*NOTE:
- $K_2Cr_2O_7$ is used as a primary standard in labs.

oxygen atom having partially double bon character.
- in dichromate ion all six Cr-O bond length are equal due to resonance.

(C.) Chemical Properties:

1.) Effect on heating: when heated it decomposes and Oxygen is evolved.

$$4K_2Cr_2O_7 \longrightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

2.) Oxidising Property: Acts as a strong oxidizing agent in acidic medium. It oxidising action is:

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

- acidified potassium dichromate will oxidise iodide to iodine, sulphides to sulphur; tin(II) to tin(IV) and iron(II) salts to iron (III). The half-reactions are:

$6I^- \longrightarrow 3I_2 + 6e^-$ $\quad$ $3Sn^{+2} \longrightarrow 3Sn^{+4} + 6e^-$

$3H_2S \longrightarrow 6H^+ + 3S + 6e^-$ $\quad$ $6Fe^{+2} \longrightarrow 6Fe^{+3} + 6e^-$

- full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for reducing agent.

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

acidified $K_2Cr_2O_7$ (orange)

- $H_2S \longrightarrow S$
- $SO_2 \longrightarrow SO_4^{-2}$
- $NO_2^- \longrightarrow NO_3^-$
- $SO_3^{-2} \longrightarrow SO_4^{-2}$
- $Fe^{+2} \longrightarrow Fe^{+3}$
- $Br^- \longrightarrow Br_2$
- $I^- \longrightarrow I_2$
- $C_2H_5OH \longrightarrow CH_3COOH$
- $Sn^{+2} \longrightarrow Sn^{+4}$

Cr^{+3} or $Cr_2(SO_4)_3$ Green

Eq. wt. of $K_2Cr_2O_7$ in acidic med. = Mol. wt / 6.

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3.) **Rxn with hot H_2SO_4:**

- $K_2Cr_2O_7 + Hot\ H_2SO_4 \longrightarrow K_2SO_4 + H_2O + O_2 + Cr_2(SO_4)_3$

Green Crystal

4.) **Rxn with cold H_2SO_4:**

- $K_2Cr_2O_7 + cold\ H_2SO_4 \longrightarrow CrO_3 + K_2SO_4 + H_2O$

Red Crystal.

5.) **Rxn with H_2O_2 in presence of Ethereal Soln:**

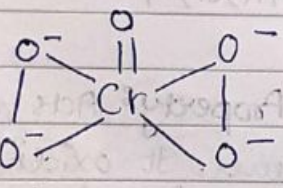
- $K_2Cr_2O_7 + 4H_2O_2 + 2H^+ \longrightarrow 5H_2O + 2CrO_5 + H_2O$

Deep blue.

* CrO_5 : Chromium pentaoxide.

O.S : +6

butterfly structure.



(5.) **Chromyl Chloride Test:** Chromyl chloride test is chemical test that detects the presence of chlorine in sample.

- For a test, mix small amount of pot. dichromate into small amount of salt then add small amount of sulfuric acid to a test tube, Red fumes of chromyl chloride is generated.

- Now, add sod. hydroxide to tube that contains yellow ppt. The yellow ppt indicates presence of chloride ion.

- $NaCl + K_2Cr_2O_7 + H_2SO_4 \longrightarrow CrO_2Cl_2$ (red fumes)
- $CrO_2Cl_2 + NaOH \longrightarrow Na_2CrO_4$ (yellow ppt)

- Chromyl chloride test is specific to chlorides and no similar compound is formed in the presence of fluoride, bromide, iodide or cyanide.

• Potassium Permanganate ($KMnO_4$):

(A.) **Preparation:** it is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3.

- These produces dark green K_2MnO_4 which dis-proportionate in neutral or acidic solution to give permanganate.

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

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

- commercially it is prepared by alkaline oxidative fusion of MnO_2 followed by electrolytic oxidation of manganate (VI).

- $MnO_2 \xrightarrow[\text{with air or } KNO_3]{\text{fused with KOH, oxidised}} MnO_4^{2-}$ manganate ion.

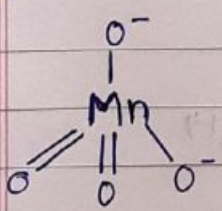
- $MnO_4^{2-} \xrightarrow[\text{soln}]{\text{electrolytic oxid}^n \text{ in alkaline}} MnO_4^-$ permanganate ion.

- In laboratory, it is prepared by oxidation of Mn^{+2} ion salt by peroxodisulphate.

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

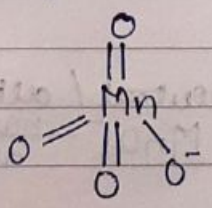
(B.) **Structure:**

I.) MnO_4^{-2}: ON = +6



- sp^3
- tetrahedral
- paramagnetic
- green
- manganate ion

II.) MnO_4^-: ON = +7



- sp^3
- tetrahedral
- diamagnetic
- purple
- permanganate ion

(C.) Chemical Properties:

* NOTE:
• Equivalent weight of $KMnO_4$ in different mediums:

I.)	MnO_4^- —(H⁺ acidic)→	Mn^{+2}	M/5
II.)	MnO_4^- —(neutral/ alkali/basic)→	MnO_2	M/3
III.)	MnO_4^- —(strong base)→	×	M/1

I.) Oxidising Rxns:

a.) in acidic medium:

$$MnO_4^- + H^+ \longrightarrow Mn^{+2} + H_2O$$

acidified $KMnO_4$ (purple)

H_2S	S
SO_2	SO_4^{2-}
NO_2^-	NO_3^-
Fe^{+2}	Fe^{3+}
Cl^-	Cl_2
Br^-	Br_2
I^-	I_2
$HCOOH$	$CO_2 + H_2O$
$H_2C_2O_4$	$CO_2 + H_2O$
$S_2O_3^{2-}$	$S_2O_6^{-2}$

Mn^{+2} ($MnSO_4$) colourless.

eg: $MnO_4^- + 8H^+ + 5Fe^{+2} \longrightarrow Mn^{+2} + 4H_2O + 5Fe^{+3}$

b.) in neutral / alkali medium:

$$MnO_4^- \xrightarrow{\text{neutral/ alkaline}} MnO_2 \text{ or } Mn^{+4}$$

Note: here, $I^- \longrightarrow I_2$ (X)

$I^- \longrightarrow IO_3^-$ (✓) iodate ion

neutral or alkali $KMnO_4$

Br^-	BrO_3^-
I^-	IO_3^-
$S_2O_3^{2-}$	SO_4^{-2}
Mn^{+2}	MnO_2

MnO_2

eg: (1) Iodide to Iodate:

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