The d- & f- Block Elements

* Transition elements : a) A transition element is defined as the one which has incompletely filled d orbitals in its ground state or in any one of its oxidation states. b) electronic configuration $(n-1)d^{1-10}\ ns^{1-2}$.

c) Zn, Cd, Hg are not transition metals as their d-orbital is full* (d^{10}). d) Transition elements are placed at 3 to 12th group from 3rd to 6th period (3d series, 4d series, 5d series, 6d incomplete series). e) The presence of unpaired & unfilled d-orbitals favours covalent bonding.

* General properties of the transition elements (d- Block) :

a) Physical Properties: All transition elements (except Zn, Cd, Hg, Mn) display typical metallic properties, such as high tensile strength, high thermal & electrical conductivity, metallic lustre. They have high melting & boiling pts, high enthalpies of atomisation.

b) Variation in atomic & ionic sizes: Generally decreases along the period

c) Ionisation enthalpies: Generally increase along the series

* full at ground state & common oxidation states. (Cu, Ag, Au are transition elements.)

d. Oxidation States: Elements show different os's. (Mn shows +2 to +7, Sc(21) does not show variable os.)

- Cr^{2+} reducing, Mn^{3+} oxidising: Cr^{2+} is reducing as its config changes from d^4 to d^3, the latter having a half filled t_{2g} level. The change from Mn^{2+} to Mn^{3+} results in the half filled d^5 config which has extra stability.

e. Magnetic properties: Transition metal ions & their compounds are paramagnetic due to their unpaired electrons on the (n-1)d orbitals & is calculated by using the spin only formula, $\mu = \sqrt{n(n+2)}$ BM where n is no. of unpaired electrons. [$n=1 \Rightarrow \mu = 1.73$ BM, $n=2 \Rightarrow \mu = 2.84$, $n=3 \Rightarrow \mu = 3.87$, $n=4 \Rightarrow \mu = 4.90$].

f. Formation of coloured compounds: Form coloured compounds due to d-d transitions. (Cr^{3+} violet, Mn^{3+} violet, Cr^{2+} blue, Mn^{2+} pink, Fe^{3+} yellow, Fe^{2+} green, Co^{3+} Co^{2+} pink-blue, Cu^{2+} blue, Zn^{2+} colourless).

g) formation of complex compounds: Transition metals form a large number of complexes due to presence of unpaired electrons, availability of empty d-orbitals to accept lone pair of electrons donated by ligands, high nuclear charge, small size.

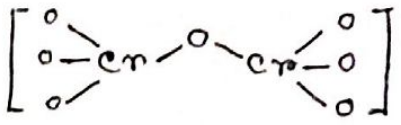
h. Catalytic properties: Show catalytic properties due to variable oxidation states & to form complexes.

i. Formation of interstitial compounds: Due to empty spaces in their lattices, small atoms can be easily accomodated. (eg. $VH_{0.56}$, $TiH_{1.7}$)

j. Alloy formation: Because of similar atomic radii & other characteristics of transition metals, alloys are readily formed by these metals.

* Some Important Compounds:

a) Potassium dichromate ($K_2Cr_2O_7$):



dichromate ion.

i) Preparation:

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

$$2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O.$$

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

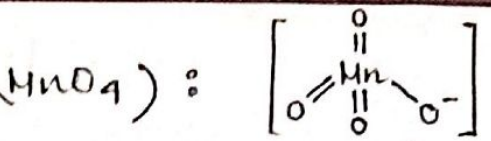
ii) Properties: Orange-red crystalline solid, oxidising agent having m.pt. 398°C.

oxidising agent in acidic medium-

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

oxidises I^- to I_2, Sn^{2+} to Sn^{4+}, Fe^{2+} to Fe^{3+}.

iii) Uses: In dyeing, photography, leather industry.

b) Potassium permanganate ($KMnO_4$): 

i) Preparation: From Potassium manganate (obtained from pyrolusite)

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

ii) Properties: Deep purple, crystalline solid, oxidising agent, having m.pt 240°C.

Oxidising agent in acidic medium:

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

oxidises I^- to I_2, Fe^{2+} to Fe^{3+}, S^- to S.

oxidising agent in alkaline or neutral medium

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

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

Iodide — Iodate.

$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$$

iii) Uses: As a desinfectant, germicide & Bacyer's reagent (alkaline $KMnO_4$).

- Permanganate titrations in presence of HCl are unsatisfactory since HCl is oxidised to Cl_2.

* Inner Transition Elements:

- Lanthanoids: The elements with atomic numbers 58 to 71, i.e. cerium to lutetium (which come immediately after lanthanum) are called lanthanoids.

• Actinoids: The elements with atomic number 90 to 103, ie thorium to lawrencium are called actinoids.

• Electronic config: $(n-2)f^{1-14}(n-1)d^{1-10}ns^2$.

• General Characteristics of lanthanoids:

i) Oxidation states: Common OS's are +3. $Eu^{2+}(4f^7)$, $Yb^{2+}(4f^{14})$, $Ce^{4+}(4f^0)$ & $Tb^{4+}(4f^7)$ are also quite stable.

ii) Reducing properties: Ions with +2 OS are reducing.

iii) Oxidising properties: Ions with +4 OS are oxidising.

iv) Paramagnetism: Most metals & ions are paramagnetic due to the presence of unpaired electrons.

v) Colour - All metals are silvery white.

vi) Lanthanoid Contraction: The contraction of size of lanthanoids & trivalent ions with increase in atomic no. This is due to increase in nuclear charge & negligible screening of 4f electrons.

• Effect of lanthanoid contraction:

i) Because of small difference in size of lanthanoids, their separation is possible by ion exchange method.

ii) Basic strength for hydroxides is more for larger cation. $Ce(OH)_3 > Lu(OH)_3$; $La(OH)_2 > La(OH)_3$.

iii) Radii of elements in same group from 4th to 12th groups in 4d & 5d series are very close & these elements in each group are called chemical twins, eg Zr & Hf, Nb & Ta.

iv) The properties of complex formation increase from La to Lu because of decrease in size & increase in charge: size ratio.

v) There is very slight increase in EN from La to Lu.

- General Characteristics of Actinoids:

i) They show higher OS's of +4, +5, +6 & +7 besides +3. ii) Along the series atomic radius continuously decreases. iii) Oxides & hydroxides are more basic than lanthanoids. Ions having unpaired electrons are coloured (except f^0 & f^7) & are paramagnetic

- Imp. points: i) Anhydrous $FeSO_4$ & $CuSO_4$ are white because of absence of crystal field splitting. ii) Among d-block, tungsten has highest m.pt & Hg has lowest m.pt. iii) Tc_{43} was the first artificial element.