

Chapter 8: d- and f- Block Elements

1. General Electronic Configuration: $(n-1)d^{1-10} ns^{1-2}$, where $(n - 1)$ stands for penultimate (last but one) shell.

Palladium (46) does not follow this general electronic configuration, it has electron configuration $[\text{Kr}]^{36}4d^{10}5s^0$ in order to have stability.

2. Transition element: d block elements are also called transition elements. 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. Zinc, cadmium, mercury are not regarded as transition metals due to completely filled d – orbital but Cu, Ag and Au are transition metals because in their commonly occurring states, they have partly filled d- sub shells.

First transition series- 3d series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
21	22	23	24	25	26	27	28	29	30
$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$

Second Transition series – 4d series

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
39	40	41	42	43	44	45	46	47	48
$4d^15s^2$	$4d^25s^2$	$4d^45s^2$	$4d^55s^1$	$4d^65s^1$	$4d^75s^1$	$4d^85s^1$	$4d^{10}5s^0$	$4d^{10}5s^1$	$4d^{10}5s^2$

Third transition Series – 5d series

La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
57	72	73	74	75	76	77	78	79	80

Fourth transition Series- 6d Series

Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub
89	104	105	106	107	108	109	110	111	112

Note: Only Nb, Cr, Cu, Ag, Au, Pt, Mo, Tc, Ru and Rh (total 10 nos.) elements have single electron in 's' orbital

3. General Characteristics of transition elements:

1) Atomic radii: The atomic radii decrease from Sc to Cr because the effective nuclear charge increases. The atomic size of Fe, Co, Ni is almost same because the attraction due to increase in nuclear charge is cancelled by the repulsion because of increase in shielding effect. Cu and Zn have bigger size because the shielding effect increases and electron electron repulsions increases.

2) Ionic radii: The ionic radii of transition elements follow the same order as their atomic radii. In general, it decreases with increases in oxidation states.

Effect of Lanthanoid Contraction in atomic and ionic size:

- The steady decrease in the atomic and ionic radii of the transition metals as the atomic number increases due to the added electron enters the deep seated f-orbitals and therefore experiences considerable pull by the nucleus.
- Due to very poor shielding effect of (n-1)f electrons, they exert very little screening effect on the outermost $5s^2$ electrons. Hence with increasing atomic number, the enhanced nuclear charge leads to contraction in the size of atoms and ions. This contraction in size is quite regular. This is called lanthanoid contraction.
- It is because of lanthanoid contraction that the atomic radii of the second row of transition elements are almost similar to those of the third row of transition elements.

3) Density- All metals have high density within a period; the densities vary inversely with atomic radii.

Reason- The atomic volumes of transition elements are low b/c electrons are added in (n- 1)d sub shell and not in ns sub shell . Therefore, increased nuclear charge is partly screened by the d-electrons and outer electrons are strongly attracted by the nucleus. Moreover, electrons are added in inner orbital. Consequently, densities of transition metals are high.

4) Metallic character:

- All transition elements are metallic in nature, i.e. they have strong metallic bonds. This is due to greater effective nuclear charge and presence of unpaired electrons.
- Metallic strength increase up to the middle till d^5 configuration and then decreases with the decrease in availability of unpaired d- electrons (from Fe onwards).
- The strength of bonding depends on the number of outer most electrons. Greater is the number of valance electrons, stronger is the metallic bonding and consequently.
- This gives rise to properties like high density, high enthalpies of atomization, and high melting and boiling points.

5) Melting and boiling points

- The transition metals have high m.p. & b.p. due to strong metallic bonds between the atoms of these elements.
- In 3d series Sc to Cr, m.p. and b.p. increases then Mn to Zn decreases because of increase in pairing of electrons.
- Mn and Tc have low m.p. & b.p. due to weak metallic bond because of stable half filled electronic configuration ($3d^5 4s^2$) and high IP.
- M.P. and B.P. of d-block is more than s-block elements due to stronger metallic bond formed in d-block elements.
- M.P. and B.P. of Zn, Cd and Hg are very low in series due to their fully filled $(n-1)d^{10} ns^2$ configuration.

6) Ionisation enthalpy:

- There is slight and irregular variation in ionization energies of transition metals due to irregular variation of atomic size.
- The first ionisation energy of Zn, Cd and Hg are very high due to their fully filled $(n-1)d^{10} ns^2$ configuration.

- Order of second ionisation energy: $\text{Sc} < \text{Ti} < \text{V} < \text{Mn} < \text{Cr}$
- The I.E. of 5d transition series is higher than 3d and 4d transition series because of Lanthanoid Contraction.

7) Oxidation state:

- Transition metals show variable oxidation states due to tendency of (n-1)d as well as ns electrons to take part in bond formation.
- This is due to the participation of inner (n -1)d electrons in addition to outer ns electrons because the energies of ns and (n -1)d electrons are almost equal.
- Transition elements show low oxidation states in some compounds or complexes having ligands such as CO, for e.g. in $\text{Ni}(\text{CO})_4$, Ni has zero oxidation state.
- Osmium (Os) and Ru show higher oxidation state +8 in d-block.

Oxidation state of first row transition elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
21	22	23	24	25	26	27	28	29	30
$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$
+3	+2 +3 +4	+2 +3 +4 +5	+2 +3 +4 +5 +6	+2 +3 +4 +5 +6 +7	+2 +3 +4 +6	+2 +3 +4	+2 +3 +4	+1 +2	+2

8) Magnetic properties: Substances is paramagnetic in nature if it has unpaired electrons and diamagnetic if all the electrons are paired. Most of the transition metals are paramagnetic in nature due to the presence of unpaired d-orbital electrons. It increases from Sc to Cr then decreases because number of unpaired electrons decreases.

9) Formation of complexes: Transition metals form complexes due to

- Presence of vacant d – orbitals of suitable energy for accepting electrons donated by ligands.
- Smaller size
- Higher charge on cations.

10) Catalytic Properties: Most of transition metals are used as catalyst b/c of present of empty d-orbitals, large surface area, valuable oxidation state, ability to form complexes for example Fe, Ni, V_2O_5 , Pt, Pd, Mo, Co are used as catalyst.

11) Colour: They form coloured ions due to presence of incompletely filled d-orbitals and unpaired electrons; they can undergo d-d transition by absorbing colour from visible region and radiating complementary colour.

12) Interstitial compounds: Interstitial compounds are those in which small atoms occupy the interstitial sites in the crystal lattice. Interstitial compounds are well known for transition metals b/c small sized atoms of H, B, C, N etc. can easily occupy positions in the voids present in the crystal lattice of transition metals.

They are non – stoichiometric, i.e., their composition is not fixed, e.g., steel. They are harder and less malleable and ductile.

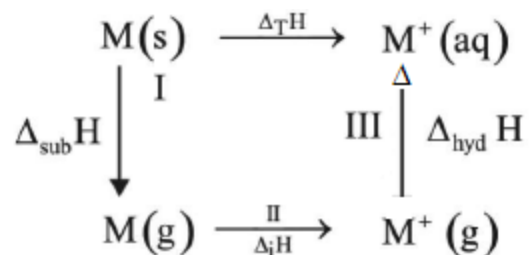
13) Alloys formation: They form alloys due to similar ionic size. Metals can replace each other in crystal lattice, e.g., brass (Cu +Zn), bronze (Cu+Sn), steel etc.

14) Standard electrode potential (E^0): Thermodynamic stability of the compounds of transition metals can be evaluated in terms of the magnitude of ionisation enthalpies of the metals, if smaller the ionisation enthalpy of metal, stables its compound.

In solution, the stability of the compounds depends upon electrode potentials rather than ionisation enthalpies. Electrode potential values depend upon the factors such as sublimation enthalpy (or atomization), hydration enthalpy and the ionisation enthalpy.



In solution this process actually takes place in the following three steps as given in following flow chart-



The overall energy change can be written as

$$\Delta_T H = \Delta_{sub} H + \Delta_i H + \Delta_{hyd} H$$

If more negative the $\Delta_T H$, the more positive will be standard oxidation potential (means oxidation easy) and hence, more negative will be standard reduction potential (means reduction easy).

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

- There is no regular trend in the E^0 (M^{2+}/M) values b/c their ionisation enthalpies ($IE_1 + IE_2$) and sublimation enthalpies do not show any regular trend.
- The general trend towards less negative E^0 values along the series is due to the general increase in the sum of first and second ionisation enthalpies.
- Cu show a unique behaviour in the series as it is the only metal having positive value for E^0 this is b/c copper has high enthalpy of ionisation [$Cu(g) + \Delta_i H \rightarrow Cu^{2+}(g) + 2e^-$] and low

enthalpy of hydration so, E^0 ($\text{Cu}^{2+} / \text{Cu}$) is positive. The high energy to transform Cu (s) to Cu^{2+} (aq) is not balanced by its hydration enthalpy.

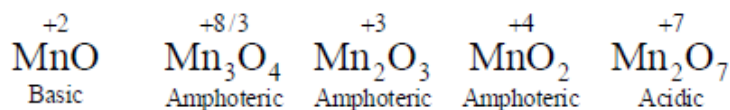
- The values of E^0 for Mn, Ni and Zn are more negative than expected from the general trend. This is due to greater stability of half-filled d-sub shell in Mn^{2+} and completely filled d-sub shell in Zn^{2+} . The exceptional behaviour of Ni towards E^0 value from the regular trend is due to its high negative enthalpy of hydration.

Trends in the $\text{M}^{3+}/\text{M}^{2+}$ Standard Electrode Potentials: An examination of the E^0 ($\text{M}^{3+}/\text{M}^{2+}$) values shows the varying trends as like

- Very low value of E^0 for Sc ($\text{Sc}^{3+}/\text{Sc}^{2+}$) reflects the stability of Sc^{3+} which have a noble gas configuration.
- The highest value for Zn is due to the removal of an electron from the stable d^{10} configuration of Zn^{2+} .
- The comparatively high value for Mn shows that Mn^{2+} (d^5) is particularly stable.
- Comparatively low value for Fe shows the extra stability of Fe^{3+} (d^5).
- The comparatively low value for V is related to the stability of V^{2+} (half-filled t_{2g} level).

Compounds of d-block elements

Oxides: Oxides in the lower oxidation states are generally basic in nature and higher oxidation states are amphoteric or acidic in nature. Transition metals form following oxides-

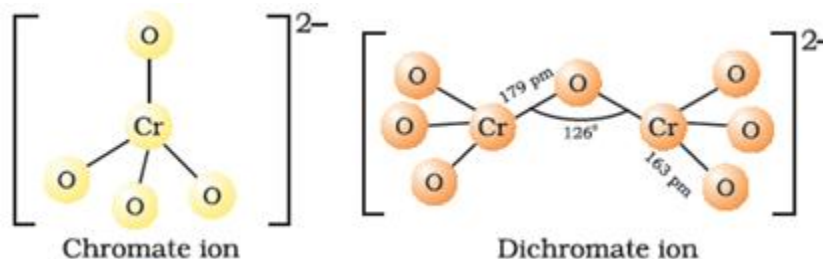


Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)

1) Preparation of Potassium dichromate: It is prepared by fusion of chromate ore (FeCr_2O_4) with sodium carbonate in excess of air.



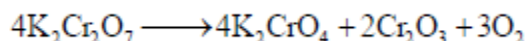
2) Structure of chromate and dichromate ions:



- In acidic medium dichromate ion (orange color) is more stable but in basic medium chromate ion (yellow) is more stable.
- In both type of ions chromium atom having sp^3 hybridization and +6 oxidation State.
- Chromate ion structure should be tetrahedral.
- In chromate ion all four Cr-O bond length are equal due to resonance. Hence all four Cr-O bonds are partially double bond in nature.
- In dichromate ion both Cr atoms having sp^3 hybridization and + 6 oxidation State.
- Bridging oxygen atom length (Cr-O Cr) is higher as compared to terminal oxygen (Cr-O) due to terminal oxygen atom having partially double bond character.
- In dichromate ion all six CR - O bond length are equal due to resonance

3) Chemical Properties:

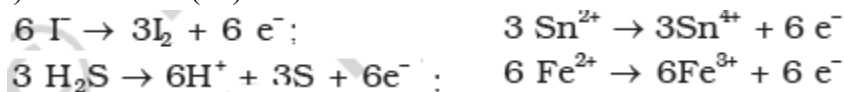
- **Effect on heating:** when heated it decomposes and O_2 is evolved.



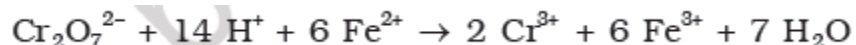
- **Oxidising Property:** Potassium dichromate acts as a strong oxidizing agent in acidic medium. Its oxidising action can be represented as follows-

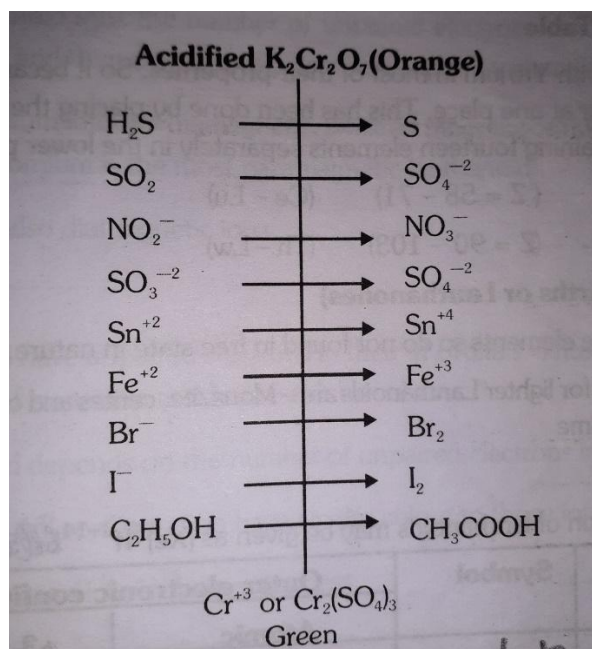


Acidified potassium dichromate will oxidise iodides to iodine, sulphides to sulphur, tin (II) to tin (IV) and iron (II) salts to iron (III). The half-reactions are noted below:



The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent, for e.g.,





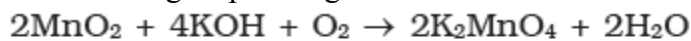
- Reaction with Hot H_2SO_4 :
 $K_2Cr_2O_7 + \text{Hot } H_2SO_4 \longrightarrow K_2SO_4 + H_2O + O_2 + Cr_2(SO_4)_3$ (Green crystal)
- Reaction with Cold H_2SO_4 :
 $K_2Cr_2O_7 + \text{Cold } H_2SO_4 \longrightarrow CrO_3$ (Red crystal) + $K_2SO_4 + H_2O$
- Reaction with H_2O_2 in presence of Ethereal Solution
 $K_2Cr_2O_7 + 4H_2O_2 + 2H^+ \longrightarrow 5H_2O + 2CrO_5$ (Deep Blue) H_2O

- **Chromyl chloride test** : The chromyl chloride test is a chemical test that detects the presence of chlorine compounds in a sample.
- For a test, mix a small amount of potassium dichromate into a small amount of salt then add a small amount of sulfuric acid to a test tube, Red fumes of chromyl chloride is generate.
- Now add sodium hydroxide to the tube that contains yellow ppt. A yellow precipitate indicates the presence of chloride ion.
- $NaCl + K_2Cr_2O_7 + H_2SO_4 \longrightarrow CrO_2Cl_2$ (Red fumes)
- $CrO_2Cl_2 + NaOH \longrightarrow Na_2CrO_4$ (Yellow ppt)
- The chromyl chloride test is specific to chlorides and no similar compound is formed in the presence of fluoride, bromide, iodide, or cyanide.

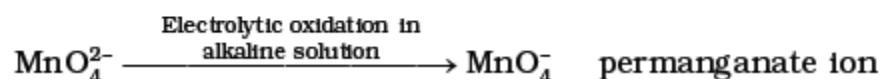
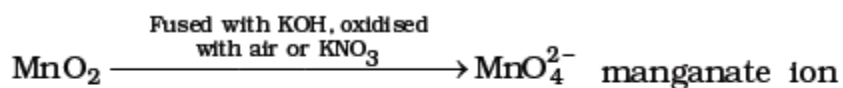
Potassium Permanganate (KMnO₄)

1) Preparation of Potassium permanganate (KMnO₄):

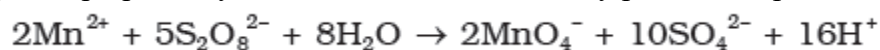
- Potassium permanganate is prepared by fusion of MnO₂ with an alkali metal hydroxide and an oxidising agent like KNO₃. This produces the dark green K₂MnO₄ which disproportionates in a neutral or acidic solution to give permanganate.



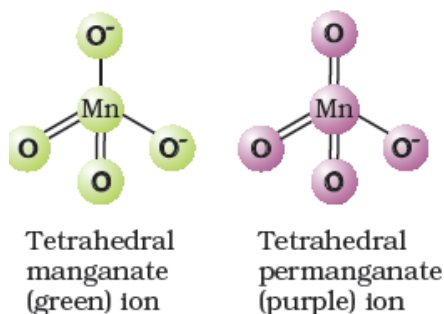
- Commercially it is prepared by the alkaline oxidative fusion of MnO₂ followed by the electrolytic oxidation of manganate (VI).



- In laboratory, it is prepared by oxidation of Mn²⁺ ion salt by peroxodisulphate.



2) Structure of Manganate ion and Permanganate ions: The manganate and permanganate ions are tetrahedral (sp³ hybrid); the green manganate ion (O.No. +6) is paramagnetic with one unpaired electron but the purple permanganate ion (O.No. +7) is diamagnetic.

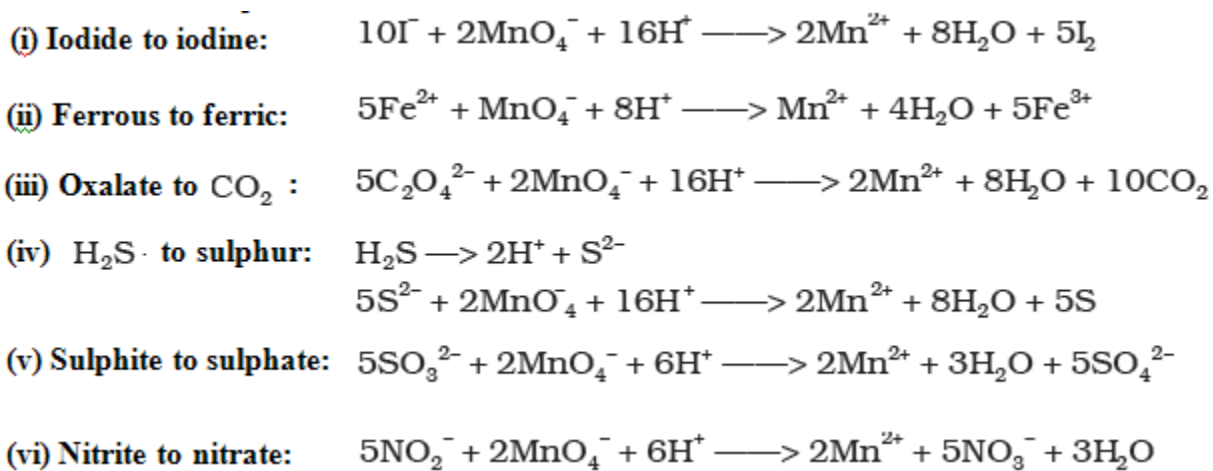
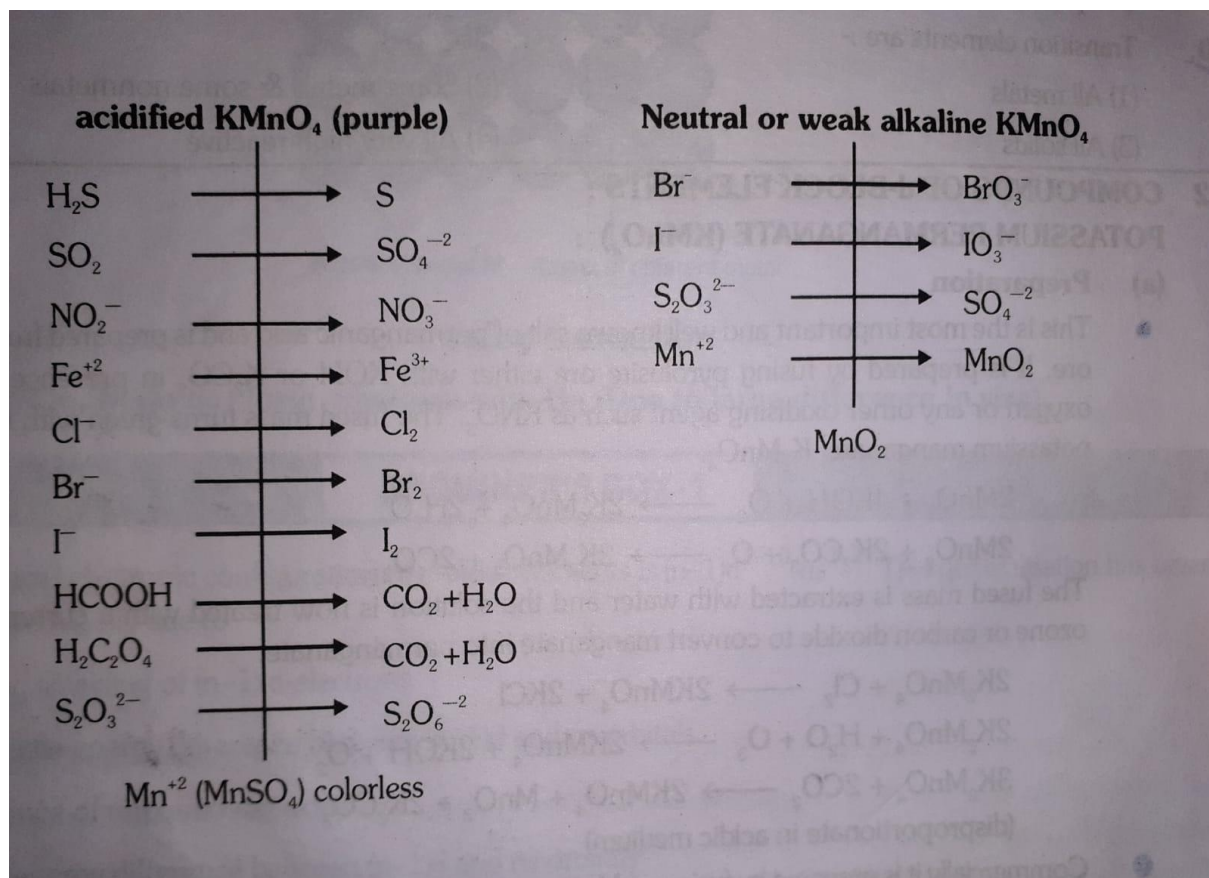


3) Properties:

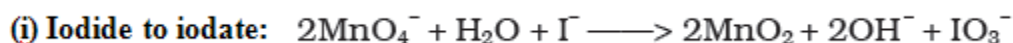
- Effect on heating:** when heated it decomposes at 513 K and O₂ is evolved.



- Oxidising Property:** Potassium permanganate acts as a strong oxidizing agent in acidic, neutral or faintly basic medium.
 - In acidic medium potassium permanganate oxidises:



➤ In neutral or faintly alkaline solutions potassium permanganate oxidises:



f- Block Elements (Inner transition elements)

Introduction: The two rows of elements at the bottom of the Periodic Table, called the Lanthanoids, Ce (Z = 58) – Lu (Z = 71) and Actinoids, Th (Z = 90) – Lr (Z = 103), their outer electronic configuration is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$. The last electron added to each element is filled in f- orbital.

Lanthanoids (Rare earths metals or Lanthanones)

1. General electronic configuration: $[Xe] 4f^{1-14}5d^{0-1}6s^2$

Note: Only Ce, Gd and Lu (total 03 nos.) elements have single electron in 'd' orbital

2. Oxidation states: The most common and most stable oxidation state of lanthanoids is +3. They also show oxidation states of +2, and +4 if the corresponding lanthanoid ions have extra stable $4f^0$, $4f^7$ and $4f^{14}$ configuration.

Element	Electronic Configuration	Electronic Configuration of M^{3+}	Oxidation States
Lanthanum La	$[Xe] 5d^1 6s^2$	$[Xe]$	+3
Cerium Ce	$[Xe] 4f^1 5d^1 6s^2$	$[Xe] 4f^1$	+3 (+4)
Praseodymium Pr	$[Xe] 4f^3 6s^2$	$[Xe] 4f^2$	+3 (+4)
Neodymium Nd	$[Xe] 4f^4 6s^2$	$[Xe] 4f^3$	(+2) +3
Promethium Pm	$[Xe] 4f^5 6s^2$	$[Xe] 4f^4$	(+2) +3
Samarium Sm	$[Xe] 4f^6 6s^2$	$[Xe] 4f^5$	(+2) +3
Europium Eu	$[Xe] 4f^7 6s^2$	$[Xe] 4f^6$	(+2) +3
Gadolinium Gd	$[Xe] 4f^7 5d^1 6s^2$	$[Xe] 4f^7$	+3
Terbium Tb	$[Xe] 4f^9 6s^2$	$[Xe] 4f^8$	+3 (+4)
Dysprosium Dy	$[Xe] 4f^{10} 6s^2$	$[Xe] 4f^9$	+3 (+4)
Holmium Ho	$[Xe] 4f^{11} 6s^2$	$[Xe] 4f^{10}$	+3
Erbium Er	$[Xe] 4f^{12} 6s^2$	$[Xe] 4f^{11}$	+3
Thulium Tm	$[Xe] 4f^{13} 6s^2$	$[Xe] 4f^{12}$	(+2) +3
Ytterbium Yb	$[Xe] 4f^{14} 6s^2$	$[Xe] 4f^{13}$	(+2) +3
Lutetium Lu	$[Xe] 4f^{14} 5d^1 6s^2$	$[Xe] 4f^{14}$	+3

Note:

- All lanthanoids and actinoids are belongs to iii B group.
- All lanthanoids elements are belongs to same number of group and same number of period.

3. Magnetic properties:

- Lanthanum ions (La^{3+}) and lutetium ions (Lu^{3+}) are diamagnetic due to having $4f^0$ and $4f^{14}$ electronic configuration while all other tripositive lanthanoids ions are paramagnetic due to presence of unpaired electrons.
- Exception- Neodymium (Nd) is the most paramagnetic lanthanoid.
- Ce^{4+} and Yb^{2+} are also diamagnetic ions.

4. Colour: The lanthanoids ions have unpaired electrons in their 4f orbitals thus these ions absorb visible region of light and undergo f-f transition and exhibit colour. Lanthanoids ions having $4f^0$, $4f^{14}$ are colourless.

5. Lanthanoid contraction:

- In the lanthanoids series with increasing atomic number, there is a progressive decrease in the size from lanthanum to lutetium or from La^{3+} to Lu^{3+} ions. This contraction in size is known as lanthanoids contraction.
- The general electronic configuration of these elements is $4f^{1-14} 5s^2 6d^{0-1} 6s^2$. In these elements the added electron enters the deep seated f-orbitals and therefore experiences considerable pull by the nucleus.
- Due to very poor shielding effect of (n-2)f electrons, they exert very little screening effect on the outermost $6s^2$ electrons. Hence with increasing atomic number, the enhanced nuclear charge leads to contraction in the size of atoms and ions.

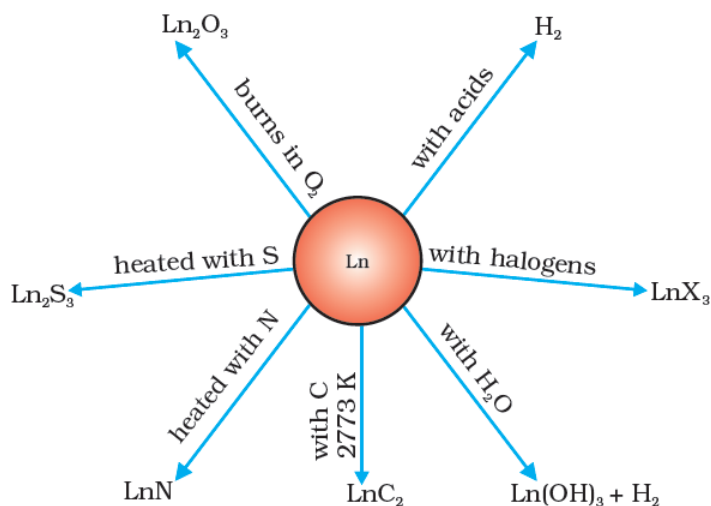
6. Effect of Lanthanoid contraction:

1) **Atomic size:** Decrease from La to Lu is due to the Lanthanoid Contraction.

2) **Basic nature of hydroxide:** Due to the effect of lanthanoids contraction, the basic nature of hydroxide regularly decreases.

3) **Similarity in properties of lanthanoids:** Due to small difference in size the chemical properties of lanthanoids are similar and their separation is difficult.

7. Important reactions of Lanthanoids:



8. Uses of lanthanoids:

- The pure metals have no specific use. So they are used as alloy or compounds.
- As alloy lanthanoids are used in making a mischmetal which consists of a lanthanoid metal mainly cerium (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al.
- Mischmetal is used in Mg-based alloy to produce bullets, shell and lighter flint.

Actinoids (5f- Series)

1. Physical appearance: These are silvery white metals, which are highly reactive.

2. General electronic configuration: $[Rn] 5f^{1-14}6d^{0-2}7s^2$

3. Oxidation states: Actinoids show most common O.S. of + 3 but it is not always most stable. Actinoids also show higher oxidation states, e.g., Th (+4), Pa (+5), U (+6) and Np (+7).

Atomic	Element	Symbol	Outer electronic structure	Oxidation states*
89	Actinium	Ac	$6d^1 7s^2$	+3
90	Thorium	Th	$6d^2 7s^2$	+3, +4
91	Protactinium	Pa	$5f^2 6d^1 7s^2$	+3, +4, +5
92	Uranium	U	$5f^3 6d^1 7s^2$	+3, +4, +5, +6
93	Neptunium	Np	$5f^4 6d^1 7s^2$	+3, +4, +5, +6, +7
94	Plutonium	Pu	$5f^6 7s^2$	+3, +4, +5, +6, +7
95	Americium	Am	$5f^7 7s^2$	+2, +3, +4, +5, +6
96	Curium	Cm	$5f^7 6d^1 7s^2$	+3, +4
97	Berkelium	Bk	$5f^9 7s^2$	+3, +4
98	Californium	Cf	$5f^{10} 7s^2$	+2, +3
99	Einsteinium	Es	$5f^{11} 7s^2$	+2, +3
100	Fermium	Fm	$5f^{12} 7s^2$	+2, +3
101	Mendelevium	Md	$5f^{13} 7s^2$	+2, +3
102	Nobelium	No	$5f^{14} 7s^2$	+2, +3
103	Lawrencium	Lr	$5f^{14} 6d^1 7s^2$	+3
104	Rutherfordium	Rf	$4f^{14} 6d^2 7s^2$	

Note:

- Thorium element does not have electron in f orbital while it belongs to f block element because of it has almost similar properties with other actinoids.
- All actinoids belong to the III B group.
- All actinoid elements belong to the same number of groups and the same number of periods.

4. Actinoid contraction: In the actinoid series, there is a decrease in atomic and ionic size with an increase in atomic number due to an increase in the effective nuclear charge on the outermost shell and poor shielding by 5f electrons. This is referred to as actinoid contraction.

5. Ionisation energy: The ionisation energy value of actinoids is very low so they are highly electropositive and form salts as well as complexes.

6. Colour: Generally actinoids are coloured due to presence of 5f unpaired electrons.

7. Magnetic property: Many of the actinoids elements are paramagnetic due to presence of unpaired 5f electrons. The variation of magnetic properties with the no. of unpaired 5f electrons is similar to that of lanthanoids (Ln).

8. Density: Actinoids are highly dense metals except thorium (Th) and americium (Am)

9. Radioactive nature: All the actinoids are radioactive elements and the earlier members have relatively long half-lives, the latter ones have half-life values ranging from a day to 3 minutes for lawrencium ($Z=103$). The latter members could be prepared only in nanogram quantities. These facts render their study more difficult.

10. Melting and Boiling point: They have high melting and boiling point and form alloys with other metals, specially iron.

11. Uses of lanthanoids:

- Thorium is used in the treatment of cancer and in incandescent (glowing) gas mantles.
- Uranium is used in the glass industry, in medicines and as nuclear fuel.
- Plutonium is used in atomic reactors and in atomic bombs.

12. Difference b/w Lanthanoids and Actinoids:

Sr.No.	Lanthanoids	Actinoids
1	4f orbital is progressively filled.	5f orbital is progressively filled.
2	+3 oxidation state is most common along with +2 and +4.	They show +2, +3, +4, +5, +6, +7 oxidation state.
3	Only promethium (Pm) is radioactive.	All are radioactive.
4	They are less reactive.	They are more reactive.
5	They have less tendency towards complex formation.	They have stronger tendency towards complex formation.
6	Lanthanoids compounds are less basic.	Actinoids compounds are more basic.