DAV CENTENARY PUBLIC SCHOOL, PASCHIM ENCLAVE, NEW DELHI-87

Topic Name : Potassium Dichromate

Preparation of potassium dichromate

Potassium dichromate is prepared from chromates which in turn are prepared from chrome iron, $FeCr_2O_4$. The various steps involved are as follows:

i. **Preparation of sodium chromate:**
The ore, $FeCr_2O_4$ is finely powdered, mixed with sodium carbonate and quick lime and then heated to redness in presence of air to evolve carbon dioxide. The reaction involved can be written as follows:

$$4FeO.Cr_2O_3 + O_2 \longrightarrow 2Fe_2O_3 + 4Cr_2O_3$$

$$4Na_2CO_3 + 2Cr_2O_3 + 3O_2 \longrightarrow 4Na_2CrO_4 + 4CO_2] \times 2$$

$$4FeO.CrO_3 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

The roasted mass is then extracted with water when sodium chromate is completely dissolved while Fe_2O_3 is left behind.

ii. **Conversion of sodium chromate into sodium dichromate:**
Sodium chromate solution obtained is filtered and treated with concentrated sulphuric acid to obtain sodium dichromate as shown below:

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

Sodium sulphate being less soluble crystallizes and is then filtered off.

iii. **Conversion of sodium dichromate into potassium dichromate:**
Sodium dichromate is more soluble and less stable than potassium dichromate and it is converted to potassium dichromate easily upon treatment with potassium chloride.

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

Potassium dichromate being much less soluble than sodium salt, crystallizes out on cooling.

Properties of potassium dichromate

Potassium dichromate is an orange red crystalline solid which melts at 669 K. It is moderately soluble in cold water but freely soluble in hot water. Some important properties are as follows:

i. **Action of heat:** When heated potassium dichromate decomposes with evolution of oxygen.

$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

ii. **Action of alkalis:** An orange red solution of potassium dichromate turns yellow upon treatment with alkali due to the formation of chromate.

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

The reaction is reversed on acidification, i.e.

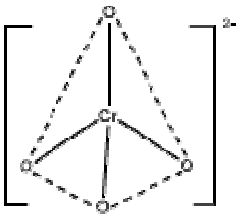
$$K_2CrO_4 + H_2SO_4 \longrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

Thus, the inter conversion of chromate and dichromate is an equilibrium process which is pH dependent.

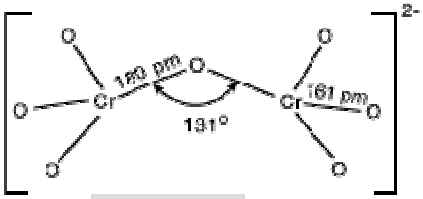
$$2CrO_4^{2-} + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Chromate (Yellow) — Hydrogen Chromate — Dichromate (Orange)

In acidic conditions (low pH), dichromate is more stable while under alkaline conditions (high pH) chromate is more stable. Structure of chromate and dichromate ions are shown below:



Chromate ion



Dichromate ion

iii. **Action of concentrated sulphuric acid:** Red crystals of chromic anhydride (chromium trioxide) are formed when potassium dichromate is treated with cold concentrated sulphuric acid.

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow \underset{\text{Red}}{2CrO_3} + 2KHSO_4 + H_2O$$

On the other hand, heating of potassium dichromate with concentrated sulphuric acid results in evolution of oxygen.

$$2K_2Cr_2O_7 + 8H_2SO_4 \longrightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

iv. **Oxidizing properties:** Potassium dichromate is a powerful oxidizing agent. In the presence of dilute sulphuric acid, one mole of potassium dichromate produces three moles of oxygen atoms as indicated by the equation.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

Where chromium in + 6 oxidation state in $Cr_2O_7^{2-}$ ion is being reduced to Cr^{3+} (+ 3 oxidation state.)
Let us examine the action of acidified potassium dichromate solution as an oxidizing agent by taking few examples:

1. It liberates I_2 from KI.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

$$6KI + 3H_2SO_4 + 3O \longrightarrow 3K_2SO_4 + 3I_2 + 3H_2O$$

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$$

or

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

2. It oxidizes ferrous salts to ferric salts.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

$$2FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 3$$

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

or

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

The above two reactions are used in the volumetric estimation of iodine and iron (II).

3. It oxidizes H_2S to sulphur.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3S + 7H_2O$

or

$Cr_2O_7^{2-} + 8H^+ + 3H_2S \longrightarrow 2Cr^{3+} + 3S + 7H_2O$

4. It oxidizes ethyl alcohol to acetaldehyde and acetic acid.

$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$

$CH_2CH_2OH + O \longrightarrow CH_3CHO + H_2O$
Ethyl alcohol — Acetaldehyde

$CH_3CHO + O \longrightarrow CH_3COOH$
Acetaldehyde — Acetic acid

5. It oxidizes sulphites to sulphates.

$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$

$Na_2SO_3 + O \longrightarrow Na_2SO_4] \times 3$

$K_2Cr_2O_7 + 4H_2SO_4 + 3Na_2SO_3 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3Na_2SO_4$

or

$Cr_2O_7^{2-} + 8H^+ + 2SO_3^{2-} \longrightarrow 2Cr^{+3} + 3SO_4^{2-} + 7H_2O$

6. It oxidizes SO_2 to sulphuric acid.

$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$

$SO_2 + O + H_2O \longrightarrow H_2SO_4] \times 3$

$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

or

$Cr_2O_7^{2-} + 2H^+ + 3SO_2 \longrightarrow Cr_2(SO_4)_3 + H_2O$

7. It oxidizes halogen acids to halogen.

$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$

8. **Chromyl chloride test:** When potassium dichromate is treated with a strong (concentrated) sulphuric acid and a chloride, reddish brown vapours of chromyl chloride are formed.

$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2CrO_3 + H_2O$

$KCl + 4HCl \longrightarrow KHSO_4 + HCl] \times 4$

$2CrO_3 + 4HCl \longrightarrow 2CrO_2Cl_2 + 2H_2O$

$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \longrightarrow 2CrO_2Cl_2 + 6KHSO_4 + 3H_2O$
Chromyl chloride
(Red)

This test is used in detection of chloride ions in qualitative analysis.

Board Questions

1. What chemical changes take place when pH of a chromate solution is progressively lowered? **CBSE 2002 (Delhi)**, **1 mark**
2. With the help of ionic equation describe what happens when pH of of a solution of dichromate ions is raised. **CBSE 2002 (Delhi), 1 mark**

3. Describe how potassium dichromate is made from chromite ore and give the equation for the chemical reactions involved. Write balanced ionic equations for reacting ions to represent the action of acidified potassium dichromate solution on:
   (i) potassium iodide solution
   (ii) acidified ferrous sulphate solution.
   and write two uses of potassium dichromate. **CBSE 2001 (Outside Delhi), 5 marks**
4. An iodide is treated with an acidified dichromate solution. **CBSE 2001 (Delhi), 2 marks**
5. Describe the preparation of $K_2Cr_2O_7$ from chromite ore. Write the necessary chemical equations. **CBSE 2001 (Outside Delhi), 2 marks**
6. Why is it that an orange solution of $K_2Cr_2O_7$ turns yellow on adding NaOH to it?
   CBSE 2000 (Outside Delhi), 1 mark
7. Describe with chemical equations what happens when dilute sodium hydroxide solution is added to a solution of $K_2Cr_2O_7$ in water. **CBSE 1999 (Delhi), 2 marks**

Topic Name : Potassium Permanganate

Preparation of potassium permanganate

Potassium permanganate is prepared on a large scale from mineral pyrolusite (MnO_2). The preparation involves following steps.

i. **Conversion of MnO_2 to potassium magnate:**
Pyrolusite is fused with potassium hydroxide and the molten liquid is stirred well in the presence of air.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

Oxidizing agents like potassium nitrate can also be used instead of air:

$$MnO_2 + 2KOH + KNO_3 \longrightarrow K_2MnO_4 + KNO_2 + H_2O$$

ii. **Oxidation of potassium manganate to potassium permanganate:**
Potassium manganate can be chemically oxidized to permanganate by bubbling CO_2, Cl_2 etc., through the solution of potassium manganate.

$$3K_2MnO_4 + 2CO_2 \longrightarrow 2KMnO_4 + MnO_2\downarrow + 2K_2CO_3$$

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

These chemical processes are not very economical at the industry scale and hence electrolytic oxidation is preferred over them.
Potassium manganate is oxidized electrochemically to permanganate. The electrode reactions taking place are:

At anode:

$$2K_2MnO_4 + H_2O + O \longrightarrow 2KMnO_4 + 2KOH$$

or

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

Green Purple

At cathode:

$$2H^+ + 2e^- \longrightarrow H_2\uparrow$$

Examples of oxidation by potassium permanganate in neutral solution are discussed below:

i. It oxidizes hot manganese sulphate to manganese dioxide.

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3O$$

$$3MnSO_4 + 3H_2O + 3O \longrightarrow 3MnO_2 + 3H_2SO_4$$

$$2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$$

$$3MnSO_4 + 2KMnO_4 + 2H_2O \longrightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$$

ii. It oxidizes sodium thiosulphate to sodium sulphate.

$$3Na_2S_2O_3 + 8KMnO_4 + H_2O \longrightarrow 3Na_2SO_4 + 8MnO_2 + 3K_2SO_4 + 2\ KOH$$

iii. It oxidizes hydrogen sulphide to sulphur.

$$2\ KMnO_4 + 4H_2S \longrightarrow 2\ MnS + S + K_2SO_4 + 4H_2O$$

Properties of potassium permanganate

Potassium permanganate is a purple crystalline solid melting at 523 K. It is slightly soluble in cold water. The solubility increases in hot water.

i. **Action of heat:** Potassium permanganate decomposes to oxygen, potassium manganate and manganese dioxide when heated to 746 K.

$$2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$$

ii. **Action of concentrated sulphuric acid:** When treated with cold concentrated sulphuric acid potassium permanganate is converted to Mn_2O_7 (green oil) which decomposes on warming to MnO_2 (it is highly explosive).

$$2KMnO_4 + 2H_2SO_4 \longrightarrow Mn_2O_7 + 2KHSO_4 + H_2O$$

$$2Mn_2O_7 \xrightarrow{\Delta} 4MnO_2 + 3O_2$$

iii. **Oxidizing properties:** Potassium permanganate is a strong oxidizing agent and the reaction is pH dependent.
In alkaline solution: In strongly alkaline solution, MnO_4^{2-} ion is produced as shown in the reaction.

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + O$$

or

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

The MnO_4^{2-} ion gets further reduced to MnO_2,

$$K_2MnO_4 + H_2O \longrightarrow MnO_2 + 2KOH + O$$

or

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

Thus, the complete reaction is:

$$2KMnO_4 + H_2O \longrightarrow 2MnO_2 + KOH + 3O$$

or

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

A few examples of oxidation by $KMnO_4$ in alkaline medium are:

a. potassium iodide is oxidized to potassium iodate.

$$2KMnO_4 + H_2O + KI \longrightarrow 2MnO_2 + 2KOH + KIO_3$$

or

$$I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-$$

b. potassium permanganate is used in oxidation of olefinic compounds to glycols. It is known by the name of Baeyer's reagent in these reactions.

c. In acidic medium:In the presence of dilute sulphuric acid, the following reaction takes place,

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

or

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

Potassium permanganate acts as a very strong oxidizing agent in acidic media. Few examples of oxidation by acidic potassium permanganate solution are:

d. oxidation of H_2S to S.

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

$$H_2S + O \longrightarrow H_2O + S] \times 5$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$$

or

$$2MnO_4^- + 16H^+ + 5S^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 5S$$

g. oxidation of ferrous sulphate to ferric sulphate.

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

$$2FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 5$$

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

or

$$2MnO_4^- + 16H^+ + 10Fe^{2+} \longrightarrow 2Mn^{2+} + 8H_2O + 10Fe^{3+}$$

j. Oxidation of potassium iodide to iodine:

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

$$2KI + H_2SO_4 \longrightarrow K_2SO_4 + 2HI\ ] \times 5$$

$$2HI + O \longrightarrow H_2O + I_2\ ] \times 5$$

$$2KMnO_4 + 3H_2SO_4 + 10KI \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$$

or

$$2MnO_4^- + 16H^+ + 10I^- \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

In neutral medium: In neutral medium, potassium permanganate is weakly oxidizing and the reaction involved is:

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3O$$

or

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

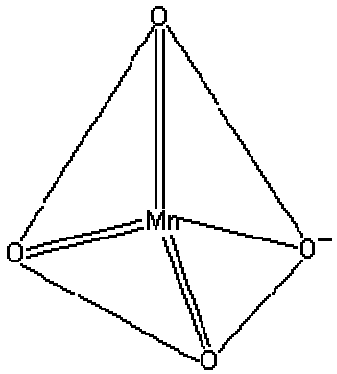
The alkali (KOH) produced renders the solution basic as the reaction proceeds and the reaction given above is then essentially same as that for alkaline medium.

Uses

i. Potassium permanganate is used in volumetric analysis for estimation of ferrous salts, oxalates, iodide and hydrogen peroxide.
ii. It is used as a strong oxidizing agent in the laboratory.
iii. It is also used as a disinfectant and germicide.

Structure of permanganate ion

The four oxygen atoms are arranged tetrahedrally around manganese in MnO_4^- as manganese is sp^3 hybridized.



Structure of permanganate ion

Board Questions

1. What chemical changes take place when MnO_2 is fused with KOH in air? **CBSE 2002 (Delhi), 1 mark**
2. Potassium manganate is electrochemically oxidized. **CBSE 2002 (Delhi), 1 mark**
3. Mention two uses of potassium permanganate in the laboratory. **CBSE 2002 (Outside Delhi), 1 mark**
4. Describe how potassium permanganate is made from pyrolusite. Write chemical equations for the reactions involved.
   Describe with an example each, the oxidizing actions of permanganate ion in alkaline and acidic media. What acid and alkali are usually used? **CBSE 2001 (Delhi), 5 marks**
5. Write balanced ionic equations for what happens when:
   acidified potassium permanganate solution is treaded with an oxalate solution.
   CBSE 2001 (Delhi), 2 marks
6. Write chemical equations for the conversion of:
   (i) chromite ore to sodium chromate
   (ii) pyrolusite to potassium manganate
   (iii) potassium permanganate to manganese dioxide **CBSE 1999 (Delhi), 3 marks**
7. Pyrolusite is fused with KOH in presence of air. **CBSE 1999 (Delhi), 2 marks**