d and f Block Elements

The d-block and f-block elements of the periodic table refer to the transition metals and inner transition metals, respectively. The d-block elements are those found in groups 3 through 12, where the d orbitals are progressively filled across the four long periods. The f-block elements are those where the 4f and 5f orbitals are progressively filled and are located in a separate section at the bottom of the periodic table. The main transition metal series are the 3d, 4d, 5d, and 6d series, and the inner transition metal series are the 4f and 5f series, also known as the lanthanoids and actinoids, respectively.

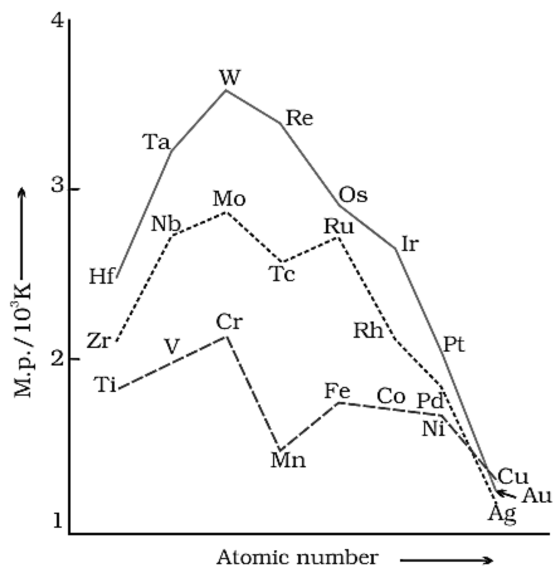
The Transition Elements (d-Block) –

Electronic configuration –

- The electronic configuration of the outer orbitals for transition metals follows the general configuration of **$(n-1)\ d^{1-10}ns^{1-2}$**.
- The only exception is palladium, which has an electronic configuration of $[Kr]4d^{10}5s^{0}$.
- The electronic configuration of Cr and Cu are - $3d^{5}4s^{1}$ and $3d^{10}4s^{1}$.
- The electronic configurations of outer orbitals of Zn, Cd, Hg, and Cn are represented by the general formula $(n-1)\ d^{10}ns^{2}$. Since their orbitals are completely filled in ground states as well as common oxidation states. So, they are not regarded as transition elements.

General Properties of the Transition Elements (d-Block) –

- **Zn, Cd, Hg, and Mn** do not have a typical metallic structure at room temperature.
- The melting points of the transition elements are shown below:

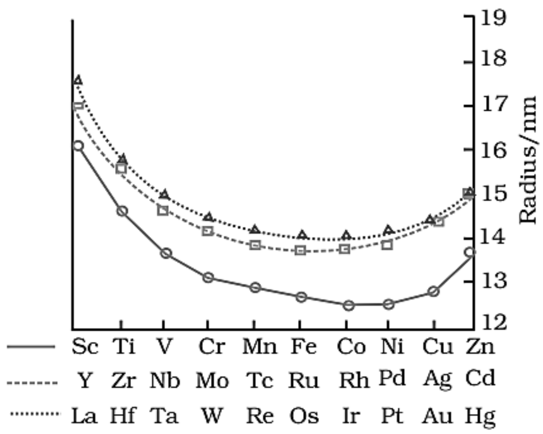


- The melting points of these metals rise to a maximum at d^5 except for anomalous values of **Mn** and **Tc**.
- In the Enthalpies of atomization graph, the maxima are at about the middle of each series

indicating that one unpaired electron per d orbital favours strong interatomic interactions.

Variation in Atomic and Ionic Sizes of Transition Metals –

- The curve shows an increase from the first (3d) to the second (4d) series of the elements but the radii of the third (5d) series is the same as that of corresponding members of the second series.



- **Lanthanoid Contraction** - The filling of 4f orbital before 5d orbital causes regular decreases in atomic radii. This is mainly due to the imperfect shielding of a 4f electron (which is less than one d electron). So, as the nuclear charge increases there is a regular decrease in the size of $4f^n$ orbitals.
- The decrease in a metallic radius coupled with an increase in the atomic mass causes a general increase in the density of these elements.

Oxidation states –

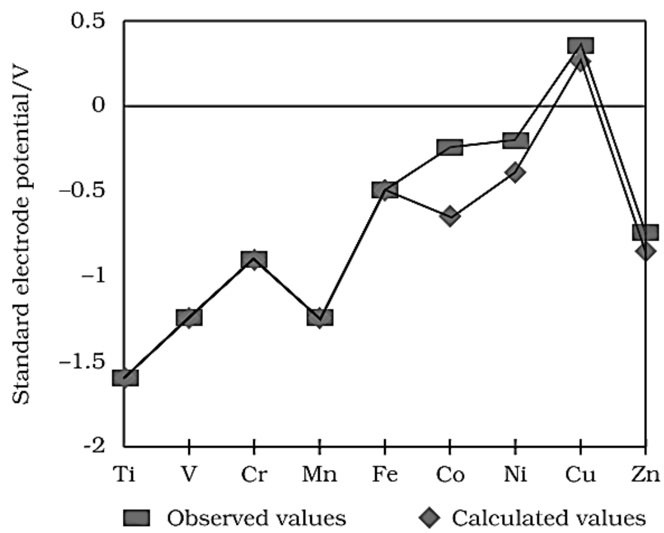
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**	**+1**	**+2**
+3	**+3**	**+3**	**+3**	**+3**	**+3**	**+3**	**+3**	**+2**	
	+4	**+4**	**+4**	**+4**	**+4**	**+4**	**+4**		
		+5	**+5**	**+5**					
			+6	**+6**	**+6**				
				+7					

Trends in the M^{2+}/M Standard Electrode Potentials –

- Copper has a positive standard electrode potential (E^{Θ}), which explains its inability to liberate hydrogen gas from acids. Only oxidizing acids like nitric acid and hot concentrated sulfuric acid will react with copper, reducing the acids in the process. The high energy required to transform copper in its elemental state, $Cu(s)$ to copper ions in solution,

$Cu^{2+}(aq)$ is not balanced by its hydration enthalpy.

- The stability of Mn^{2+} and Zn^{2+} due to their half-filled subshells and completely filled d^{10} orbital respectively is related to their $E^{\ominus}$ values. $E^{\ominus}$ for Ni is related to the highest negative $\Delta_{Hyd}H^0$.



Chemical Reactivity and $E^{\ominus}$ Values –

- The metals in the first transition series (except Cu) are generally more reactive and can be oxidized by 1M hydrogen ions (H^+).
- The standard electrode potentials $E^{\ominus}$ indicate a decreasing tendency to form divalent cations across the series, related to the increasing sum of first and second ionization enthalpies.
- The $E^{\ominus}$ value of Mn, Ni, and Zn is more negative than that expected from the general trend.

Magnetic Properties –

- Diamagnetic substances are repelled by the magnetic field.
- Paramagnetic substances are attracted by the magnetic field. Substances that are attracted very strongly are ferromagnetic in nature.
- Many transition metal ions exhibit Para magnetism. This arises from each unpaired electron possessing both spin and orbital angular momentum, which gives it a magnetic moment. For first-row transition metal compounds, the orbital contribution is quenched so spin angular momentum is what determines magnetic behaviour.
- The magnetic moment calculated by the spin-only formula is as under:

$$\mu = \sqrt{n(n+2)}$$

where n is the number of unpaired electrons, μ is the magnetic moment in the units of Bohr Magneton (BM).

Formation of Coloured Ions –

- When an electron in a transition metal ion is excited from a lower energy d-orbital to a higher one, the energy absorbed corresponds to a frequency in the visible light region. The colour observed is the complementary colour to the one absorbed.
- The colours of aquated first-row transition metals are as under –

Configuration	Ion/Colour
$3d^0$	**Sc^{3+}, Ti^{4+}/ Colourless**
$3d^1$	**Ti^{3+}, Purple/V^{4+} blue**
$3d^2$	**V^{3+}, Green**
$3d^3$	**V^{2+},Cr^{3+},Violet**
$3d^4$	**Mn^{3+}, Violet/Cr^{2+},Blue**
$3d^5$	**Mn^{2+},Pink/Fe^{3+},Yellow**
$3d^6$	**Fe^{2+},Green**
$3d^6$,$3d^7$	**Co^{3+},Co^{2+}/Bluepink**
$3d^8$	**Ni^{2+},Green**
$3d^9$	**Cu^{2+},Blue**
$3d^{10}$	**Zn^{2+},Colourless**

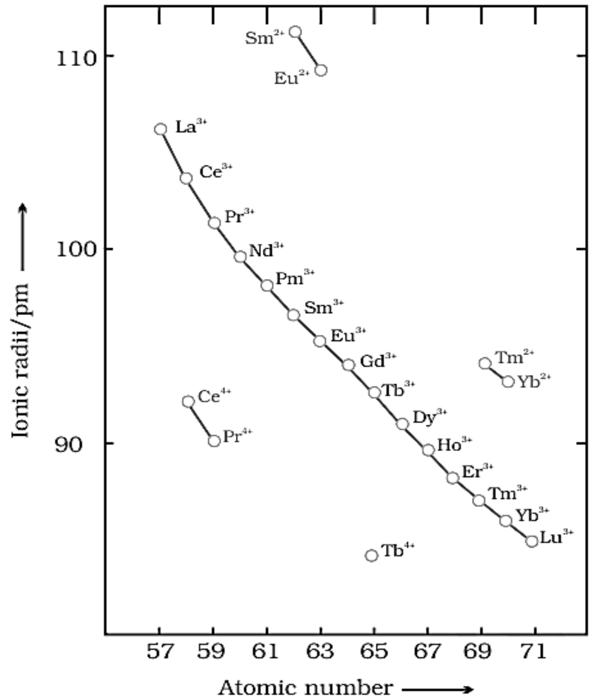
Catalytic Properties –

- The catalytic activity of transition metals is attributed to their ability to adopt multiple oxidation states and form complexes. This allows them to act as effective catalysts by increasing the concentration of reactants at the catalyst surface. It also helps weaken the bonds in reacting molecules, lowering the activation energy required.

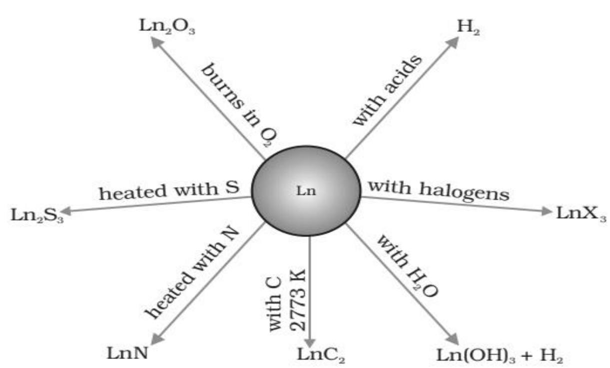
The Inner Transition Elements (f-Block) –

The Lanthanoids –

- **Electronic Configurations** – The lanthanoid atoms have an electronic configuration with $6s^2$ that is common across the series. However, the occupancy of the 4f orbitals varies with increasing atomic number from 1 to 14 electrons. The tri-positive ion is the most stable ion of the Lanthanoids**.**
- **Atomic and Ionic Sizes –**



- **Chemical reactions of Lanthanoids –**
- In general, the earlier lanthanoid metals are more reactive, similar to calcium. Reactivity decreases across the series, becoming more like Aluminium.
- The metals combine with hydrogen when gently heated. Carbides like Ln_3C, Ln_2C_3, and LnC_2 are formed upon heating with carbon.
- They liberate hydrogen from dilute acids and burn in halogens to form halide products.
- Lanthanoid metals form oxides with the general formula M_2O_3 and hydroxides written as $M(OH)_3$. The hydroxides are definite compounds rather than just hydrated oxides.



The Actinoids -

- **Electronic Configurations –**
- All actinoid elements are believed to have an electronic configuration of $7s^2$ with a variable occupancy of the 5f and 6d subshells.
- The 14 electrons are formally added to the 5f orbitals, except in thorium which does not

fill its 5f subshell until protactinium and beyond.

- The irregularities in actinoid electronic configurations, similar to the lanthanoids, relate to the stability of partial or complete occupancy of the 5f orbitals (f^0, f^7, f^{14} configurations).
- The 5f orbitals resemble the 4f orbitals in angular distribution, the 5f orbitals are not as buried, and thus 5f electrons can participate more extensively in bonding.

- **Oxidation States –** The common oxidation states for Actinium and Actinoids.

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3		**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
	4	**4**	**4**	**4**	**4**	**4**	**4**	**4**						
		5	**5**	**5**	**5**	**5**								
			6	**6**	**6**	**6**								
				7	**7**									