d & f Block

Transition Elements

Becaused block elements are situated in b/w metals and nonmetals. Typically, the transition elements having completely filled d-level, are not considered as transition elements but they are d-block elements.

Since Zn group has d^{10} configuration in their ground state as well as in stable oxidation state, they are not considered as transition elements but they are d-block elements.

General Characteristics

$(n-1)d^{1-10}ns^{1-23}$

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
साइन्स	टीचर	very	cruel	मन	फे	को	नी	क्यू	जान जलाती हो।

As usual / Others are: $4s^1$ / $3d^5$ (Cr); $4s^1$ / $3d^{10}$ (Cu)

Cr, Mo, W → Maximum

6 no. of unpaired e^-s are involved in metallic bonding

Zn, Cd, Hg — Lowest m.p.

Due to no unpaired e^-

For metallic bonding

Sc ⟶ Mn Fe Co Ni Cu Zn

decreases — Remains same — Increases again

1^{st}, 2^{nd}, 3^{rd} IE's are increasing from left to right for 1^{st} Transition series, but not regularly.

For 2^{nd} IE Cr > Fe > Mn and Cu > Zn

For 3^{rd} IE Mn > Cr > Fe and Zn has highest.

The atomic volume of the transition elements are low, compared with s-block, so their density is comparatively high (D = M/V).

The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7.

Thus, early in the series Scandium (II) is virtually unknown and Titanium (IV) is more stable than Ti (III) or Ti (II).

Oxidation states of the I^{st} transition series most common ones are in bold types

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			+1					+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3		
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

MIND MAP

d & f Block

Formation of Coloured Ion

Colour (aquated)

$Ti^{4+} \longrightarrow$ Colourless

$V^{4+} \longrightarrow$ Blue

$V^{2+} \longrightarrow$ Violet

$Cr^{3+} \longrightarrow$ Green

$Mn^{2+} \longrightarrow$ Light pink

$Fe^{3+} \longrightarrow$ Yellow

$Ni^{2+} \longrightarrow$ Green

$Zn^{2+} \longrightarrow$ Colourless

Catalytic Properties

The transition metals and their compounds are known for their catalytic activity.

This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes.

Vanadium(V)oxide (in Contact Process), finely divided Iron (in Haber's Process), and Nickel (in Catalytic Hydrogenation) are some of the examples.

Formation of Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals.

Alloy Formation

An Alloy is a blend of metals prepared by mixing the components.

Alloys of transition metals with non transition metals such as brass (Copper-Zinc) and bronze (Copper-Tin), are also of considerable industrial importance.

Oxides and Oxoanions of Metals

Chromate-Dichromate

Preparation

$$\underset{\text{(Chromite Ore)}}{4FeCr_2O_4} + 8Na_2CO_3 + 7O_2 \xrightarrow[\text{Red hot in presence of air}]{1000° - 1300°C}$$

Residue (Fe_2O_3)

Filtrate (Na_2CrO_4)

Dissolve in water and filtered

$$8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2\uparrow$$

$$2Na_2CrO_4 + \underset{\text{conc.}}{H_2SO_4} \longrightarrow Na_2SO_4\downarrow + Na_2Cr_2O_7 + H_2O$$

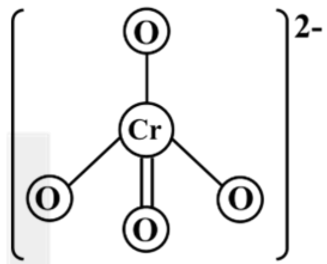
It's solubility upto 32°C increases and then decreases } Hence, suitable temp. is to be employed to crystallise out Na_2SO_4 first.

$$\underset{\text{Hot conc.}}{Na_2Cr_2O_7} + 2KCl \xrightarrow[\text{Decomposition}]{\text{Double}} K_2Cr_2O_7 + 2NaCl$$

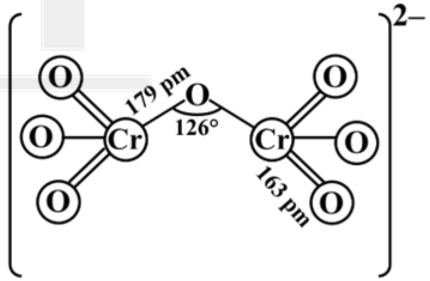
The oxidation state of Chromium in Chromate and Dichromate is the same.

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

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$



Chromate ion



Dichromate ion

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \quad (E^{\ominus} = 1.33V)$$

MIND MAP

d & f Block

Manganate & Permanganate

Preparation of MnO_4^{2-}

$MnO_2 \xrightarrow[\text{or NaOH } \Delta \text{ in presence of air}]{KOH} MnO_4^{2-}$ (Green melt)

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

$MnO_2 + 2KOH + KNO_3 \longrightarrow K_2MnO_4 + KNO_2 + H_2O$

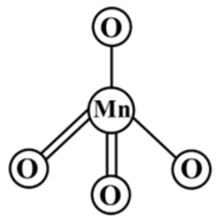
$3MnO_2 + 6KOH + KClO_3 \longrightarrow 3K_2MnO_4 + KCl + 3H_2O$

Green melt $\xrightarrow[\text{little alkali}]{\text{Cold Water} + }$ Green soln. $\xrightarrow[\text{evaporation}]{\text{On}}$

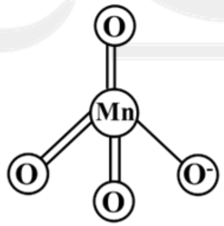
- $\xrightarrow[\text{used}]{\text{If KOH}}$ K_2MnO_4 (isomorphrous with K_2SO_4)
- $\xrightarrow[\text{used}]{\text{If NaOH}}$ $Na_2MnO_4.10H_2O$ Isomorphrous with $Na_2SO_4.10H_2O$

Manganate is also obtained when $KMnO_4$ is boiled with KOH.

$$4KMnO_4 + 4KOH \xrightarrow{\text{Boiled}} 4K_2MnO_4 + 2H_2O + O_2$$



Tetrahedral Manganate (green) ion



Tetrahedral PerManganate (Purple) ion

$$3K_2MnO_4 + 2H_2O \longrightarrow \underset{\text{Purple}}{2KMnO_4} + \underset{\text{Dark Brown}}{MnO_2 \downarrow} + 4KOH$$

Inner Transition Elements

The elements in which the last electron enters in $(n-2)f$ orbitals are called inner transition elements or f-block elements.

Position In The Periodic Table

The Lanthanides resemble with Yttrium in most of their properties.

Lanthanides (Rare Earths or Lanthanones)

Electronic Configuration

The general configuration of Lanthanides may be given as $6s^2 5d^{0-1} 4f^{1-14}$.

The Lanthanides contain two s electrons in the outermost shell, they are therefore expected to exhibit a characteristic Oxidation state of +2.

But for the Lanthanides, the +3 Oxidation is common.

All the Lanthanides attains +3 oxidation state and only Cerium, Praseodymium, and Terbium exhibit higher oxidation state (+4).

Eu and Yb exhibit +2 oxidation state.

MIND MAP

d & f Block

Magnetic Properties

In Tripositive Lanthanide ions the number of unpaired electrons regularly increases from Lanthanum to Gadolinium (0 to 7) and then continuously decreases upto Lutecium (7 to 0).

Lanthanum and Lutecium ions are diamagnetic, while all other tripositive Lanthanide ions are Paramagnetic.

(Exception – Neodyomium is the most Paramagnetic Lanthanide).

Colour

The Lanthanide ions have unpaired electrons in their 4f orbitals.

Thus these ions absorb visible region of light and undergo f–f transition and hence exhibit colour.

Other Properties

All the Lanthanoids are silvery white soft metals and tarnish rapidly in air.

Ionisation Energies

Lanthanides have fairly low Ionisation Energies comparable to alkaline earth metals.

Electro Positive Character

High due to low I.P.

Complex formation

Do not have much tendency to form complexes due to low charge density because of their large size.

Lu^{+3} is smallest in size and can form complexes.

Reducing Agent

They readily lose electrons so are good reducing agent.

Alloy

Alloys of Lanthanides with Fe are called Misch metals, which consists of a Lanthanoid metal (~ 95%) and Iron (~ 5%) and traces of S, C, Ca and Al.

Basic Nature

$La(OH)_3$ is most basic in nature while $Lu(OH)_3$ least basic.

The Lanthanide elements Eu and Yb dissolve directly in very high concentration in liquid Ammonia.

Lanthanide Contraction

In the Lanthanide series with increasing atomic number, there is a progressive decrease in the size from Lanthanum to Lutecium or from La^{+3} to Lu^{+3}.

This contraction in size is known as Lanthanide Contraction.

Chemical Reactions of The Lanthanoids