Some Compounds of d-Block Elements.

Potassium dichromate, ($K_2Cr_2O_7$)

Potassium dichromate is one of the most important compound of chromium, and also among dichromates. In this compound Cr is in the hexavalent (+6) state.

Preparation: It can be prepared by any of the following methods,

(i) From potassium chromate: Potassium dichromate can be obtained by adding a calculated amount of sulphuric acid to a saturated solution of potassium chromate.

$$\underset{\substack{potassium\ chromate \\ (yellow)}}{2K_2CrO_4} + H_2SO_4 \rightarrow \underset{\substack{potassium\ dichromate \\ (orange)}}{K_2CrO_7} + K_2SO_4 + H_2O$$

$K_2Cr_2O_7$ Crystals can be obtained by concentrating the solution and crystallization.

(ii) Manufacture from chromite ore: $K_2Cr_2O_7$ is generally manufactured from chromite ore ($FeCr_2O_4$). The process involves the following steps.

(a) Preparation of sodium chromate. Finely powdered chromite ore is mixed with soda ash and quicklime. The mixture is then roasted in a reverberatory furnace in the presence of air. Yellow mass due to the formation of sodium chromate is obtained.

$$4FeCr_2O_4 + O_2 \rightarrow 2Fe_2O_3 + 4Cr_2O_3$$

$$4Cr_2O_3 + 8Na_2CO_3 + 6O_2 \rightarrow 8Na_2CrO_4 + 8CO_2(g)$$

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8CO_2(g) + \underset{sodium\ chromate}{8Na_2CrO_4}$$

The yellow mass is extracted with water, and filtered. The filtrate contains sodium chromate.

The reaction may also be carried out by using NaOH instead of Na_2CO_3.The reaction in that case is,

$$4FeCr_2O_4 + 16NaOH + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$$

(b) Conversion of chromate into dichromate. Sodium chromate solution obtained in step(a) is treated with concentrated sulphuric acid when it is converted into sodium dichromate.

$$\underset{sodium\ chromate}{2Na_2CrO_4} + H_2SO_4 \rightarrow \underset{sodium\ dichromate}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

On concentration, the less soluble sodium sulphate, $Na_2SO_4.10H_2O$ crystallizes out. This is filtered hot and allowed to cool when sodium dichromate, $Na_2Cr_2O_7.2H_2O$, separates out on standing.

(c) Concentration of sodium dichromate to potassium dichromate. Hot concentrated solution of sodium dichromate is treated with a calculated amount of potassium chloride. When potassium dichromate being less soluble crystallizes out on cooling.

$$\underset{sod.dichromate}{Na_2CrO_7} + 2KCl \rightarrow \underset{pot.dichromate}{K_2Cr_2O_7} + 2NaCl$$

Physical properties

(i) Potassium dichromate forms orange-red colored crystals.

(ii) It melts at 699 K.

(iii) It is very stable in air (near room temperature) and is generally, used as a primary standard in the volumetric analysis.

(iv)It is soluble in water though the solubility is limited.

Chemical properties

(i) Action of heat: Potassium dichromate when heated strongly. decomposes to give oxygen.

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

(ii) Action of acids

(a) In cold, with concentrated H_2SO_4, red crystals of chromium trioxide separate out.

$$K_2Cr_2O_7(aq) + conc.H_2SO_4 \rightarrow KHSO_4(aq) + 2CrO_3(s) + H_2O$$

On heating a dichromate-sulphuric acid mixture, oxygen gas is given out.

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

(b) With HCl, on heating chromic chloride is formed and Cl_2 is liberated.

$$K_2Cr_2O_{7(aq)} + 14HCl(aq) \rightarrow 2CrCl_{3(aq)} + 2KCl(aq) + 7H_2O + 3Cl_2(g)$$

(iii) Action of alkalies: With alkalies, it gives chromates. For example, with KOH,

$$\underset{orange}{K_2Cr_2O_4} + 2KOH \rightarrow \underset{yellow}{2K_2CrO_4} + H_2O$$

On acidifying, the colour again changes to orange-red owing to the formation of dichromate.

$$2K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

Actually, in dichromate solution, the $Cr_2O_7^{2-}$ ions are in equilibrium with CrO_4^{2-} ions.

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

(iv) Oxidizing nature: In neutral or in acidic solution, potassium dichromate acts as an excellent oxidizing agent, and $Cr_2O_7^{2-}$ gets reduced to Cr^{3+}. The standard electrode potential for the reaction,

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$ is +1.31 V. This indicates that dichromate ion is a fairly strong oxidizing agent, especially in strongly acidic solutions. That is why potassium dichromate is widely used as an oxidizing agent, for quantitative estimation of the reducing agents such as, Fe^{2+}. It oxidizes,

(a) Ferrous salts to ferric salts

$$K_2CrO_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$2FeSO_4 + H_2SO_4 + [O] \rightarrow Fe_2[SO_4]_3 + H_2O \times 3$$

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

Ionic equation: $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

(b) Sulphites to sulphates and arsenites to arsenates.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$Na_2SO_3 + [O] \rightarrow Na_2SO_4] \times 3$$

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

Ionic equation: $Cr_2O_7^{2-} + 8H^+ + 3SO_3^{2-} \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$

Similarly, arsenites are oxidised to arsenates.

$$Cr_2O_7^{2-} + 8H^+ + 3AsO_3^{3-} \rightarrow 2Cr^{3+} + 3AsO_4^{3-} + 4H_2O$$

(c) Hydrogen halides to halogens.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$2HX + O \rightarrow H_2O + X_2] \times 3$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 6HX \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3X_2$$

Where, X may be Cl, Br, I.

Ionic equation: $Cr_2O_7^{2-} + 8H^+ + 6HX \rightarrow 2Cr^{3+} + 3X_2 + 7H_2O$

(d) Iodides to iodine

$$K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$2KI + H_2O + [O] \rightarrow 2KOH + I_2] \times 3$$

$$2KOH + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O] \times 3$$

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

Ionic equation: $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$

Thus, when KI is added to an acidified solution of $K_2Cr_2O_7$ iodine gets liberated.

(e) It oxidizes H_2S to S.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$H_2S + [O] \rightarrow H_2O + S] \times 3$$

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

Ionic equation: $Cr_2O_7^{2-} + 8H^+ + 3H_2S \rightarrow 2Cr^{3+} + 3S + 7H_2O$

(v) Formation of insoluble chromates: With soluble salts of lead, barium etc., potassium dichromate gives insoluble chromates. Lead chromate is an important yellow pigment.

(vi) Chromyl chloride test: When potassium dichromate is heated with conc. H_2SO_4 in the presence of a soluble chloride salt, the orange-red vapours of chromyl chloride (CrO_2Cl_2) are formed.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \xrightarrow{heat} 2KHSO_4 + 4NaHSO_4 + \underset{\substack{chromyl\ chloride \\ (orange-red\ vapours)}}{2CrO_2Cl_2}$$

Chromyl chloride vapours when passed through water give yellow-coloured solution containing chromic acid.

$$CrO_2Cl_2 + 2H_2O \rightarrow 2HCl + \underset{Chromic\ acid.(yellow\ solution)}{H_2CrO_4}$$

Chromyl chloride test can be used for the detection of chloride ion is any mixture.

Uses: Potassium dichromate is used as,

(i) An oxidizing agent

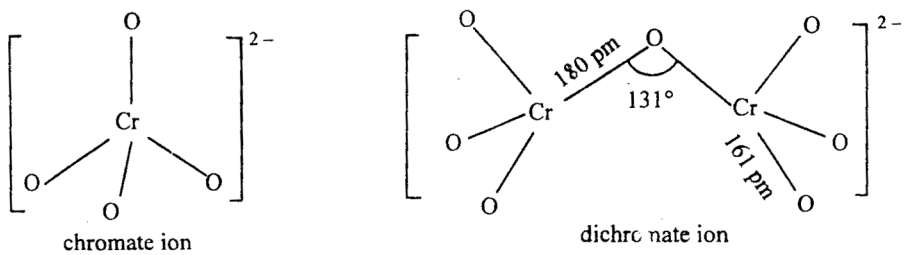
(ii) In chrome tanning

(iii) The raw material for preparing large number of chromium compounds

(iv) Primary standard in the volumetric analysis.

Structures of Chromate and Dichromate Ions

Chromates and dichromates are the salts of chromic acid (H_2CrO_4). In solution, these ions exist in equilibrium with each other. Chromate ion has four oxygen atoms arranged tetrahedrally around Cr atom. (see Fig). Dichromate ion involves a Cr–O–Cr bond as shown in Fig.



The structures of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) ions.

Potassium Permanganate, ($KMnO_4$)

Potassium permanganate is a salt of an unstable acid $HMnO_4$ (permanganic acid). The Mn is an +7 state in this compound.

Preparation: Potassium permanganate is obtained from pyrolusite as follows.

Conversion of pyrolusite to potassium manganate : When manganese dioxide is fused with potassium hydroxide in the presence of air or an oxidising agent such as potassium nitrate or chlorate, potassium manganate is formed, possibly via potassium manganite.

$$MnO_2 + 2KOH \xrightarrow{fused} \underset{potassium\ manganite}{K_2MnO_3} + 4H_2O] \times 2$$

$$2K_2MnO_3 + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$\underset{pyrolusite}{2MnO_2} + 4KOH + O_2 \xrightarrow{fused} \underset{\substack{potassium\ manganate \\ [dark-green\ mass]}}{2K_2MnO_4} + 2H_2O$$

Oxidation of potassium manganate to potassium permanganate: The potassium manganate so obtained is oxidised to potassium permanganate by either of the following methods.

By chemical method: The fused dark-green mass is extracted with a small quantity of water. The filtrate is warmed and treated with a current of ozone, chlorine or carbon dioxide. Potassium manganate gets oxidised to potassium permanganate and the hydrated manganese dioxide precipitates out. The reactions taking place are,

When CO_2 is passed

$$\underset{potassium\ manganate}{3K_2MnO_4} + 2H_2O \rightarrow \underset{potassium\ permangana\ te}{2KMnO_4} + MnO_2 \downarrow + 4KOH$$

$$2CO_2 + 4KOH \rightarrow 2K_2CO_3 + 2H_2O$$

When chlorine or ozone is passed

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

$$2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + 2KOH + O_2(g)$$

The purple solution so obtained is concentrated and dark purple, needle-like crystals having metallic lustre are obtained.

Electrolytic method: Presently, potassium manganate (K_2MnO_4) is oxidisedelectrolytically. The electrode reactions are,

At anode: $\underset{green}{2MnO_4^{2-}} \rightarrow \underset{purple}{2MnO_4^-} + 2e^-$

At cathode: $2H^+ + 2e^- \rightarrow H_2(g)$

The purple solution containing $KMnO_4$ is evaporated under controlled condition to get crystalline sample of potassium permanganate.

Physical properties

$KMnO_4$ crystallizes as dark purple crystals with greenish luster (m.p. 523 K).

It is soluble in water to an extent of 6.5g per 100g at room temperature. The aqueous solution of $KMnO_4$ has a purple color.

Chemical properties: Some important chemical reactions of $KMnO_4$ are given below,

Action of heat : $KMnO_4$ is stable at room temperature, but decomposes to give oxygen at higher temperatures.

$$2KMnO_4(s) \xrightarrow{heat} K_2MnO_4(s) + MnO_2 + O_2(g)$$

Oxidizingactions: $KMnO_4$ is a powerful agent in neutral, acidic and alkaline media. The nature of reaction is different in each medium. The oxidizing character of $KMnO_4$ (to be more specific, of MnO_4^-) is indicated by high positive reduction potentials for the following reactions.

Acidic medium: $MnO_4^- + 8H^+ + 5e^- \square Mn^{2+} + 4H_2O \quad E^o = 1.51\ V$

Alkaline medium: $MnO_4^- + 2H_2O + 3e^- \square MnO_2 + 4OH^- \quad E^o = 1.23\ V$

In strongly alkaline solutions and with excess of MnO_4^-, the reaction is

$$MnO_4^- + e^- \square MnO_4^{2-} \qquad E^o = 0.56\ V$$

There are a large number of oxidation-reduction reactions involved in the chemistry of manganese compounds. Some typical reactions are,

In the presence of excess of reducing agent in acidic solutions permanganate ion gets reduced to manganous ion, e.g., $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

An excess of reducing agent in alkaline solution reduces permanganate ion only to manganese dioxide e.g.,

$$3NO_2^- + MnO_4^- + 2OH^- \rightarrow 3NO_3^- + MnO_2 + H_2O$$

In faintly acidic and neutral solutions, manganous ion is oxidized to manganese oxidized to manganese dioxide by permanganate.

$$2MnO_4^- + 3Mn^{+2} + 2H_2O \rightarrow 5MnO_2 + 4H^+$$

In strongly basic solutions, permanganteoxidizes manganese dioxide to manganate ion.

$$MnO_2 + 2MnO_4^- + 4OH^- \rightarrow 3MnO_4^{2-} + 2H_2O$$

In acidic medium, $KMnO_4$oxidizes,

Ferrous salts to ferric salts

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

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

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

Ionic equation: $2MnO_4^- + 16H^+ + 10Fe^{2+} \rightarrow 2Mn^{2+} + 10Fe^{3+} + 8H_2O$

The reaction forms the basis of volumetric estimation of Fe^{2+} in any solution by $KMnO_4$.

Oxalic acid to carbon dioxide

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

$$(COOH)_2 + [O] \rightarrow 2CO_2 + H_2O] \times 5$$

$$2KMnO_4 + 3H_2SO_4 + 5(COOH)_2 \rightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

Ionic equation: $2MnO_4^- + 6H^+ + 5(COOH)_2 \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

Sulphites to sulphates

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

$$Na_2SO_3 + [O] \rightarrow Na_2SO_4] \times 5$$

$$2KMnO_4 + 3H_2SO_4 + 5Na_2SO_3 \rightarrow K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 3H_2O$$

Ionic equation: $2MnO_4^- + 6H^+ + 5SO_3^{2-} \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$

Iodides to iodine in acidic medium

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

$$2KI + H_2O + [O] \rightarrow I_2 + 2KOH \times 5$$

$$2KOH + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O\ ] \times 5$$

$$2KMnO_4 + 8H_2SO_4 + 10KI \rightarrow 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O$$

Ionic equation: $2MnO_4^- + 16H^+ + 10I^- \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

Hydrogen peroxide to oxygen

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

$$H_2O_2 + [O] \rightarrow H_2O + O_2 \uparrow \times 5$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

Manganous sulphate ($MnSO_4$) to manganese dioxide (MnO_2)

$$2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3[O]$$
$$MnSO_4 + H_2O + [O] \rightarrow MnO_2 + H_2SO_4 \times 3$$
$$2KOH + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O$$
$$2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$$

Ionic equation: $2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+$

Ammonia to nitrogen

$$2KMnO_4 + H_2O \rightarrow 2MnO_2 + 2KOH + 3[O]$$
$$2NH_3 + 3[O] \rightarrow N_2(g) + 3H_2O$$
$$2KMnO_4 + 2NH_3 \rightarrow 2MnO_2 + 2KOH + 2H_2O + N_2(g)$$

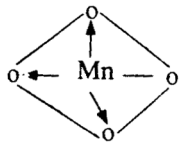
Uses: $KMnO_4$ is used,

(i) As an oxidizing agent.

(ii) As a disinfectant against disease-causing germs.

(iii) For sterilizing wells of drinking water.

(iv) In volumetric estimation of ferrous salts, oxalic acid etc.



Structure of MnO_4^- ion.

Structure of Permanganate Ion (MnO_4^-): Mn in MnO_4^- is in +7 oxidation state. Mn^{7+} exhibits sp^3hybridization in this ion. The structure of MnO_4^- is, shown in fig.