

## Unit - VIII

### d-Block and f-block elements

d-block elements  $\rightarrow$  The elements in which the last electron enters in d-orbital are called d-block elements.

The d-block elements consist of elements from group 3 to 12.

d-block elements are also called transition elements.

Transition elements  $\rightarrow$  The elements which have partly filled d-orbital in their ground state or in common oxidation state are called transition elements.

Q Why Cu, Ag, Au are transition elements?

A  $\text{Cu} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

$\text{Cu}^{2+} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^9$

Acc. to definition, transition elements are those which have partly filled d-orbital in ground state or common oxidation state.

but in case of Cu, Ag, Au d orbital is completely filled. Since in common oxidation state the d orbital is partly filled. ∴ These are called transition elements.

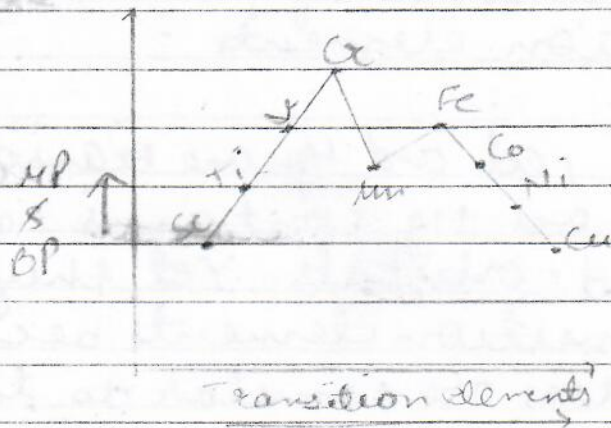
Q. Why Zn, Cd and Hg are transition elements?

A. Zn, Cd and Hg contains completely filled d-orbitals. Yet they are considered as transition elements because their properties are similar to transition elements.

Characteristics of transition elements

- 1) Electronic configuration  $\rightarrow (n-1)d^{1-10} ns^{1-2}$
- 2) Atomic radii  $\rightarrow$  Atomic radii of d-block elements lies b/w atomic radii of s-block elements & p-block elements.
  - (i) The atomic radii of d-block elements is less than s-block elements and more than p-block elements.
  - (ii) Within the transition elements the atomic radii decreases with increase in atomic number but decrease is small after midway.
- 3) Ionisation enthalpy  $\rightarrow$  The ionisation enthalpy of d-block element is more than s-block elements and less than p-block elements.
- 4) Metallic character  $\rightarrow$  Transition elements except Hg are typical metallic in nature. Due to low ionisation enthalpy and have one or two  $e^-$  in their outermost energy shell.

- As a result metallic bond is formed b/w them
- 5) Melting and boiling point  $\rightarrow$  Transition metals have very high melting point and boiling point. This is due to presence of a strong metallic bond b/w their atoms.



### Transition metals 1st series

The inter atomic forces is roughly related with number of unpaired electron. More be the number of unpaired electron, more be the inter atomic forces and more be the melting and boiling point.

Due to this melting point and boiling point first increases from Sc to Cr and then decreases from Fe to Cu.

There dip in MP and BP at manganese because Mn have stable E.C. and in this case the  $e^-$  tightly held by the nucleus and the ~~we~~ bond b/w the atoms is weak.  $\therefore$  its MP and BP is low.

- 6) Oxidation state  $\rightarrow$  Transition metal shows variable oxidation state such as +2, +3, +4, +5, +6, +7.
- Transition metal shows variable

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oxidation state due to participation of both  $(n-1)d$  and  $ns$  orbital  $e^-$  in bond formation.

- ⇒ The common oxidation state of the 1st series of transition element is +2.
- ⇒ The compounds of low oxidation state are generally ionic and the compounds of higher oxidation are generally covalent.
- ⇒ some transition metals have zero oxidation state.

7) Magnetic properties → The magnetic properties of transition element is related with nature of electrons present in it.

If transition metal contains all paired  $e^-$  then its compound is diamagnetic in nature.

If transition metal contains unpaired  $e^-$  then its compound is paramagnetic in nature.

8) Coloured compounds or ions → Most of the transition metal compounds or ions are coloured in nature.

The colour of transition metal compound or ions is due to  $d-d$  transition.

9) Tendency to form complexes → Transition elements have a high tendency to form

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the complexes. Eg  $\rightarrow [Cu(NH_3)_6]^{2+}$   
and  $[Fe(CN)_6]$

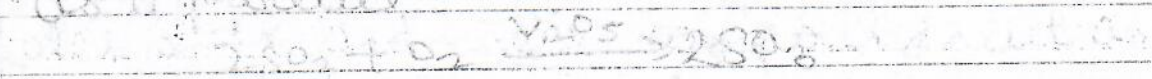
The high tendency of transition elements to form complexes is due to

- ① High nuclear charge on metal ion
- ② Availability of vacant d-orbitals to accept the  $e^-$ .

10) Catalytic properties  $\rightarrow$  Many transition elements and their compounds act as a catalyst in various rxn.

For eg.  $\rightarrow$  Haber's process  $\rightarrow$  In this process  $N_2$  &  $H_2$  react with  $H_2$  in presence of Fe and Mo at high pressure and low temperature to give  $NH_3$  as a product.

Contact process  $\rightarrow$  Oxidation of  $SO_2$  to  $SO_3$  is an oxidation in presence of vanadium pentoxide ( $V_2O_5$ ) forms  $SO_3$  as a product.



Transition metals and their compounds act as a catalyst because

- (i) They have high tendency to combine with reactant and form intermediate complex with low activation energy.
- (ii) They provides large surface area to reactant so that they get adsorbed on their surface and carry out chemical rxn.

11) Formation of alloys  $\rightarrow$   
Alloys are the homogeneous solid solution in which atoms of one metal is present randomly within the atoms of other elements.

eg.  $\Rightarrow$  Bronze is a alloy of Cu and Sn (Te)  
Brass is a alloy of Cu and Zn

The transition elements are quite similar in size and properties thus atom of one metal can easily be replaced by the atoms of other metal.

12) Formation of interstitial compounds.  
Transition metals forms interstitial compounds with elements such as H, C, B, N etc.

In transition metals there are certain interstitial sites due to various defects. These interstitial sites are occupied by the atoms of small elements such as H, C, N, B etc. and leads to the formation of interstitial compounds.

Compounds  $\Rightarrow$

$\Rightarrow$  Potassium dichromate ( $K_2Cr_2O_7$ )

Methods of preparation  $\rightarrow$

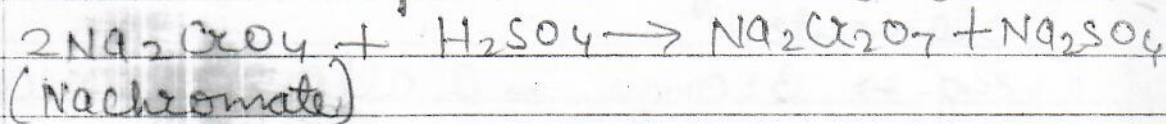
From chromite ore ( $FeCr_2O_4$ )

$K_2Cr_2O_7$  can be prepared from chromite ore which involve following steps  $\rightarrow$

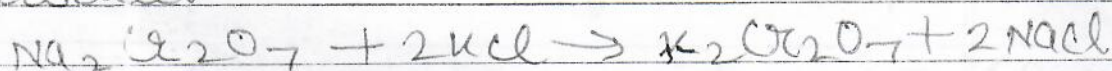
① Conversion of chromite ore to  $Na_2Cr_2O_7$   
chromite ore when fused with  $NaOH$

in presence of air forms Na chromate  
 $4\text{FeCr}_2\text{O}_4 + 16\text{NaOH} + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{H}_2\text{O}$

② Conversion of Na chromate into Na dichromate  $\rightarrow$  Na chromate on acidification with  $\text{H}_2\text{SO}_4$  forms Na dichromate.

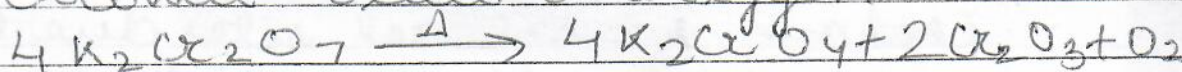


③ Conversion of Na dichromate into K dichromate  $\rightarrow$  on heating Na dichromate with salt of K gives K dichromate as a product.

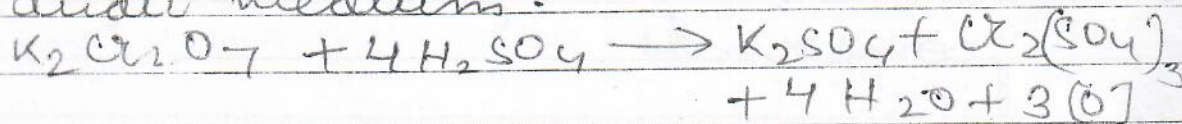


Properties  $\rightarrow$

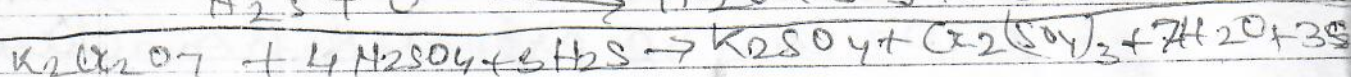
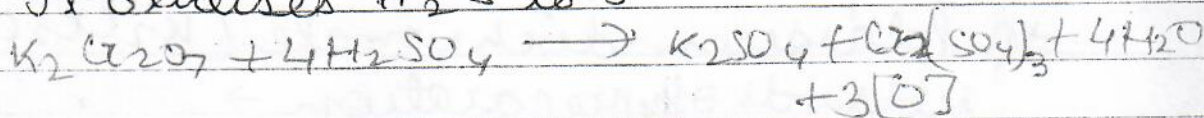
① Action with metal heat  $\rightarrow$  K dichromate on heating decompose to K chromate, chromic oxide and oxygen.



② Oxidising character  $\rightarrow$  K dichromate act as strong oxidising agent in acidic medium.

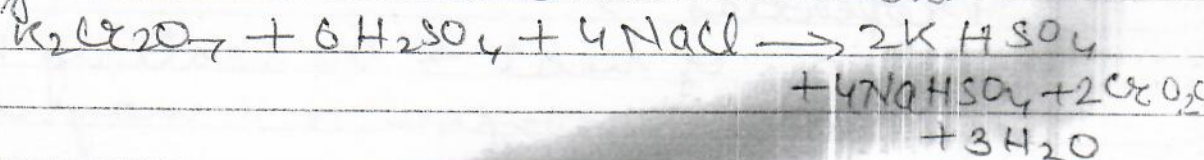


It oxidises  $\text{H}_2\text{S}$  to S

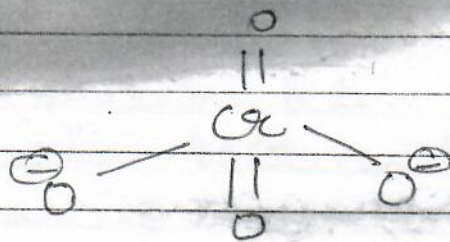


(CrO<sub>2</sub>Cl<sub>2</sub>)  
 ③ Chromyl chloride test → This test is used for the identification of chloride ion.

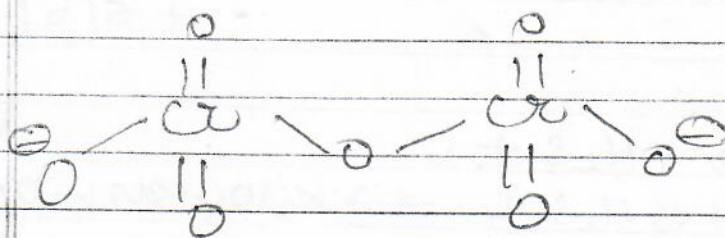
In this test K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is heated with H<sub>2</sub>SO<sub>4</sub> and a given salt. If reddish orange vapour appears then Cl<sup>-</sup> ion is present in given salt. If reddish orange vapours are not formed then Cl<sup>-</sup> ion is absent.



Structure → Chromate ion CrO<sub>4</sub><sup>2-</sup>



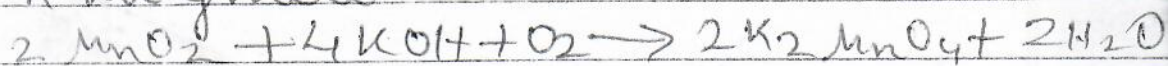
Dichromate Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>



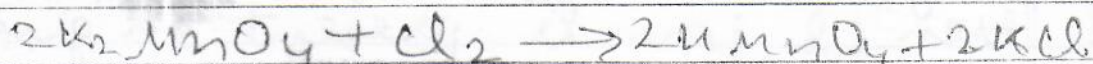
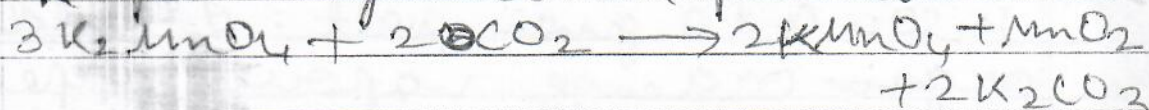
⇒ Potassium permanganate (KMnO<sub>4</sub>)  
 Method of preparation → KMnO<sub>4</sub> is prepared from pyrolusite ore (MnO<sub>2</sub>) which involve following steps:  
 ① Conversion of pyrolusite ore into potassium manganate → Pyrolusite ore when fused with potassium hydroxide is present in presence of oxygen forms



K manganate -

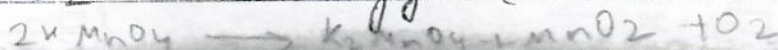


- ② Conversion of K manganate into K permanganate  $\rightarrow$  K manganate on oxidation with  $\text{CO}_2$ ,  $\text{Cl}_2$  etc. form K permanganate as a product.

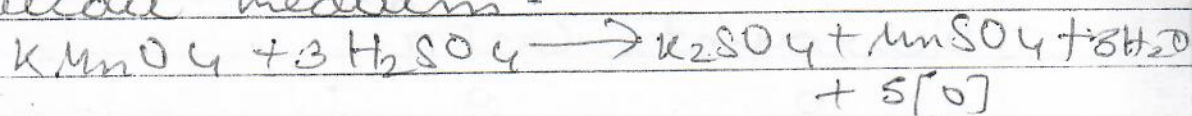


Properties  $\rightarrow$

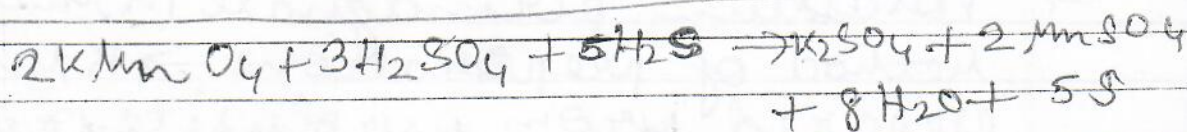
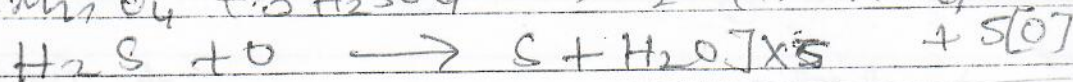
- ① Action of heat  $\rightarrow$  on heating K permanganate decompose to K manganate,  $\text{MnO}_2$  and oxygen.



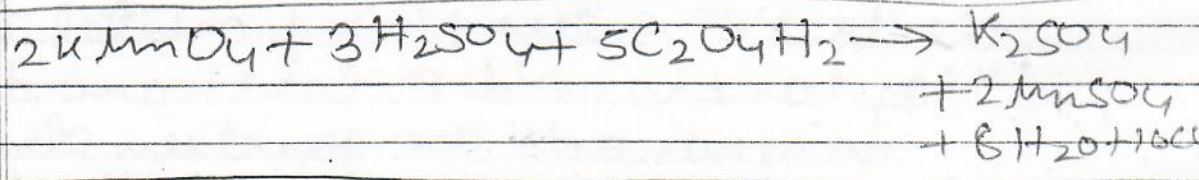
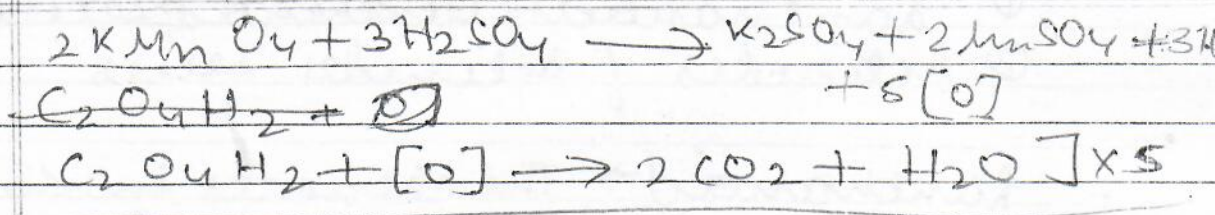
- ② oxidising character  $\rightarrow$  K permanganate act as a mild oxidising agent in basic and neutral medium. But it act as a strong oxidising agent in acidic medium.



It oxidise  $\text{H}_2\text{S}$  to S



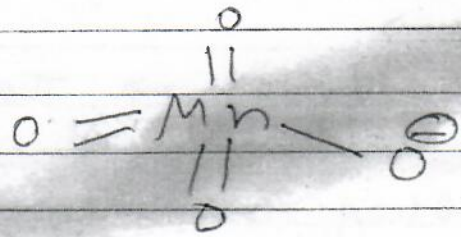
It oxidise oxalic acid to  $\text{CO}_2$



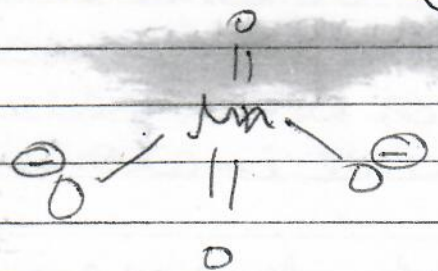
Structure →

Potassium permanganate →  $\text{KMnO}_4$

Permanganate ion: →  $\text{MnO}_4^-$



Manganate ion →  $(\text{MnO}_4^{2-})$



⇒ Alkaline  $\text{KMnO}_4$  is known as Baeyer's reagent.

⇒ f-block elements → The elements in which the last  $e^-$  enters in f-orbital are known as f-block elements.

The general electronic configuration of f-block elements is  $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$ . f-block elements are also known as inner transition elements.

f-block elements or inner transition elements consists of two series

- ① Lanthanoids / Lanthanoid series
- ② Actinides / Actinides series

Lanthanoid  $\rightarrow$  The elements in which the last  $e^-$  enters in  $4f$  orbital are called as Lanthanoids or Lanthanoid series.

Lanthanoids are fourteen elements followed by lanthanum, starting from Cerium to Lutetium. The general electronic configuration of Lanthanoids are  $4f^{1-14} 5d^{0-1} 6s^2$ .

Properties  $\rightarrow$

① Oxidation state  $\rightarrow$  The common oxidation state of Lanthanoid is +3. In addition to this they also show +2 and +4 oxidation state.

② Atomic radii or ionic radii  $\rightarrow$  As we move along the Lanthanoid series the atomic or ionic radii decreases but the decrease in atomic radii is very small.

The steady decrease in atomic radii or ionic radii with increase in atomic number along the Lanthanoid is called as Lanthanoid contraction.

\* Consequences of Lanthanoid contraction  $\rightarrow$   
Following are the consequences of Lanthanoid contraction  $\rightarrow$

- ① Resemblance of elements of 2nd and 3rd

## transition

②. Similarity b/w lanthanoids  $\rightarrow$  Due to lanthanoid contraction there is a very small change in atomic radii of lanthanoids. Therefore, all the lanthanoids have similarities in properties -

③. Difference in basic strength  $\rightarrow$  The basic strength of the hydroxides of inner transition elements decreases with increase in atomic number.

eg  $\rightarrow$   $\text{La}(\text{OH})_3$  is more basic than  $\text{Lu}(\text{OH})_3$

$\rightarrow$  As we move along the lanthanoid series the atomic size decreases due to lanthanoid contraction and thus M-OH bond strength increases and thus the basic strength decreases. Due to this  $\text{La}(\text{OH})_3$  is more basic than  $\text{Lu}(\text{OH})_3$ .

③. Colour  $\rightarrow$  In general most of the lanthanoids are white but few of its trivalent ions are coloured.

Actinides  $\rightarrow$  The elements in which the last  $e^-$  enters in 5f orbital are called actinides.

Actinides are the 14 elements followed by actinium (Ac) starting from Thorium 90 (Th) to Lawrencium 103 (Lr).

All the actinides are radioactive in nature.

Properties →

- ① Electronic configuration → General e.c. is  $5f^{1-14} 6d^{0-1} 7s^2$
- ② Oxidation state → The common O.S. of actinides is +3. In addition to this they show variable oxidation state.
- ③ Atomic radius → As we move along the actinides series, the atomic size decrease. This steady decrease in atomic size is known as actinide contraction.
- ④ Colour → All the actinides are coloured and their colour is due to f-f transition.

	Lanthanoid	Actinides
1)	Lanthanoids are non radioactive in nature.	Actinides are radioactive in nature.
2)	Lanthanoids do not show variable oxidation state.	Actinides show variable oxidation state.
3)	Most of the lanthanoids are white.	All the actinides are coloured.
4)	Lanthanoids have less tendency to form complexes.	Actinides have high tendency to form complexes.