The d-and f-Block Elements

The Transition Elements (d-Block)

Position in the Periodic Table

- Their position is in between *s*- and *p*- block elements.
- There are four rows of transition elements – 3*d*, 4*d*, 5*d*, and 6*d*. The fourth row of 6*d* is still incomplete.

Electronic Configuration

- General outer electronic configuration is $(n-1)d^{1-10}\,ns^{1-2}$.
- But this generalization has several exceptions as there is very little difference in energy between $(n-1)d$ and *ns* orbitals. For example, Cr has electronic configuration $3d^5\,4s^1$ instead of $3d^4\,4s^2$. Cu has electronic configuration $3d^{10}\,4s^1$ instead of $3d^9\,4s^2$.
- Outer electronic configurations of the transition elements in the ground state are listed in the following tables:

1st series			**2nd series**		
Element	Atomic number	Outer electronic configuration	Element	Atomic number	Outer electronic configuration
Sc	21	$3d^14s^2$	Y	39	$4d^15s^2$
Ti	22	$3d^24s^2$	Zr	40	$4d^25s^2$
V	23	$3d^34s^2$	Nb	41	$4d^45s^1$
Cr	24	$3d^54s^1$	Mo	42	$4d^55s^1$

Mn	25	$3d^{5}4s^{2}$	Tc	43	$4d^{6}5s^{1}$
Fe	26	$3d^{6}4s^{2}$	Ru	44	$4d^{7}5s^{1}$
Co	27	$3d^{7}4s^{2}$	Rh	45	$4d^{8}5s^{1}$
Ni	28	$3d^{8}4s^{2}$	Pd	46	$4d^{10}5s^{0}$
Cu	29	$3d^{10}4s^{1}$	Ag	47	$4d^{10}5s^{1}$
Zn	30	$3d^{10}4s^{2}$	Cd	48	$4d^{10}5s^{2}$
3rd series			**4th series**		
Element	Atomic number	Outer electronic configuration	Element	Atomic number	Outer electronic configuration
La	57	$5d^{1}6s^{2}$	Ac	89	$6d^{1}7s^{2}$
Hf	72	$5d^{2}6s^{2}$	Rf	104	$6d^{2}7s^{2}$
Ta	73	$5d^{3}6s^{2}$	Db	105	$6d^{3}7s^{2}$
W	74	$5d^{4}6s^{2}$	Sg	106	$6d^{4}7s^{2}$

Re	75	$5d^{5}6s^{2}$	Bh	107	$6d^{5}7s^{2}$
Os	76	$5d^{6}6s^{2}$	Hs	108	$6d^{6}7s^{2}$
Ir	77	$5d^{7}6s^{2}$	Mt	109	$6d^{7}7s^{2}$
Pt	78	$5d^{9}6s^{1}$	Ds	110	$6d^{8}7s^{2}$
Au	79	$5d^{10}6s^{1}$	Rg	111	$6d^{10}7s^{1}$
Hg	80	$5d^{10}6s^{2}$	Uub	112	$6d^{10}7s^{2}$

- Zn, Cd, and Hg are not regarded as transition elements.
- Reason – The orbitals of these elements are completely-filled. [Electronic configuration is $(n - 1)\, d^{10}\, ns^{2}$]
- Ions of configuration d^{1-9} have similar magnetic and electronic properties.
- Elements with partially-filled *d*-orbitals exhibit certain characteristic properties such as showing a variety of oxidation states, formation of coloured ions, and formation of complex with a variety of ligands.
- They and their compounds have catalytic property and are paramagnetic in nature.

General Properties of Transition Metals - I

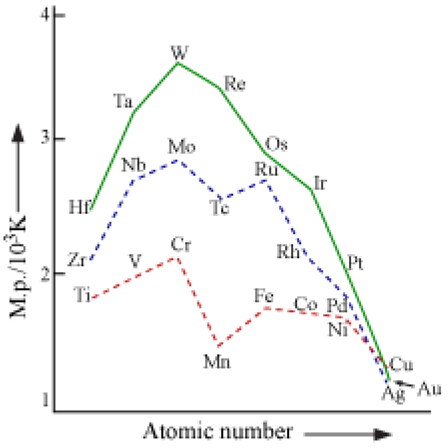
Physical Properties

- Nearly all transition metals display metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre.
- Very hard and have low volatility (Exception: Zn, Cd and Hg)

- The melting and boiling points of the first transition series are lower than those of the heavier transition elements.

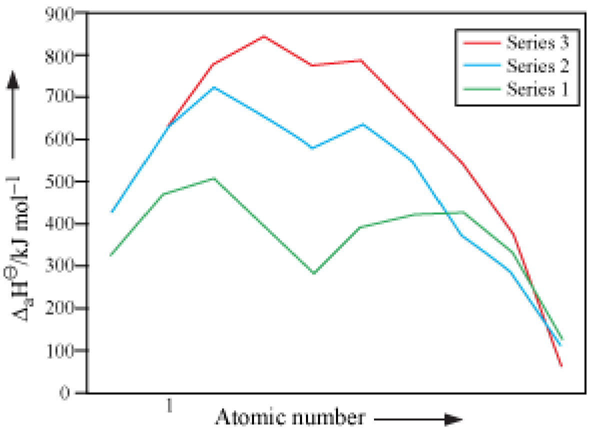
  Reason: Occurrence of stronger metallic bonding (M−M bonding) in heavier metals

- Trends in melting points of transition metals are shown in the given figure.



- Transition elements have high effective nuclear charge and a large number of valence electrons. Therefore, they form very strong metallic bonds. As a result, the enthalpy of atomisation of transition metals is high.

- Trends in enthalpies of atomisation of transition elements are shown in the given figure.

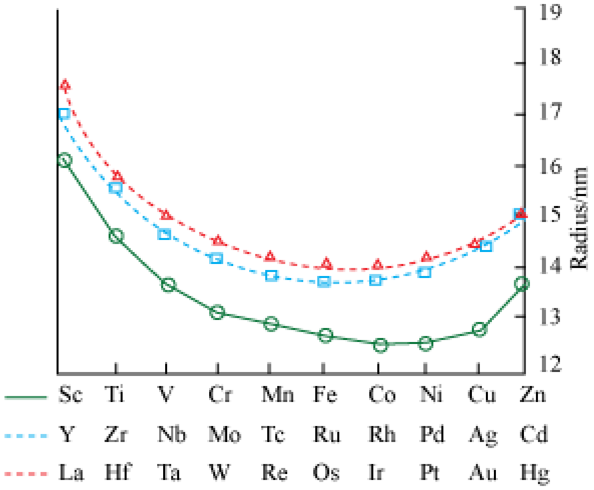


- The enthalpies of atomisation of the elements in the first transition series are lower than those of the corresponding elements in the second and third transition series.

Variation in Atomic and Ionic Sizes of Transition Metals

- Atomic size generally decreases from left to right across a period.

- The atomic sizes of the elements of the first transition series are smaller than those of the corresponding heavier elements (elements of the 2nd and 3rd transition series).
- However, the atomic sizes of the elements in the third transition series are virtually the same as those of the corresponding members in the second transition series. This is due to lanthanoid contraction.
- Trends in atomic radii of transition elements are shown in the given figure.



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 4*f* electrons in the third transition series
- Certain elements in the second transition series have higher first ionisation enthalpies than the elements corresponding to the same vertical column in the first transition series.
- There are also elements in the 2nd transition series whose first ionisation enthalpies are lower than those of the elements corresponding to the same vertical column in the 1st transition series.

General Properties of Transition Metals - II

Oxidation States

- All transition metals exhibit a variety of oxidation states.

- The oxidation states of the first row transition metals are listed in the given table.

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**	-	-	-	-	-

(The most common ones are in bold types)

- The variable oxidation states of transition elements are due to the participation of *ns* and $(n-1)d$-electrons in bonding.

- Lower oxidation state is exhibited when *ns*-electrons take part in bonding.

- Higher oxidation states are exhibited when $(n-1)d$-electrons take part in bonding.

- In each group, the highest oxidation state increases with the increase in atomic number; reaches the maximum in the middle, and then starts decreasing.

  Example: In the first transition series, manganese has the maximum oxidation state (+7).

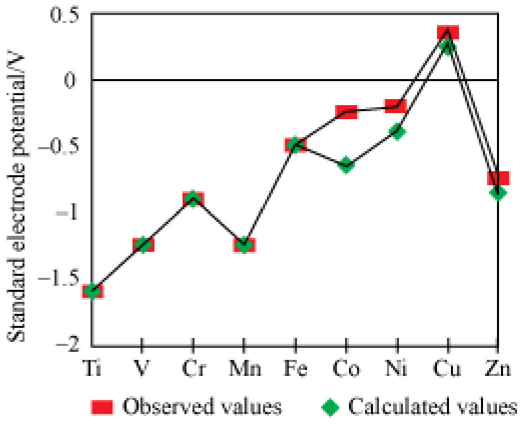
- For the elements of the first transition series, the most common oxidation state is +2. (Exception: Scandium)

- The highest oxidation state shown by any transition metal is +8. (Example: osmium and ruthenium)

- Some transition elements show zero oxidation state in their compounds.

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

- The observed and calculated values of standard electrode potential (E^{θ}) for the elements Ti to Zn are shown in the given figure.



- The sum of enthalpies of sublimation and ionization is not balanced by hydration enthalpy in case of copper. Hence, the $E^{\theta}(M^{2+}/M)$ value for copper is positive.

- The values of E^{θ} for Mn, Ni, Zn are more negative than the expected trend.

- Reason: The stability of the half-filled *d*-subshell in Mn^{2+} and the completely filled d^{10} configuration in Zn^{2+}

  Negative value of E^{θ} for Ni is due to the highest negative hydration energy.

Trends in the M^{3+}/M^{2+} Standard Electrode Potentials

- The given table lists the values of E^{θ} for M^{2+}/M and M^{3+}/M^{2+}.

Element	-	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Standard electrode	M^{2+}/M	-	-1.63	-1.18	-0.90	-1.18	-0.44	-0.28	-0.25	+0.34	-0.76

Potential E^{Θ}/ V	M^{3+}/M^{2+}	-	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97	-	-	-

- The highest value for Zn is due to the formation of the stable d^{10} configuration of Zn^{2+}.
- Similarly, comparatively higher value for Mn is due to the formation of the stable d^5 configuration of Mn^{2+}.

Chemical Reactivity

- Many of the transition metals are electropositive. Hence, they dissolve in mineral acids.
- Few of them are ‘noble’, and are unaffected by simple acids.
- Metals of the first series are relatively more reactive and are oxidised by 1M H^+.
- The E^{θ} values for M^{2+}/M indicate the decreasing tendency to form divalent ions across the series.
- The E^{θ} values for M^{3+}/M^{2+} show that Mn^{3+} and Co^{3+} ions are the strongest oxidising agents in aqueous solution.
- Ti^{2+}, V^{2+} and Cr^{2+} are strong reducing agents, and will liberate hydrogen gas from dilute acids.

General Properties of Transition Metals -III

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

μ = Magnetic moment in Bohr magneton (BM)

- Magnetic moment increases with the increase in the number of unpaired electrons.
- Magnetic moments (calculated from ‘spin-only’ formula) for some ions of the first row transition elements are listed in the given table.

Ion	**Configuration**	**Unpaired electron(s)**	**Magnetic moment (BM)**	
			Calculated	**Observed**
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.73	1.75
Tl^{2+}	$3d^2$	2	2.84	2.76
V^{2+}	$3d^3$	3	3.87	3.86
Cr^{2+}	$3d^4$	4	4.90	4.80
Mn^{2+}	$3d^5$	5	5.92	5.96
Fe^{2+}	$3d^6$	4	4.90	5.3 – 5.5
Co^{2+}	$3d^7$	3	3.87	4.4 – 5.2

Ni^{2+}	$3d^8$	2	2.84	2.9 – 3, 4
Cu^{2+}	$3d^9$	1	1.73	1.8 – 2.2
Zn^{2+}	$3d^{10}$	0	0	-

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.
- Colours of some of the first row transition metal ions (aquated) are listed in the given table

Configuration	Example	Colour
$3d^0$	Sc^{3+}	Colourless
$3d^0$	Ti^{4+}	Colourless
$3d^1$	Ti^{3+}	Purple
$3d^1$	V^{4+}	Blue
$3d^2$	V^{3+}	Green

$3d^3$	V^{2+}	Violet
$3d^3$	Cr^{3+}	Violet
$3d^4$	Mn^{3+}	Violet
$3d^4$	Cr^{2+}	Blue
$3d^5$	Mn^{2+}	Pink
$3d^5$	Fe^{3+}	Yellow
$3d^6$	Fe^{2+}	Green
$3d^6$, $3d^7$	Co^{3+}, Co^{2+}	Blue, pink
$3d^8$	Ni^{2+}	Green
$3d^9$	Cu^{2+}	Blue
$3d^{10}$	Zn^{2+}	Colourless

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
- Example: $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[PtCl_4]^{2-}$, etc.

Catalytic Properties

- Transition metals and their compounds are known for their catalytic activity.
- Example: Vanadium (V) oxide (in Contact Process), nickel (in Catalytic Hydrogenation), etc.
- Iron (III) catalyses the reaction of iodide with persulphate ions.

$$2I^- + S_2O_8^{2-} \longrightarrow I_2 + 2SO_4^{2-}$$

- Mechanism:

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$
$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$$

Formation of Interstitial Compounds

- Interstitialcompounds
- 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_4N, Fe_3H, etc.
- Characteristics of interstitial compounds
- Higher melting points than pure metals
- Very hard
- Retain metallic conductivity
- Chemically inert

Alloy Formation

- Alloys are readily formed by these metals.
- Reason: Because of similar radii and other characteristics of transition metals
- Alloys, so formed, are hard and have high melting points.
- Ferrous alloys – Cr, V, W, Mo and Mn are used for the production of a variety of steels and stainless steel.
- Alloys of transition metals with non-transition metals: Brass (Cu – Zn) and bronze (Cu – Sn)

Some Important Compounds of Transition Elements

Oxides and Oxoanions of Metals

- Oxides are generally formed by the reaction of metals with oxygen at higher temperatures.
- All the metals (except scandium) form MO oxides, which are ionic in nature.
- As the oxidation number of a metal increases, ionic character decreases.

Potassium Dichromate ($K_2Cr_2O_7$)

- Prepared from chromite ore $(FeCr_2O_4)$ in the following steps:
    - Preparation of sodium chromate

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

- Conversion of sodium chromate into sodium dichromate

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

- Conversion of sodium dichromate to potassium dichromate

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

- 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 $(Cr_2O_7^{2-})$ exists in equilibrium with chromate (CrO_4^{2-}) ion at pH = 4. However, by changing the pH, they can be inter-converted.

$$\begin{array}{ccccc} 2CrO_4^{2-} & \xrightleftharpoons[\text{Alkali}]{\text{Acid}} & 2HCrO_4^{-} & \xrightleftharpoons[\text{Alkali}]{\text{Acid}} & Cr_2O_7^{2-} \\ \text{Chromate} & & \text{Hydrogen} & & \text{Dichromate} \\ \text{(Yellow)} & & \text{chromate} & & \text{(Orange)} \end{array}$$

- $K_2Cr_2O_7$ acts as a very strong oxidising agent in the acidic medium.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

- $K_2Cr_2O_7$ takes up electrons to get reduced and acts as an oxidising agent.
- Examples:
- Oxidises iodide to iodine

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

- Oxidises iron (II) solution to iron (III) solution i.e., ferrous ions to ferric ions

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

- Oxidises H_2S to sulphur

$$Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 3S + 7H_2O$$

Potassium Permanganate

- It can be prepared from pyrolusite (MnO_2). The ore is fused with KOH in the presence of either atmospheric oxygen or an oxidising agent such as KNO_3 or $KClO_4$ to give K_2MnO_4.

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\text{heat}} \underset{\text{(Green)}}{2K_2MnO_4} + 2H_2O$$

- The green mass can be extracted with water and then oxidised either electrolytically or by passing chlorine/ozone into the solution.
- Electrolytic oxidation:

$$K_2MnO_4 \longleftrightarrow 2K^+ + MnO_4^{2-}$$
$$H_2O \longleftrightarrow H^+ + OH^-$$

- At anode, manganate ions are oxidised to permanganate ions.

$$\begin{array}{lcl} MnO_4^{2-} & \longleftrightarrow & MnO_4^- + e^- \\ \text{Green} & & \text{Purple} \end{array}$$

- Oxidation by chlorine:

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$
$$2MnO_4^{2-} + Cl_2 \longrightarrow 2MnO_4^- + 2Cl^-$$

- Oxidation by ozone:

$$2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$$
$$2MnO_4^{2-} + O_3 + H_2O \longrightarrow 2MnO_4^{2-} + 2OH^- + O_2$$

- Acidified $KMnO_4$ solution oxidises Fe (II) ions to Fe (III) ions i.e., ferrous ions to ferric ions.

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

- Acidified potassium permanganate oxidises SO_2 to sulphuric acid.

$$2MnO_4^- + 10SO_2 + 4O_2 + 4H_2O \longrightarrow 2Mn^{2+} + 10SO_4^{2-} + 8H^+$$

- Acidified potassium permanganate oxidises oxalic acid to carbon dioxide.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Lanthanoids

- Lanthanoids are the fourteen elements from lanthanum (La) to lutetium (Lu).

Electronic Configuration

- In general, the outermost electronic configuration is $4f^{1-14}6s^2$.
- Electronic configurations of lanthanum and lanthanoids are listed in the table

Atomic Number	**Name**	**Symbol**	**Electronic configurations**			**Radii/pm**		
			Ln	**Ln^{2+}**	**Ln^{3+}**	**Ln^{4+}**	**Ln**	**Ln^{3+}**
57	Lanthanum	La	$5d^1 6s^2$	$5d^1$	$4f^0$	-	187	106
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^2$	$4f^1$	$4f^0$	183	103
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^3$	$4f^2$	$4f^1$	182	101
60	Neodymium	Nd	$4f^4 6s^2$	$4f^4$	$4f^3$	$4f^2$	181	99
61	Promethium	Pm	$4f^5 6s^2$	$4f^5$	$4f^4$	-	181	98
62	Samarium	Sm	$4f^6 6s^2$	$4f^6$	$4f^5$	-	180	96
63	Europium	Eu	$4f^7 6s^2$	$4f^7$	$4f^6$	-	199	95
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^3 5d^1$	$4f^7$	-	180	94
65	Terbium	Tb	$4f^9 6s^2$	$4f^9$	$4f^8$	$4f^7$	178	92
66	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^{10}$	$4f^9$	$4f^8$	177	91

67	Holmium	Ho	$4f^{11}6s^{2}$	$4f^{11}$	$4f^{10}$	-	176	89
68	Erbium	Er	$4f^{12}6s^{2}$	$4f^{12}$	$4f^{11}$	-	175	88
69	Thulium	Tm	$4f^{13}6s^{2}$	$4f^{13}$	$4f^{12}$	-	174	87
70	Ytterbium	Yb	$4f^{14}6s^{2}$	$4f^{14}$	$4f^{13}$	-	173	86
71	Lutetium	Lu	$4f^{14}5d^{1}6s^{2}$	$4f^{14}5d^{1}$	$4f^{14}$	-	-	-

Atomic and ionic sizes

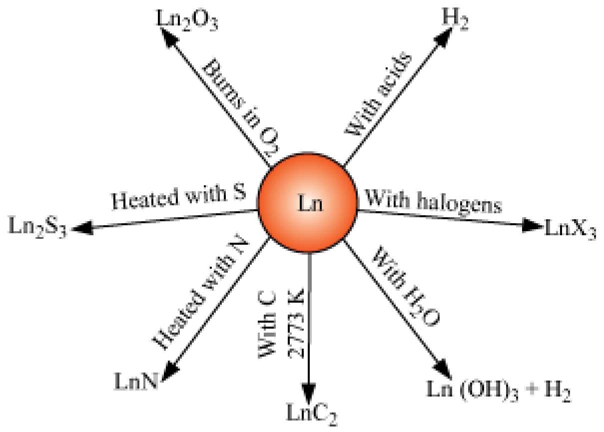
- There is a gradual decrease in atomic and ionic radii of Lanthanoids with an increase in atomic number. This is known as lanthanoid contraction.
- Due to lanthanoid contraction, the radii of the elements of the 3rd transition series are very similar to those of the corresponding elements of the 2nd series.

Oxidation states

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

General Characteristics

- Silvery-white, soft metals; tarnish rapidly in air
- Hardness increases with increasing atomic number
- Good conductors of heat and electricity
- 1st and 2nd ionisation enthalpies around 600 kJ mol^{-1} and 1200 kJmol^{-1} respectively
- Chemical reactions:



Chemical reations of the lanthanoids

Uses

- In the production of alloy steels for plates and pipes
- Mixed oxides of lanthanoids are used as catalysts in petroleum cracking.
- Some lanthanum oxides are used as phosphors in television screens and other fluorescing surfaces.

The Actinoids & Some Applications of d-and f-block Elements

Actinoids

- These include fourteen elements after actinium (from thorium to lawrencium).
- These are the radioactive elements.

Electronic Configuration:

- They have the electronic configuration of $7s^2$ with variation of occupancy in $5f$ and $6d$ orbitals.
- There is a gradual decrease in atomic and ionic radii of actinoids with increase in atomic number.

This is known as actinoid contraction.

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.

- Oxidation states of actinium and actinoids are given in the following table.

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									

General Characteristics and Comparison with Lanthanoids

- Silvery metals
- Have a variety of structures
- Highly reactive (especially when finely divided)
- Give a mixture of oxide and hydride when treated with boiling water
- Combine with most non-metals at moderate temperatures
- React readily with hydrochloric acid, but slowly with nitric acid due to the formation of protective oxide film
- Do not react with alkalies
- Paramagnetic in nature

Their magnetic properties are complex in comparison to lanthanoids.

- Lower ionisation enthalpies than lanthanoids
- Reason – 5*f* electrons are less effectively shielded than 4*f* electrons.

Some Applications of *d*-and *f*-block Elements

- Iron is used in the construction materials.
- Fe, Cr, Ni, and Mn are used in the manufacture of steel, which is used in construction.
- TiO is used in pigment industry whereas MnO_2, Zn, and Ni/Cd are used in battery industry.
- Ag, Au, Cu, and Ni are used in making coins.
- Some metals and/or their compounds (V, Ti, Al, Fe, Ni, and Pd) are used as catalysts.
- AgBr is used in photographic industry as it has special light sensitive properties.