CHAPTER - 05

THE d AND f -BLOCK ELEMENTS

The elements of gp 3 - 12 in which the orbitals are progressively filled in each of the four long periods is known as d-block.

There are mainly 3 series of the transition metals 3d series (Sc to Zn), 4d series (Y to Cd) and 5d series (La to Hg) and an incomplete 6d series.

Transition element is defined as the one which has incompletely filled d orbitals in its ground state or any one of the oxidation state.

ELECTRONIC CONFIGURATION

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

Outer electronic configuration of 3d series

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z →	21	22	23	24	25	26	27	28	29	30
	$3d^1$	$3d^2$	$3d^3$	$3d^5$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^{10}$	$3d^{10}$
	$4s^2$	$4s^2$	$4s^2$	$4s^1$	$4s^2$	$4s^2$	$4s^2$	$4s^2$	$4s^1$	$4s^2$

4d series

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z →	39	40	41	42	43	44	45	46	47	48
	$4d^1$	$4d^2$	$4d^4$	$4d^5$	$4d^6$	$4d^7$	$4d^8$	$4d^{10}$	$4d^{10}$	$4d^{10}$
	$5s^2$	$5s^2$	$5s^1$	$5s^1$	$5s^1$	$5s^1$	$5s^1$	$5s^0$	$5s^1$	$5s^2$

5d series

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z →	57	72	73	74	75	76	77	78	79	80
	$5d^1$	$5d^2$	$5d^3$	$6d^4$	$5d^5$	$5d^6$	$5d^7$	$5d^9$	$5d^{10}$	$5d^{10}$
	$6s^2$	$6s^2$	$6s^2$	$6s^2$	$6s^2$	$6s^2$	$6s^2$	$6s^1$	$6s^1$	$6s^2$

6d series

	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub
Z $\rightarrow$	89	104	105	106	107	108	109	110	111	112
	$6d^1$	$6d^2$	$6d^3$	$6d^4$	$6d^5$	$6d^6$	$6d^7$	$6d^8$	$6d^{10}$	$6d^{10}$
	$7s^2$	$7s^2$	$7s^2$	$7s^2$	$7s^2$	$7s^2$	$7s^2$	$7s^2$	$7s^1$	$7s^2$

Physical properties

Nearly all the transition elements display typically metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and lustre with the exception of Zn, Cd, Hg and Mn.

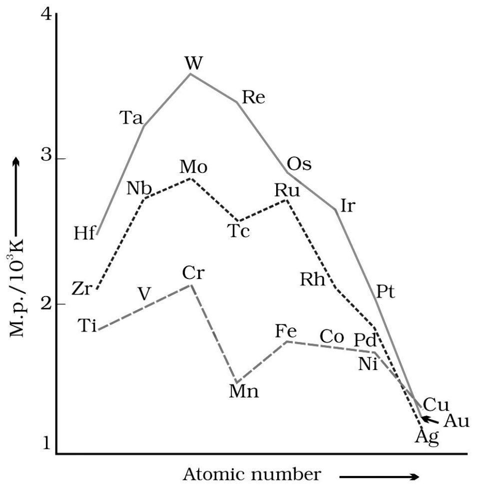
Lattice structure

Sc hcp (bcc)	Ti hcp (bcc)	V bcc	Cr bcc (ccp)	Mn x (hcp)	Fe bcc (hcp)	Co ccp	Ni ccp	Cu ccp	Zn x (hcp)
Y hcp (bcc)	Zr hcp (bcc)	Nb bcc	Mo bcc	Tc hcp	Ru hcp	Rh ccp	Pd ccp	Ag ccp	Cd x (hcp)
La hcp (bcc) (ccp)	Hf hcp (bcc)	Ta bcc	W bcc	Re hcp	Os hcp	Ir ccp	Pt ccp	Au ccp	Hg x

M.P and B.P

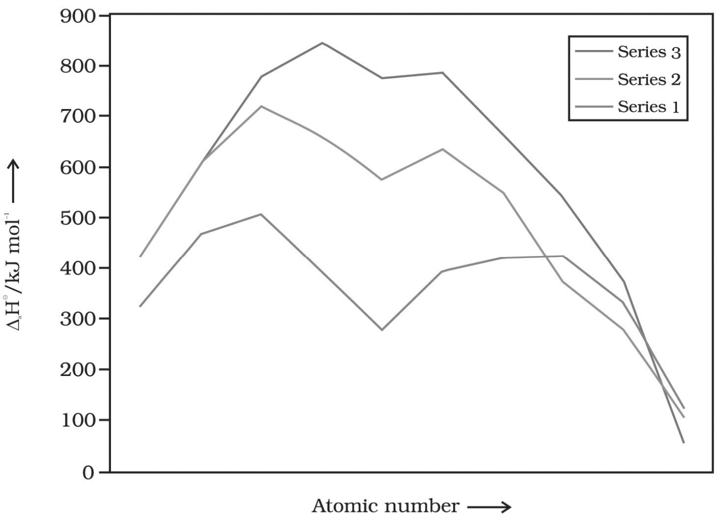
The high M.P of these metals are due to the involvement of greater number of electrons from (n-1)d in addition to ns electrons in the interatomic metallic bonding.

Greater the number of unpaired electrons stronger is the resultant bonding and greater is the M.P.



Enthalpies of atomisation

Metals of the 2nd and 3rd series have greater enthalpies of atomisation than corresponding elements of the first series.



Atomic and ionic sizes

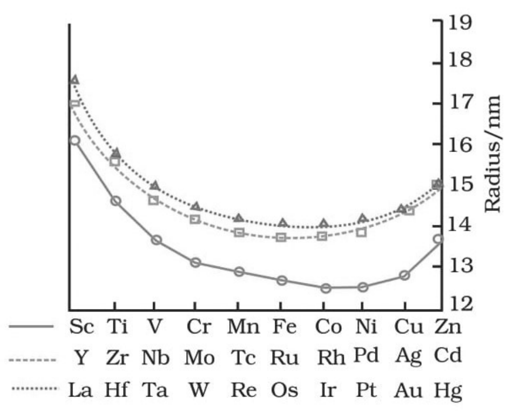
In a series, the atomic radii of d block generally decrease with increase in atomic number but the decrease in atomic size is small after midway and there is a slight increase towards the end of a period.

Radius first decrease due to increasing the nuclear charge then nearly same due to the increased nuclear charge will be equal to the electron-electron repulsion and finally increase is due to increasing $e^- - e^-$ repulsion.

From top to bottom the radii first increase from 3d to 4d series due to increasing the number of shells.

From 4d to 5d there is almost equal radii even if the number of shells increases. This is due to the lanthanoid contraction. Lanthanoid contraction is due to the poor shielding power of 4f electrons.

Ionic radii also follows the same trend as atomic radii.



Density

Along any series from left to right, the atomic radii decreases due to increase in nuclear charge. Thus the atomic volume decreases while atomic mass increases which result in increase of density. In 3d series density increases up to Cu. The last Zn is an exception due to large atomic volume.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Density	3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

In d block Ir has the highest density (22.61 gcm^{-3}) and Sc has lowest (3.43 $g\ cm^{-3}$)

Os have slightly lower than Ir (22.59 gcm^{-3})

Ionisation enthalpy

1) First I.E of d block higher than s block and lower than p-block.
2) In a given series the difference in the I.E between any 2 successive members is very much less than the difference in case of successive members of 's' or 'p' block.
3) 1st I.E of Zn, Cd, Hg are very high due to completely filled configuration.
4) More the I.E, lesser the thermodynamic stability of the compound.
5) Lowest 1st I.E of d block - Sc (361 KJ mol^{-1})
6) Higher 1st I.E of d block - Hg (1007 KJ mol^{-1})
7) 1st I.E of gp-12 Hg > Zn > Cd (exception)

Oxidation State

- Variable oxidation state.
- Most common oxidation state +2 except for Sc
- Mostly ionic bonds are formed +2 & +3 oxidation state. In compounds having higher oxidation state mostly covalent.
- The element which exhibit greater no. of oxidation state in or near the middle of each series.
- Adjacent oxidation states are differ by only one unit.
- Lower members prefer lower oxidation state and heavier members prefer higher oxidation state
- Transition metal exhibit zero oxidation state when they form compounds with $\pi-$acceptor ligands like CO.
- The highest oxidation state ie., +8 exhibit Os & Ru
- The highest oxidation state are found in fluorides and oxides

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+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**

Trend in stability of higher oxidation state Halides

- In Halides Cr will exhibit higher oxidation state +6
- In simple halide Mn exhibit maximum oxidation state +4. But MnO_3F is a known compound.
- In lower oxidation state fluorides are unstable
- Cu(II) halides except iodide are known
- Many Cu(I) compounds are unstable in aq.solution and undergo disproportionation.

$$2Cu^{+} \rightarrow Cu^{2+} + Cu$$

Oxidation Number									
+ 6			CrF_6						
+ 5		VF_5	CrF_5						
+ 4	TiX_4	VX^{I}_4	CrX_4	MnF_4					
+ 3	TiX_3	VX_3	CrX_3	MnF_3	FeX^{I}_3	CoF_3			
+ 2	TiX_2^{III}	VX_2	CrX_2	MnX_2	FeX_2	CoX_2	NiX_2	CuX_2^{II}	ZnX_2
+ 1								CuX^{III}	

Key: X = F → I; X^{I} = F → Br; X^{II} = F, CI; X^{III} = CI → I

Oxides

- Highest oxidation state exhibit Mn, ie., +7 (Mn_2O_7)
- Highest oxidation state of the oxide coincide the gp number from Sc to Mn

  Oxygen stabilized the highest oxidation state more than fluorine. This is due to the ability of O_2 to form multiple bonds.
- If an element form different oxide, their acidic strength increase with increasing the oxidation state.

Oxidation Number	Groups 3	4	5	6	7	8	9	10	11	12
+ 7					Mn_2O_7					
+ 6				CrO_3						
+ 5			V_2O_5							
+ 4		TiO_2	V_2O_4	CrO_2	MnO_2					
+ 3	Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_2O_3				
					$Mn_3O_4^{*}$	$Fe_3O_4^{*}$	$Co_3O_4^{*}$			
+ 2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO
+ 1									Cu_2O	

Standard electrode potentials

- The electrode potential is a measure of $\Delta_T H$

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

E^0values (M^{2+}/M)

Element	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
E^0 (M^{2+}/M)	-1.63	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	0.34	-0.76

- The general trend towards less negative E^0 values along the series is due to increase in I.E
- The +ve E^0value of Cu account for its inability to liberate H_2 from acid.

The E^0 value of Mn, Ni, Zn are more negative than excepted. This is due to greater stability of half filled d orbital of Mn^{2+} and completely filled d orbital of Zn^{2+}. The exceptional E^0 value of Ni related to the highest negative $\Delta_{Hyd}H$.

E^0value of M^{3+}/M^{2+}

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
E^0 (M^{3+}/M^{2+})		-0.37	-0.26	-0.4	1.57	0.77	1.97			

- Low value of Sc is due to Sc^{3+} has noble gas configuration.
- Highest value of Zn is due to d^{10} configuration of Zn^{2+}
- Greater the value of reduction potential, greater is the tendency to act as an oxidising agent.

<u>Magnetic property</u>

Paramagnetic -due to the presence of unpaired e^-

Diamagnetic -due to the absence of unpaired e^-

Ferromagnetism is an extreme form of paramagnetism

For d block magnetic moment calculated by the formula $\mu = \sqrt{n(n+2)}$ B.M

$\mu \rightarrow$ Spin only magnetic moment

$n \rightarrow$ no. of unpaired e^-

<u>Formation of coloured ions</u>

- Colour is due to d-d transition
- Generally d^0 & d^{10} configuration are colourless due to absence of d-d transition

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
$3d^6 3d^7$	$Co^{3+} Co^{2+}$	bluepink
$3d^8$	Ni^{2+}	green
$3d^9$	Cu^{2+}	blue
$3d^{10}$	Zn^{2+}	colourless

Formation of complex compounds

Reasons:

- Small size
- High ionic charge
- Availability of d orbitals for bond formation

Catalytic properties

Reasons:

- Ability to adopt multiple oxidation state and to form complexes.

  Eg: Fe^{3+} catalysis the reaction between iodide and persulphate ions.

Formation of interstitial compounds

- These are formed when small atoms like H, C or N are trapped inside the crystal lattice.
- They are nonstochiometric
- They are neither typically ionic nor covalent

  Eg: TiC, Mn_4N, Fe_3H, $TiH_{1.7}$, $VH_{0.56}$

- They have high melting point, higher than pure metal
- They are very hard, some ... approach diamond in hardness
- They retain metallic conductivity
- They are chemically inert

Alloy formation

- Alloy is a blend metals prepared by mixing components
- Because of the similar radii and other characteristics of transition metals, alloys are readily formed by these metals
- Alloys of transition metals with non transition metals such as brass (Cu - Zn) and bronze (Cu - Sn)

Some important components of Transition elements

1. $K_2Cr_2O_7$

Preparation:

Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromate ore ($FeCr_2O_4$) with sodium or potassium carbonate in free assess of air.

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

The yellow solution of sodium chromate is filtered and acidified with H_2SO_4 give a solution from which orange $Na_2Cr_2O_7.2H_2O$ can be crystallised

$$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

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

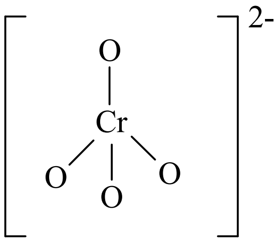
Properties

- $Na_2Cr_2O_7$ is more soluble than $K_2Cr_2O_7$
- In aqueous solution, chromate and dichromate are interconvertable depending on the pH of the solution.

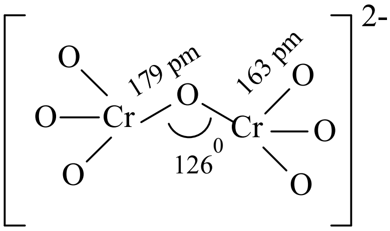
$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

$$CrO_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$$

- Structure



Chromate ion



Dichromate ion

Chromate ion is tetrahedral whereas the dichromate ion consist of two tetrahedra sharing one corner with Cr-O-Cr bond angle of 126^0.

- Acidified $K_2Cr_2O_7$ acts as an oxidising agent

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

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

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

$$3S_2O_3^{2-} + Cr_2O_7^{2-} + 8H^+ \rightarrow 3S + 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$

- Equivalent mass of $K_2Cr_2O_7 = \dfrac{\text{Molecular mass of } K_2Cr_2O_7}{6}$

- Action of heat

$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

- Orange colour of $K_2Cr_2O_7$ is not due to d-d transition, it is due to the charge transfer transition.
- $K_2Cr_2O_7$ is used as a primary standard in volumetric analysis
- **Chromyl chloride test**: When $K_2Cr_2O_7$ is heated with chloride and strong H_2SO_4 reddish brown vapour of chromyl chloride is formed.

$$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \longrightarrow 2CrO_2Cl_2 + 6KHSO_4 + 3H_2O$$

- **With hydrogen peroxide**: Acidified potassium dichromate forms a deep blue colour with H_2O_2 due to the formation of CrO_5

$$K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \longrightarrow 2CrO_5 + K_2SO_4 + 5H_2O$$

2. $KMnO_4$

Preparation

1. It is prepared by fusion of MnO_2 (Pyrolusite ore) with an alkali metal hydroxide and an oxidising agent like KNO_3. This produces the dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

2. Commercially it is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (VI)
3. In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

Properties

- Potassium permanganate form dark purple colour crystal which are isostructural with those of $KClO_4$.
- The manganate and permanganate ions are tetrahedral in shape.
- The green manganate is paramagnetic with one unpaired e^-. But permanganate is diamagnetic
- The colour of $KMnO_4$ is not due to d-d transition, it is due to charge transfer transition
- It act as an oxidising agent in acidic, basic, neutral medium

  [NCERT structure]
- Action of heat

  $$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$
- It is not used as a primary standard in volumetry
- Equivalent mass

  1. In acidic medium

  $$\text{Eq. mass} = \frac{M}{5}$$

  2. In neutral medium

  $$\text{Eq. mass} = \frac{M}{3}$$

  3. In strong alkaline medium

  $$\text{Eq. mass} = \frac{M}{1}$$

F- BLOCK Elements

- F-block elements are called inner transition element.
- General electronic configuration $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

THE LANTHANOIDS

- The elements in which the least electron enters the 4f-orbitals are called first inner transition series or lanthanoids.
- Elements and electronic configuration

Atomic Number	Name	Symbol	Electronic configurations* Ln	Ln^{2+}	Ln^{3+}	Ln^{4+}	Radii/pm 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	$4f^7 5d^1 6s^2$	$4f^7 5d^1$	$4f^7$		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 radii

  The regular decrease in the radii of lanthanoids with increasing atomic number is called lanthanoid contraction.

- Consequences of lanthanoid contraction:

  1. Tb, Dy, Ho, Er, Tm, Yb, Lu have shorter atomic radius than Yttrium
  2. Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+} have shorter ionic radius than Yttrium
  3. Reactivity decreases from Ce to Lu
  4. Basic character of oxide and hydroxide decreases across the series
  5. Chemical twins are formed
  6. Separation of lanthanoid by ion exchange method are facilitated.

- All the Ln are silvery white soft metal
- Their hardness increases with increasing their atomic number. But Sm is exceptionally extra hard.
- Their melting paints are in the range of 1000 to 1200 K. But Sm melt at 1623K.

  They have typical metallic structure

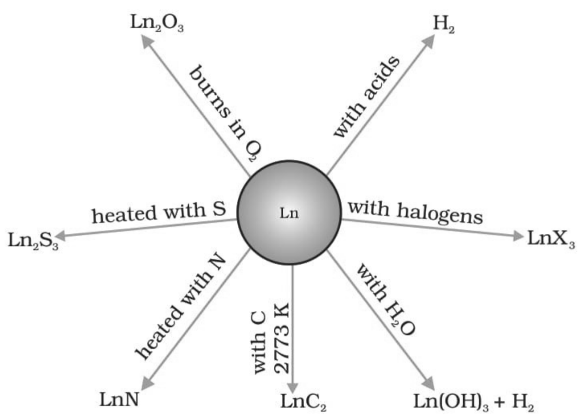
- They are good conductors of heat and electricity
- Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous sol. due to f-f transition.
- The lanthanoid ions other than f^0 type (La^{3+}, Ce^{4+}) and f^{14} type (Yb^{2+}, Lu^{3+}) are all paramagnetic.
- The paramagnetism rises to maximum in Neodymium
- The 1st ionisation enthalpy of Ln are around 600 KJ mol^{-1}, the second about 1200 KJ mol^{-1}.
- The earlier members are quite reactive similar to Ca. But with increasing atomic number they have more like Al.
- Their electrode potentials are in the range of -2.2 to -2.4V, except for Eu for which the value of -2V.
- Most common oxidation state +3.
- Some of them will exhibit +2 & +4 in addition to +3.

  Eg: Eu^{2+}, Yb^{2+}

  Pr^{4+}, Nd^{4+}, Tb^{4+}, Dy^{4+}
- Uses:

  1. Ce is used as a scavenger of O_2
  2. Ce $(SO_4)_2$ is an oxidiser in cerimetry
  3. CeO_2 & ThO_2 are used to make gas mantles
  4. Misch metal is an alloy of Ln which contain ~95% Ln, ~5% Fe and traces of S, C, Ca & Al.
  5. Sm_2O_3 is used to make phospher screen
  6. Mixed oxides of Ln's are used as catalysts in petroleum cracking.

Chemical reaction



THE ACTINOIDS (Ac)

- Elements and electronic configuration

Atomic Number	Name	Symbol	Electronic configurations* M	M^{3+}	M^{4+}	Radii/pm M^{3+}	M^{4+}
89	Actinium	Ac	$6d^1 7s^2$	$5f^0$		111	
90	Thorium	Th	$6d^2 7s^2$	$5f^1$	$5f^0$		99
91	Protactinium	Pa	$5f^2 6d^1 7s^2$	$5f^2$	$5f^1$		96
92	Uranium	U	$5f^3 6d^1 7s^2$	$5f^3$	$5f^2$	103	93
93	Neptunium	Np	$5f^4 6d^1 7s^2$	$5f^4$	$5f^3$	101	92
94	Plutonium	Pu	$5f^6 7s^2$	$5f^5$	$5f^4$	100	90
95	Americium	Am	$5f^7 7s^2$	$5f^6$	$5f^5$	99	89
96	Curium	Cm	$5f^7 6d^1 7s^2$	$5f^7$	$5f^6$	99	88
97	Berkelium	Bk	$5f^9 7s^2$	$5f^8$	$5f^7$	98	87
98	Californium	Cf	$5f^{10} 7s^2$	$5f^9$	$5f^8$	98	86
99	Einstenium	Es	$5f^{11} 7s^2$	$5f^{10}$	$5f^9$	–	–
100	Fermium	Fm	$5f^{12} 7s^2$	$5f^{11}$	$5f^{10}$	–	–
101	Mendelevium	Md	$5f^{13} 7s^2$	$5f^{12}$	$5f^{11}$	–	–
102	Nobelium	No	$5f^{14} 7s^2$	$5f^{13}$	$5f^{12}$	–	–
103	Lawrencium	Lr	$5f^{14} 6d^1 7s^2$	$5f^{14}$	$5f^{13}$	–	–

- Ac exhibit variable oxidation state, Np & Pu have +7 oxidation state

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									

- None of them is found to have +2 oxidation state.
- Chemical twins are not formed because the radii of adjacent members differ in much more.
- They are radioactive elements
- Earlier members have relatively long half life, the latter once have half life values ranging from a day to 3 minutes
- They are silvery in appearance but display variety of structures. The structural variability is due to irregularities in radii.

  The action of boiling water on them give a mixture of oxide and hydride.
- Magnetic properties are complex.
- The heaviest primordial element is Pu, which has a half life of several million years and existed before the formation of earth.
- Their compounds in +3 and +4 oxidation state are easily hydrolysed.