

## The d-and f-Block Elements

---

- The *d*-block elements are known as **transition metals**.
- The *f*-block elements are known as **inner transition metals**.
- 4*f* – metals → lanthanoids
- 5*f* – metals → actinoids

### Electronic Configuration

General outer electronic configuration is  $(n-1)d^{1-10} ns^{1-2}$ .

Zn, Cd, and Hg are not regarded as transition elements.

Reason – The orbitals of these elements are completely-filled. [Electronic configuration is  $(n-1)d^{10} ns^2$ ]

### The *d*-block elements (transition metals):

- The *d*-block elements (group 3 – 12) occupy the large, middle section of the periodic table.
- In general, their valence shell electronic configuration is  $(n-1)d^{1-10} ns^{1-2}$ .
- There are three series of transition metals, corresponding to the filling of 3*d*, 4*d* and 5*d* orbitals.
- All the transition metals exhibit typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity, metallic lustre, etc.
- The melting and boiling points of transition metals are high due to the involvement of  $(n-1)d$  electrons in interatomic bonding.
- The maxima of these properties occur at about the middle of each series, which indicates that one unpaired electron per *d*-orbital is particularly favourable for strong interatomic interaction.
- Variation of atomic radii:

Lanthanoid contraction – Regular decrease in atomic radii due to the filling of the 4*f* orbital before the 5*d* orbital. As a result, with increase in atomic number, the expected increase in size is not observed.

### Ionisation Enthalpies

- In each of the three transition series, the first ionisation enthalpy increases from left to right. However, there are some exceptions.
- The first ionisation enthalpies of the third transition series are higher than those of the first and second transition series.  
Reason: Poor shielding effect of 4f electrons in the third transition series
- Exhibit variable oxidation states
- Exhibit paramagnetic behaviour. Their magnetic moment values can be calculated using the expression:

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

where,  $\mu$  is the magnetic moment and  $n$  is the number of unpaired electrons.

- Have the tendency to form coloured ions
- Form interstitial and complex compounds
- Act as catalysts
- Form alloys
- Many of the transition metals are electropositive, and can dissolve in mineral acids while a few of them are noble.
- Transition metals form oxides and oxoanions of metals.

### **Magnetic Properties**

- Diamagnetic substance – Repelled by the applied field
- Paramagnetic substance – Attracted by the applied field
- Ferromagnetic substance – Attracted very strongly
- Paramagnetism arises due to the presence of unpaired electrons.
- Magnetic moment can be calculated by using 'spin-only' formula, i.e.,

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

Where,

$n$  = Number of unpaired electrons

$\mu$  = Magnetic moment in Bohr magneton (BM)

### **Formation of Coloured Ions**

- An electron from a lower energy  $d$ -orbital is excited to a higher energy  $d$ -orbital when the energy of excitation corresponds to the frequency of light absorbed.
- This frequency of light generally lies in the visible region.
- The colour observed is the complementary colour of the light absorbed.

### **Formation of Complex Compounds**

- Transition metals form a large number of complex compounds.
- Reason: Comparatively smaller size of metal ions, high ionic charges and availability of  $d$ -orbitals for bond formation

### Catalytic Properties

- Transition metals and their compounds are known for their catalytic activity.

### Formation of Interstitial Compounds

- Interstitial compounds formed when small atoms like H, C, N are trapped inside the crystal lattices of metals
- Usually non-stoichiometric
- Neither typically ionic nor covalent
- Example: TiC, Mn<sub>4</sub>N, Fe<sub>3</sub>H, etc.

### Alloy Formation

- Alloys are readily formed by these metals.
- Reason: Because of similar radii and other characteristics of transition metals

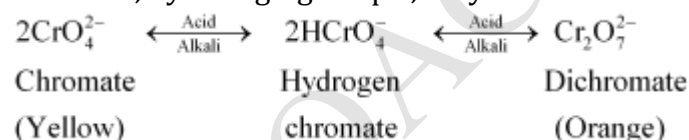
### Oxides and Oxoanions of Metals

- Oxides are generally formed by the reaction of metals with oxygen at higher temperatures.

### Potassium Dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ )

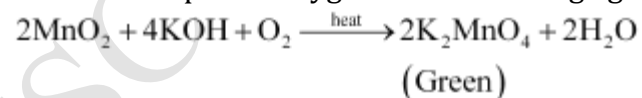
**Preparation:**  $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \longrightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$

- Potassium dichromate being less soluble than sodium dichromate can be obtained in the form of orange coloured crystals by treating sodium dichromate with potassium chloride and can be removed by filtration.
- The dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) exists in equilibrium with chromate ( $\text{CrO}_4^{2-}$ ) ion at pH = 4. However, by changing the pH, they can be inter-converted.



### Potassium Permanganate

- It can be prepared from pyrolusite ( $\text{MnO}_2$ ). The ore is fused with KOH in the presence of either atmospheric oxygen or an oxidising agent such as  $\text{KNO}_3$  or  $\text{KClO}_4$  to give  $\text{K}_2\text{MnO}_4$ .

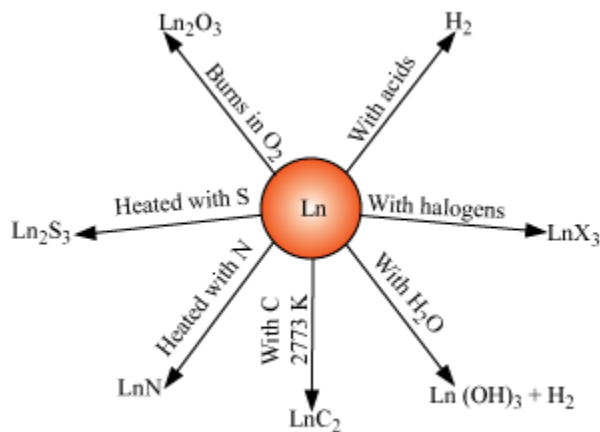


### The f-block elements (inner transition elements):

#### The lanthanoids –

- In general, their outermost electronic configuration is  $4f^{1-14} 6s^2$ .
- Due to lanthanoid contraction, there is a gradual decrease in atomic and ionic radii with increase in atomic number.

- The lanthanoids exhibit mainly +3 oxidation state. However, sometimes +2 and +4 oxidation states are also exhibited.
- Chemical reactions:



Chemical reactions of the lanthanoids

### Actinoids

- These include fourteen elements after actinium (from thorium to lawrencium).
- These are the radioactive elements.
- Electronic configuration:  
 $7s^2 \rightarrow$  Stable  
 $5f$  and  $6d \rightarrow$  Variable

### Oxidation States:

- Greater range of oxidation states
- Reason:  $5f$ ,  $6d$ , and  $7s$  subshells are of comparable energies.
- Exhibit mainly +3 oxidation state. However, +4, +5, +6, and +7 oxidation states are also exhibited.
- Their magnetic properties are complex in comparison to lanthanoids.
- Lower ionisation enthalpies than lanthanoids
- Reason –  $5f$  electrons are less effectively shielded than  $4f$  electrons.