CONCEPT MAP

ESSENTIALS OF INORGANIC CHEMISTRY (PART II)

The *d* and *f*-Block Elements

d-Block Elements

- **(Groups 3-12) :** Transition elements
  There are four main transition series 3*d*(Sc to Zn), 4*d*(Y to Cd), 5*d*(La, Hf to Hg) and 6*d*(Ac, Rf to Cn)
- **E.C.:** $(n-1)d^{1-10}\,ns^{0-2}$ (where, *n* is the outermost shell).

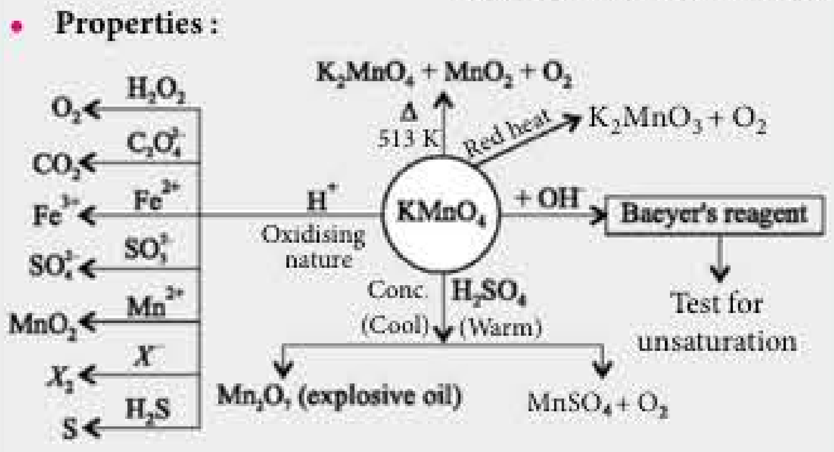
Trends and Characteristics of Transition Elements

- Atomic radii decreases with increase in atomic number.
- Having *hcp*, *ccp* or *bcc* metallic structures [except Hg].
- First *I.E.* is higher than those of *s*-block elements and lesser than those of *p*-block elements.
- High m.pt. and b.pt. M.pt. first increase, rise to maximum and then decrease.
- Show variable oxidation states. Most common oxidation state of the first series is +2 [except Sc (+3)]. Higher oxidation state shown by Ru and Os is +8.
- They form complexes, interstitial compounds and alloys.
- Transition metals and their compounds are used as catalyst.
- Transition metal compounds are coloured.
- Transition metal compounds are generally paramagnetic.

Some Important Compounds of Transition Elements

$KMnO_4$ (Potassium permanganate)

- **Preparation :** $3K_2MnO_4 + 2H_2SO_4 \longrightarrow 2KMnO_4 + MnO_2 + 2K_2SO_4 + 2H_2O$
- **Properties :**



f-Block Elements

- Inner transition elements.
- The *f*-block consists of two series of elements known as lanthanides (lanthanoids) and actinides (actinoids).
- **E.C.:** $(n-2)f^{1-14}\,(n-1)d^{0-1}\,ns^2$ (where, *n* = 6 for lanthanides and *n* = 7 for actinides).

Trends and Characteristics of Lanthanides

- Show common stable oxidation state +3.
- Regular decrease in atomic and ionic radii with increase in atomic number is called lanthanide contraction.
- They have low *I.E.* and high b.pt. and m.pt.
- All the lanthanides are strong reducing agents.

Trends and Characteristics of Actinides

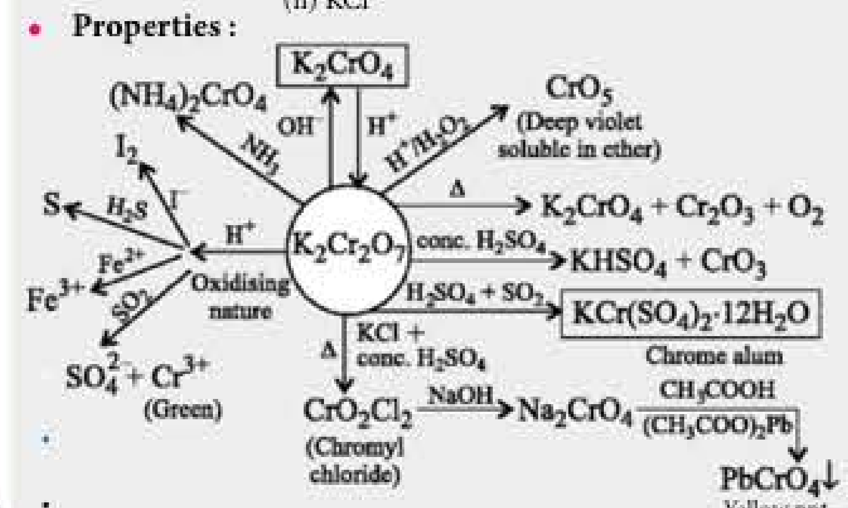
- All actinides show +3 common oxidation state.
- All actinides are radioactive.
- All are strong reducing agents.

Chemical Reactivity of Lanthanides

$K_2Cr_2O_7$ (Potassium dichromate)

- **Preparation :** $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

  $Na_2CrO_4 \xrightarrow[\text{(ii) KCl}]{\text{(i) Conc. } H_2SO_4} K_2Cr_2O_7 + 2NaCl$
- **Properties :**



Coordination Compounds

Werner's Coordination Theory

It explains the nature of bonding in complexes. Metals show two different kind of valencies :

- **Primary valency :** Non-directional and ionisable. It is equal to the oxidation state of the central metal ion. It is satisfied by negative ions.
- **Secondary valency :** Directional and non-ionisable. It is equal to the coordination number of the metal. It is commonly satisfied by neutral and negatively charged ions.

Valence Bond Theory (VBT)

- Bonding in terms of hybridised orbitals of the central metal atom or ion, it explains the shapes and magnetic behaviour of complexes.
- **Hybridisation and geometry of complexes :**

Coordination no.	Type of hybridisation	Geometry of complex
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

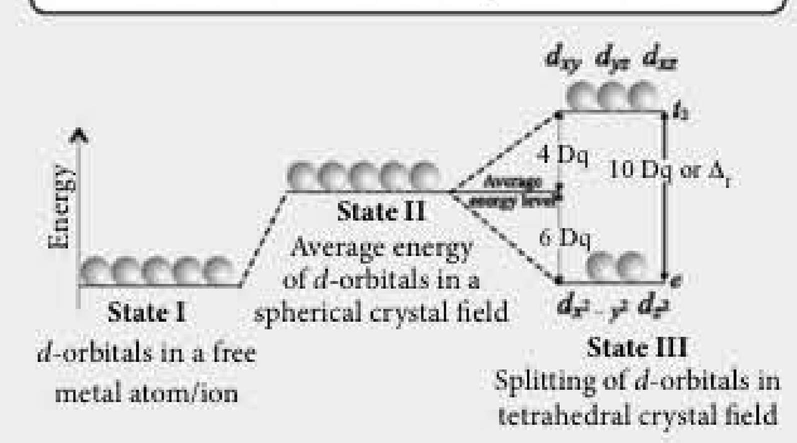
Isomerism

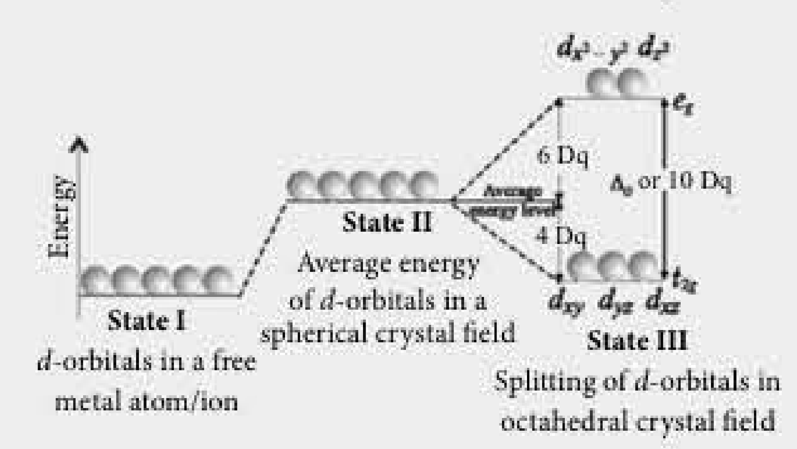
- **Structural isomerism :** Arises due to difference in structures of coordination compounds.
  - **Ionisation isomerism :** $[Co(NH_3)_5Br]Cl$; $[Co(NH_3)_5Cl]Br$
  - **Hydrate isomerism :** $[Cr(H_2O)_6]Cl_3$; $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$, $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$
  - **Coordination isomerism :** $[Co(NH_3)_6][Cr(CN)_6]$; $[Cr(NH_3)_6][Co(CN)_6]$
  - **Linkage isomerism :** $[Co(NH_3)_5ONO]Cl_2$; $[Co(NH_3)_5NO_2]Cl_2$
- **Stereoisomerism :** Shown by compounds having same structural formula but differ only in the spatial arrangement of ligands around the central atom.
  - **Geometrical isomerism :** Arises due to different possible geometric arrangement of ligands.
  - **Optical isomerism :** Shown by molecule which do not have plane of symmetry.

Crystal Field Theory (CFT)

- According to CFT, under the influence of ligand field, degeneracy of *d*-orbitals is destroyed and they split into two or more energy levels. The extent of splitting depends upon the strength of ligand.
- **Spectrochemical series :** Arrangement of ligands in the order of increasing field strength (increasing order of Δ_o).
  $I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < NH_3 < en < NO_2^- < CN^- < CO$.
  - If $\Delta_o < p$, then complex is high spin.
  - If $\Delta_o > p$, then complex is low spin ; $\Delta_t = 4/9\,\Delta_o$

Splitting of *d*-orbitals in Tetrahedral and Octahedral Crystal Field





Applications of Coordination Compounds

- In biological system. *e.g.*, chlorophyll, haemoglobin, vitamin B_{12}, etc. are coordinate compounds of Mg, Fe and Co respectively.
- *cis*-platin is used in cancer treatment, EDTA is often used for treatment of lead poisoning.