

d-and f-block elements

d-block of the periodic table contains elements of the groups 3-12 in which the orbitals are progressively filled in each of the four long periods. The elements constituting the *f*-block are those in which the *4f* and *5f* are progressively in the later two long periods; these elements are formal members of group 3 from which they have been taken out to form separate *f*-block of the periodic table.

The transition metals are those elements which have incompletely filled d-subshells in their ground state or in any one of their oxidation state.

Cu, Ag and Au are transition metals because in their commonly occurring states, they have partly filled d-sub shells. Zn, Cd and Hg of group 12 do not have partly filled d-sub shell in their elementary state or commonly occurring oxidation state, and hence, are not considered as transition elements. However, being the end members their chemistry is studied with transition elements.

Electronic Configuration- $(n-1)d^{1-10} ns^{1-2}$

Transition series- The d-block elements are called transition elements as they represent change in properties from most electropositive s-block elements to least electropositive (or most electropositive) p-block elements.

Transition elements consist to of 4 rows: These series are called transition series.

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
$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$

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
$4d^1 5s^2$	$4d^2 5s^2$	$4d^4 5s^2$	$4d^5 5s^1$	$4d^6 5s^1$	$4d^7 5s^1$	$4d^8 5s^1$	$4d^{10} 5s^0$	$4d^{10} 5s^1$	$4d^{10} 5s^2$

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

GENERAL PROPERTIES OF TRANSITION ELEMENTS

Atomic radii: The atomic radii is intermediate between those of s- and p- block elements. The

Following trends are observed:

a) The atomic radii of elements of a particular series decrease with increase in atomic number but this decrease in atomic radii become small after midway.

Reason- The atomic radii decreases in the beginning because of increase in atomic no., the nuclear charge goes on increasing progressively, but the electrons enter the penultimate shell and the added d-electrons screen the outermost s-electrons. The shielding effect is small so that net electrostatic attraction between the nuclear charge and outermost electrons increases. Consequently atomic radius decreases. As the no. of d-electrons increase the screening effect increases. This neutralizes the effect of increased nuclear charge due increase in atomic number and consequently atomic radius remains almost unchanged after chromium.

b) At the end of each period, there is slight increase in atomic number

Reason- This is because of increased electron-electron repulsions between the added electrons in the same orbital which exceeds the attractive forces due to increased nuclear charge. Therefore, electron cloud expands and size increase.

c) The atomic radii increase while going down the group.

Reason – The atomic radii of second transition series is larger than that of first transition series because of increase in no. of outermost shell.

The third transition series have nearly the same radii as metals of second transition series. This is because of lanthanide contraction. This is associated with the interventions of 4f- orbitals which are filled before 5d-series. 4f- orbital have poor screening effect, This results in regular decrease in atomic radii which compensates the expected increase in atomic size with increase in atomic no.

Ionic Radii- The ionic radii follows the same trend as atomic radii. Since metals exhibit different oxidation states, radii of ions also differ. The ionic radii decrease with increase in nuclear charge.

Metallic character- All transition elements are metals. They have high density, hardness, high m.p. & b.p. & high tensile strengths, ductility, high, thermal and electrical conductivity and lustre.

Reason – The metallic character is due to their relatively low ionization enthalpies and number of vacant orbitals in the outermost shell. The hardness of these metals suggests the presence of strong bonding due to overlap of unpaired electrons between different metal atoms. Therefore, they exhibit high enthalpy of atomization. Enthalpy of atomization is maximum in the middle indicates one unpaired electron is particularly favorable for strong atomic interaction. Hence, max enthalpy of atomization.

Density- All metals have high density. Within a period, the densities vary inversely with atomic radii, i.e., densities increase along a period. Also densities increase upon descending down the group.

Reason – The atomic volumes of transition elements are low because electrons are added in (n-1)d sub shell and not in ns subshell . 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.

Melting and boiling points

The transition metals have high m.p. & b.p. The m.p. and b.p. of metals rise to a maximum value and then decrease with increase in atomic number. However, Mn and Tc have abnormally low m.p. & b.p.

Reason – The high m.p. & b.p. is due to strong metallic bonds between the atoms of these elements. The metallic bond is formed due to interaction of electrons in the outermost orbital. The strength of bonding depends on the number of outer most electrons. Greater is the number of valence electrons, stronger is the metallic bonding and consequently, m.p. is high.

Therefore 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) . Therefore, m.p. decrease after the middle because of increase in pairing of electrons.

The dip in the curve in Mn and Tc is due to the fact that Mn has stable electronic configuration ($3d^5 4s^2$). As a result 3d electrons are more tightly held by Mn atomic nucleus and this reduces delocalization of electrons resulting in weaker metallic bonding.

Ionization Enthalpies- The following trend is observed in the ionization enthalpies of d- block elements.

The ionization enthalpies of d-block elements are higher than those of p-block elements. The I.E. increase along a series.

Reason - The increase in ionization enthalpy is due to the effect of increasing nuclear charge which would tend to attract outer electron with greater force. Consequently, ionization enthalpy is expected to increase. But the addition of electrons take place in last but one d-sub shell and this increases the screening effect. With the increase in electrons in d-sub shell the outer electrons are shielded more & more. Thus, effect of increased nuclear charge is opposed by additional screening effect of the nucleus and ionization enthalpy increases but slowly. The irregular trend in first I.E. of first transition series elements is due to the fact that removal of one electron alters the relative energies of 4s and 3d orbitals. Therefore, there is reorganization energy which gains in exchange energy due to increase in no. of electrons in d^n configuration and from transference of s-electrons in d- orbital.

Some exceptions observed in ionization enthalpies are:-

- Cr and Cu have high I.E. This is attributed to their half filled (d^5) and completely (d^{10}) electronic configuration .
- The value of second I.E. for zinc is low because ionization involves removal of an electron resulting in stable $3d^{10}$ configuration.
- The trend in third I.E. shows high value for Mn^{+2} and Zn^{+2} because of stable $3d^5$ and $3d^{10}$ electronic configuration.

Similarly, $I.E_3$ for Fe $< I.E_3$ for Mn because of stable $3d^5$ in Fe. In general, third I.E. values are very high because of filled 4f-orbitals which have poor shielding effect.

Oxidation States-

a) Transition metals exhibit a larger number of oxidation states in their compound.

Reason - This is because of 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.

The elements which gave the greatest number of oxidation states occur in or near the middle of the series. Eg. Mn ; oxidation states from +2 & +7

The lesser number of oxidation states at the extreme ends is either due to too few electrons to lose or share or too many d electrons, hence fewer orbitals are available in to available to share electrons with others, thus higher valence cannot be attained.

eg. Cu can have oxidation state of +1 & +2

Zn can have oxidation state of +2 only

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 ¹ 4s ²	3d ² 4s ²	3d ³ 4s ²	3d ⁵ 4s ¹	3d ⁵ 4s ²	3d ⁶ 4s ²	3d ⁷ 4s ²	3d ⁸ 4s 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

b) Except Sc, the most common oxidation state of first row transition elements is +2 which arises due to loss of 4s- electrons. This means Sc, 3d-orbitals are more stable and lower in energy than 4s- orbital. As a result electrons are first removed from 4s- orbital.

c) Zinc is +2 in which no d-electrons are involved.

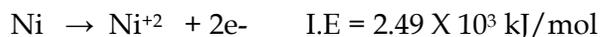
d) Within a group, maximum oxidation state increases with atomic number. For e.g. in group 8, Fe shows +2 and +3 but Ruthenium and Osmium form compounds in +4, +6 and +8 oxidation state.

e) In +2 and +3 oxidation state, bonds formed are ionic and in the compounds of higher oxidation state bonds are covalent.

Transition elements show low oxidation states in some compounds or complexes having ligands such as CO, for e.g. in Ni(CO)₄, Ni has zero oxidation state.

Standard electrode potential

The magnitude of ionization enthalpy gives the amount of energy required to remove electrons from particular oxidation state of metal in compounds. Smaller the I.E. the metal, the more stable is its compound.

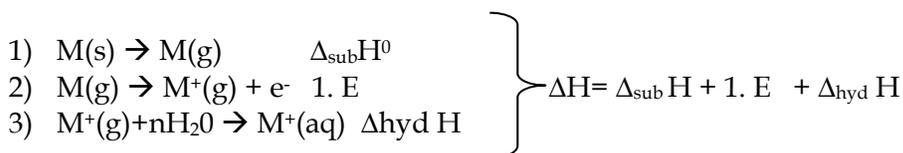


Ni(II) compounds are thermodynamically more stable than Pt(II) compounds.



Pt(IV) compounds are relatively more stable than Ni(IV) compounds. Stability of the compounds depend on electrode.

In addition to ionization enthalpy, ΔH_{sub} , ΔH_{hyd} energy, explain the stability of a particular oxidation state.



Smaller the value of total energy charge for a particular oxidation state in aqueous solution, greater will be the stability of that oxidation state. The electrode potential is a measure of total energy charge.

The lower the electrode potential, ie, more negative the standard reduction potential of the electrode, more stable is the oxidation state of the transition metal in aqueous solution. More negative values of E^0 for Mn and Zn are due to the stability of half filled ($3d^5$) in Mn^{+2} and completely filled ($3d^{10}$) configuration in Zn^{+2} .

Trend in M^{3+} / M^{2+} standard electrode potential

Except copper and Zinc, all other elements of first transition series show +3 oxidation states to from M^{+3} in aqueous solution.

- Low value of Sc reflects stability of Sc^{+3} which has a noble gas configuration.
- High value for Mn shows that Mn^{+2} (d^5) is particularly stable.
- Low value for Fe, shows extra stability for Fe^{+3} configuration.

Trends in stability of higher oxidation states-

The highest oxidation state is generally shown among halides and oxidation.

- Transition metals react with halogens at high temp as they have high activation energies. High temp is required to start the reaction but heat of reaction is sufficient to continue. The reaction.
Order of reactivity: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- In general elements of I transition series enact in low oxidation state.
- Since fluorine is the most electronegative element, the transition elements show high oxidations states with fluorine.
- The highest oxidation states are found in TiX_4 .
- The +7 oxidation states are not shown by simple halides.
- V(V) is shown by VFs only. Other halides from oxo halides OX_3 .
- Fluorides are unstable in their low oxidation state. Eg -V forms VX_2 ($X = \text{Cl, Br or I}$) Cu can form CuX ($X = \text{Cl, I}$) Cu (II) halides are known except the iodide.
- The ability of oxygen to stabilize the highest oxidation state is exhibited in their oxides. The highest oxidation states in member of group number. Eg-Sc in Sc_2O_3 is +3 and is a

member of group 3. Mn in group 7 has +7 oxidation state in Mn_2O_7 . Manganese forms highest oxidation state fluorides as MnF_4 whereas the highest oxide is Mn_2O_7 . This is due to tendency of oxygen to form multiple bonds. In the covalent oxide Mn_2O_7 , each Mn is tetrahedrally surrounded by oxygen atoms and has Mn-O-Mn bridge. Tetrahedral MnO_4^{2-} ions are also known for V(V), Cr(VI), Mn(VI) and Mn(VII).

Formation of colored ions-

Most of the compounds of transition metals are colored in solid or solution form.

Reason- The colour is due to the presence of incomplete (n-1)d sub shell. Under the influence of approaching ions towards central metal ion, the d-orbitals of central metal split into different energy levels. This phenomenon is called crystal field splitting. For e.g. When six ions or molecules approach the metal ion (octahedral field), the d-orbitals split into two sets:- One set consisting of two d-orbitals of higher energy (dx^2-y^2 , dz^2) and other set consisting of d-orbitals (d_{xy} , d_{yz} & d_{zx}) of lower energy. The electrons are easily promoted from one to another energy level in the same d-sub shell. These are called d-d transition. The amount of energy required to excite some of the electrons to higher energy states within the same d-sub shell corresponds to energy of certain colours of visible light. Therefore, when white light falls on the compounds, some part of its energy corresponding to certain colour is absorbed and the electron gets raised from lower energy to higher energy & the excess colour is transmitted. The observed colour is complementary of colour absorbed. Eg- Ti^{+3} (d^1) is purple.

Magnetic Properties-

Paramagnetism arises from the presence of unpaired electrons. Diamagnetic substances are repelled by the applied magnetic field while the paramagnetic substances are attracted whereas the ferromagnetic substances are attracted the most.

Each unpaired electron has a magnetic moment associated with its spin angular momentum and orbital angular momentum. For the compounds of the 1st transition series, the contribution of orbital angular momentum is effectively less and hence is of no significance. For these, the magnetic moment is determined by the number of unpaired electrons and can be calculated by 'spin only'

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

N = no. of unpaired e-

μ = Magnetic moment in Bohr magneton (μ_B) units

($\mu_B = eh/4m = 9.27 \times 10^{-24} \text{ Am}^2 \text{ or Jt}^{-1}$)

μ increase with the increasing number of unpaired electrons or in other words observed magnetic moment gives a useful indication about the number of unpaired electrons.

Eg- Calculate the magnetic moment of Mn^{2+} if the at. no. = 25,

Z = 25 So, d^5 has 5 unpaired electrons, n = 5

$$\mu = 5(5+2) = 5.92\mu_B$$

Formations of complex compounds :- The transition metals form a large no. of complex compounds due to

- (i) the comparatively smaller sizes of the metal ions,
- (ii) their high ionic charges and
- (iii) the availability of d-orbitals for bond formation

Eg. $[PtCl_4]^{2-}$, $[Cu(NH_3)_4]$, $[Fe(CN)_6]^{4-}$ etc.

Catalytic Properties-

a) Transition metals show catalytic property because of their ability to adopt multiple oxidation states. Catalysts at a solid surface involve the formation of bond between reactant molecules and atoms of the surface of the catalyst. This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules & the activation energy is lowered, moreover transition metals can change their oxidation states.

Eg- Fe^{3+} catalyses the reaction between I_2 & persulphate ions.

b) The catalytic property of transition metals is due to their tendency to form reaction intermediates with suitable reactants. These intermediates give reaction paths of low activation energy and therefore increase the rate of reaction. The reaction intermediates decompose yielding products and regenerating the original substance. The transition metals form reaction intermediates due to the presence of vacant orbitals & tendency to form variable oxidation state.

Formation of interstitial compounds :-

Many of the transition metals form interstitial compounds which are formed when small atoms like B, H, N or C are trapped inside the crystal lattices of metals. They are usually non-stoichiometric and are neither typically ionic nor covalent. These small atoms enter into the void sites, eg In, Ti. If C enters the void giving the composition TiC or $\text{TiH}_{1.7}$, $\text{VH}_{0.56}$ etc.

Physical & Chemical characteristics of these compounds

- (i) High m.pt, higher than pure metals.
- (ii) Very hard, some borides approach diamond in hardness
- (iii) Retain metallic conducting
- (iv) Chemically inert

Alloy Formation:-

Alloys are homogenous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other but the metals should have similar metallic radii within 15% of each other.

The alloys formed have high m.pt & are hard.

Eg. Alloys of Cr, V, W, Mo, Mn etc, stainless steel is or alloys of Fe, Ni, Cr

Alloys of transition metals with non-transition metals, such as Brass (Cu-Zn), Bronze (Cu-Sn).

Some important compounds of transition elements

Oxides & oxo metals ions



The higher oxidation state in the oxides coincides with the group no. eg, Sc_2O_3 (Sc is +3), Mn_2O_7 (Mn is +7).

Beyond group 7- no higher oxides. Eg- Fe_2O_3 (Fe is +3)

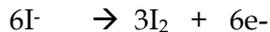
Besides the oxides, oxocations, stabilize V(V) as VO_2^+ , V(IV) as VO^{2+} and Ti(IV) as TiO^{2+} .

As the oxidation number of metal increases, ionic character decreases.

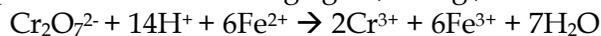
Mn_2O_7 is a covalent compound which is green oil.

Mn_2O_7 gives HMnO_4 } Acids in high oxidation state.
 CrO_3 gives $\text{H}_2\text{Cr}_2\text{O}_7$ }

Acidified $K_2Cr_2O_7$ oxidises iodides to iodine, sulphide to S, Sn(II) to Sn(IV), Fe(II) to Fe(III) to Fe(III)



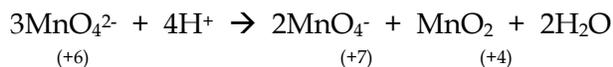
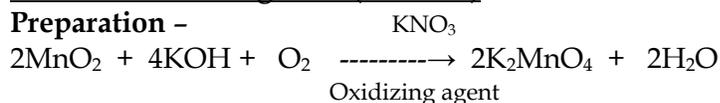
The full ionic equation can be obtained by adding half equation for potassium dichromate to half equation for the reducing agent, for eg.,



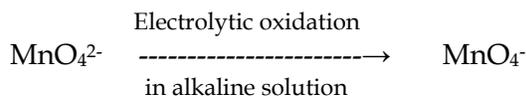
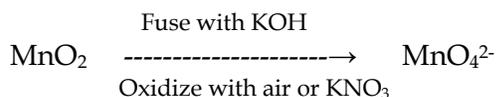
Uses - In leather industry, preparation of azo dyes.

Potassium Permanganate (KMnO₄)

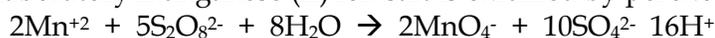
Preparation -



Commercially prepared by alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of Manganate (VI)

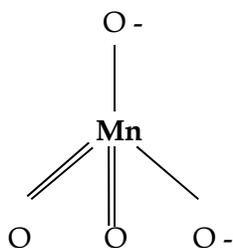


In the laboratory manganese (II) ion salt is oxidized by peroxodisulphate to permanganate

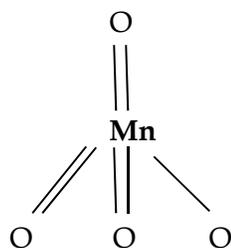


Properties-

1. Forms dark purple crystals
2. Not very soluble in water
3. Decomposes when heated at 513K



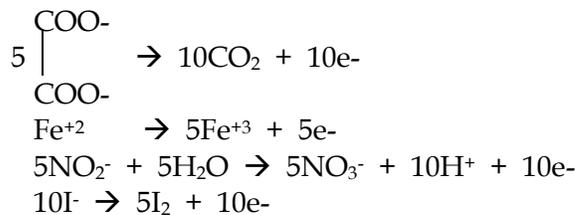
Tetrahedral manganese (green)ion



Tetrahedral Permanganate (purple) ion

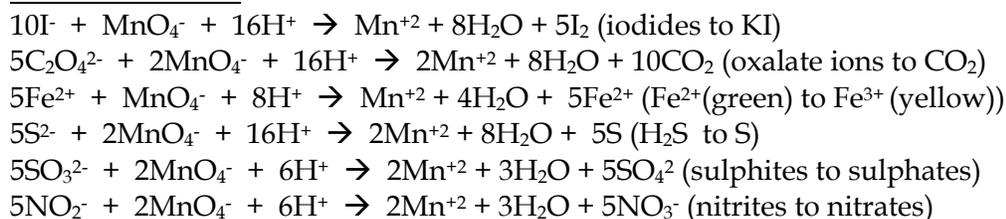
MnO₄ is a strong oxidizing agent, both in neutral & acidic medium

Acidified KMnO₄ oxidises oxalates to CO₂, Iron(II) to iron (III), nitrites to nitrates and iodides to free iodine. The half reactions of reductants are-

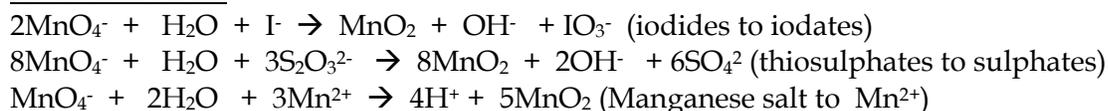


Full reactions can be written by adding the half reactions of KMnO₄ to half reactions of the reducing agents and balancing them.

Acidic solutions -



Neutral medium -



Uses- Used as oxidant, used for bleaching wool, cotton, silk and decolorization of oils.

The Inner Transition elements (f- Block)

Consists of two series:-

Lanthanoides (Ln; general Symbol)
(14 elements following La)

Actinoides
(14 elements following Ac)

Have only one stable oxidation state (+3)

Lanthanoides :-

Electronic Configuration:-

<u>Atomic No.</u>	<u>Name</u>	<u>Symbol</u>	<u>E.C.</u>
57	Lanthanum	La	5d ¹ 6s ²
58	cerium	Ce	4f ¹ 5d ¹ 6s ¹
59	praseodymium	Pr	4f ³ 6s ²
60	Neodymium	Nd	4f ⁴ 6s ²

61	Promethium	Pm	$4f^5 6s^2$
62	Samarium	Sm	$4f^6 6s^2$
63	Euroduim	Eu	$4f^7 6s^2$
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$
65	Terbium	Tb	$4f^9 6s^2$
66	Dysprosium	Dy	$4f^{10} 6s^2$
67	Holmium	Ho	$4f^{11} 6s^2$
68	Erbium	Er	$4f^{12} 6s^2$
69	Thulium	Tm	$4f^{13} 6s^2$
70	Ytterbium	Yb	$4f^{14} 6s^2$
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$

Atomic & Ionic Series :- Decrease from La to Lu is due to Lanthanoid Contraction (The shielding of one $4f$ electron by another less than that by one d electron by another & the increase in nuclear charge along the series.

The almost identical radii of Zr (160pm.) and Hf (159), a consequence of the lanthanoid contraction, account their occurrence together in nature and for the difficulty faced in their separation.

Colour and Para magnetism

Ln^{3+} are coloured both in solid and in aqueous solution due to the presence of f electrons.

La^{3+} and Lu^{3+} do not show any colour. However absorption bands are narrow probably because of the excitants with in f level.

Ln^{3+} are paramagnetic except La^{3+} & Ce^{4+} (f^0 type) & f^{14} type (Yb^{2+} & Lu^{3+}). Paramagnetism rises to maximum in Neodymium .

Ionization enthalpies

I.E. depends on the degree of stability of empty, half filled and completely filled f -level.

This is indicated from the abnormally low values of the third ionization enthalpy of La, Gd, Lu.

Oxidation states.:-

Ln^{3+} compounds are predominant species. +2 & +4 ions in solution or in solid compounds are also obtained occasionally.

Ce (IV) formation is favoured due to extra stability of noble gas configuration, but it is a strong oxidant reverting to the common +3 state .

Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO_2

Eu^{2+} is formed by losing the two s - electrons & its +7 configuration.

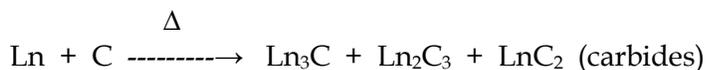
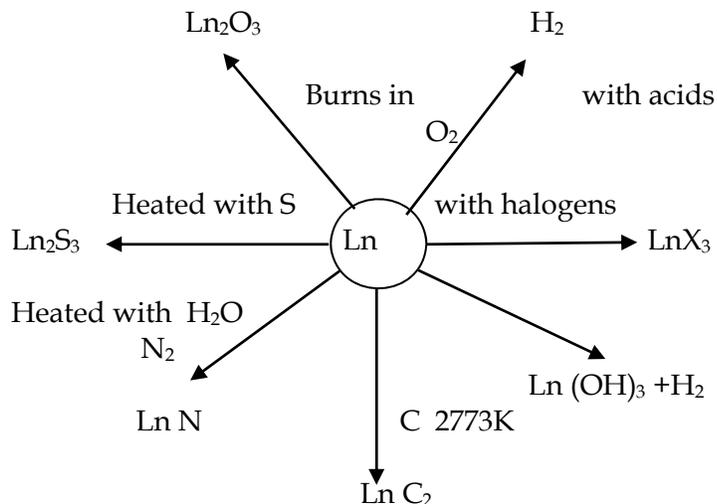
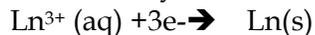
Properties and use :-

Ln are silvery white soft metals and tarnish rapidly in air. Hardness increases with increasing atomic number. M.pt. ranges from 1000K - 1200K

Sm is steel hard. (m.pt 1623K)

Chemical behavior

In general earlier members of the series are quite reactive similar to Ca, with increasing atomic number they behave more like aluminum.



Use :- Used in the production of alloy steels for plates & pipes eg. Mischmetal is an alloy which consists of a lanthanoid metal (95%) and iron (5%) and trace of S, C, Ca and Al. A good amount of this alloy is used in Mg-based alloy to produce bullets, shell & lighter flint.

- Mixed oxides of Ln are used as catalyst in petroleum cracking .
- Ln oxides are used as phosphors in television screens & similar fluorescing surfaces.

The Actinoids:-

<u>Atomic no.</u>	<u>Name</u>	<u>Symbol</u>	<u>E.C.</u>
89	Actinium	Ac	$6\text{d}^17\text{s}^2$
90	Thorium	Th	$5\text{f}^16\text{d}^17\text{s}^2$
91	Protactinium	Pa	$5\text{f}^26\text{d}^17\text{s}^2$
92	Uranium	U	$5\text{f}^36\text{d}^17\text{s}^2$
93	Neptunium	Np	$5\text{f}^46\text{d}^17\text{s}^2$
94	Plutonium	Pu	$5\text{f}^67\text{s}^2$
95	Americium	Am	$5\text{f}^77\text{s}^2$
96	Curium	Cm	$5\text{f}^76\text{d}^17\text{s}^2$
97	Berkelium	Bk	$5\text{f}^97\text{s}^2$
98	Californium	Cf	$5\text{f}^{10}7\text{s}^2$
99	Einsteinium	Es	$5\text{f}^{11}7\text{s}^2$
100	Fermium	Fm	$5\text{f}^{12}7\text{s}^2$
101	Mendelevium	Md	$5\text{f}^{13}7\text{s}^2$
102	Nobelium	No	$5\text{f}^{14}7\text{s}^2$
103	Lawrencium	Lr	$5\text{f}^{14}6\text{d}^17\text{s}^2$

Although the naturally occurring elements & the earlier member have relatively long half lives, the latter members have values ranging from a day to 3 minutes for Lr (Z=103) These facts and high radioactivity renders their study more difficult.

Electronic Configuration

The irregularities in the electronic configurations of the actinoids like those of in the lanthanoids are related to the stability of f^6 , f^7 and f^{14} occupancies of the 5f orbitals.

Eg. Am : [Rn] $5f^7 7s^2$

Cm : [Rn] $5f^7 6d^1 7s^2$

5f orbital can & do participate in bonding.

Common oxidation state is +3

The maximum oxidation state increases from +4 in Th, +5 in Pa, +6 in U and +7 in Np but decreases in succeeding elements.

Magnetic Properties:- the variation of magnetic properties with the no. of unpaired 5f electrons is similar to that of Ln.

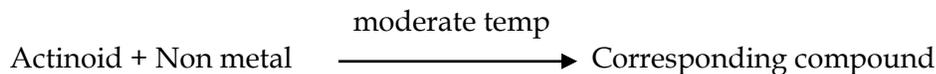
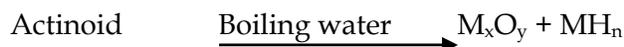
Ionic Sizes: Decrease in size due to increase in the effective nuclear charge on the outermost shell and poor shielding by 5f electrons. This is referred to as **actinoid contractions**.

Ionization Enthalpy :

The I.E. of early actinoids is lesser than that of early Ln as when 5f orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The 5f electrons, will therefore, be more effectively shielded from the nuclear charge than are the 4f electrons of the corresponding Ln. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

Physical and Chemical Reactivity

The actinoids are highly reactive when they are finely divided.



Metallic radii of actinoids is more as compared to lanthanoids.

Comparison With Lanthanoids

1. Structural variability in actinoids is obtained due to irregularities in metallic radii which are greater than lanthanoids.
2. Magnetic properties in actinoids are more complex than lanthanoids.

3. Ionization enthalpies of early actinoids, though not accurately known are lower than early lanthanoids. This is because 5f electrons penetrate less into the inner core and hence the outer electron are less firmly held, they are available for bonding in actinoids.

Applications of d-and f Block Elements

- 1 Iron and steel are important construction materials. Their production is based on reduction of iron oxides, removal of impurities, and addition of carbon and alloying metals such as Cr, Mn, and Ni.
- 2 TiO is used in pigment industry.
- 3 MnO₂ is used in battery cell. Also Zn and Ni/Cd.
- 4 Elements of group II are coinage metals.
- 5 V₂O₅ catalyses oxidation of SO₂ in contact process,
- 6 Iron catalyst is used in Haber's process.
- 7 TiCl₄ and Al(CH₃)₃ forms Ziegler-Natta Catalyst.
- 8 Ni complexes are used in polymerization of alkynes.