2SO_4 :

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

Nitrites are oxidised to nitrates :

$$2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-$$

Oxalic acid is oxidised to CO_2 :

This reaction is slow at room temperature, but is rapid at 60°C.

Mn(II) ions produced catalyse the reaction; thus the reaction is autocatalytic

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \xrightarrow{60°C} 2Mn^{2+} + 8H_2O + 10CO_2$$

POTASSIUM DICHROMATE ($K_2Cr_2O_7$)

- **Preparation :**

The chromite ore is roasted with sodium carbonate in presence of air in a reverberatory furnace

$$4FeO.Cr_2O_3 \text{ (chromite ore)} + 8Na_2CO_3 + 7O_2 \xrightarrow[\text{in air}]{\text{Roasting}} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

The roasted mass is extracted with water when Na_2CrO_4 goes into the solution leaving behind insoluble Fe_2O_3. The solution is then treated with calculated amount of H_2SO_4.

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

The solution is concentrated when less soluble Na_2SO_4 crystallises out. The solution is further concentrated when crystals of $Na_2Cr_2O_7$ are obtained. Hot saturated solution of $Na_2Cr_2O_7$ is then treated with KCl when orange red crystals of $K_2Cr_2O_7$ are obtained on crystallisation.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2\,NaCl$$

$K_2Cr_2O_7$ is preferred over $Na_2Cr_2O_7$ as a primary standard in volumetric estimation because $Na_2Cr_2O_7$ is hygroscopic in nature but $K_2Cr_2O_7$ is not.

Continue..

- **Properties**

(a) Physical :

It is orange-red coloured crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at 398°C.

(b) Chemical :

(i) Effect of heating :

On heating strongly, it decomposes liberating oxygen.

$$2K_2Cr_2O_7 \longrightarrow 2K_2CrO_4 + Cr_2O_3 + \frac{3}{2}O_2$$

On heating with alkalies, it is converted to chromate, i.e., the colour changes from orange to yellow. On acidifying, yellow colour again changes to orange.

$$K_2Cr_2O_7 + 2KOH \longrightarrow 2K_2CrO_4 + H_2O$$

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$

Orange Yellow

$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$

Yellow Orange