The d and f Block Elements

8

d -Block Elements

TRANSITION ELEMENTS AND COMPLEXES

- In the long form of periodic table elements are classified based on electronic configuration. The elements which are classified between's' and 'p' block are 'd' block elements or Transition elements. In these elements the differentiating electron enters in the 'd' orbitals of penultimate shell.
- General configuration for 'd' block elements is ns^{1-2} $(n-1)d^{1-10}$. i.e., in 'd' block elements the valence shell has constant number of electrons whereas the number of electrone in penultimate shell go on increasing.
- Elements which have atleast one unpaired electron in their 'd' orbital in atomic or any oxidation state are called as Transition elements. Thus all transition elements are 'd' block elements but all 'd' block elements may not be transition elements or the elements having incompletely filled 'd' orbitals are called as transition elements.
- Transition elements are classified between's' and 'p' blocks from fourth period onwards. Series of transition elements are four
- **1st Series -** They are classified in fourth period and are called as '3d' series of elements. Their atomic numbers are 21(Sc) to 30 (Zn).

  2nd Series- They are classified in fifth period and are called as '4d' series of elements. Their atomic numbers are 39(Y) to 48(Cd).

  3rd series- They are classified in sixth period and are called as '5d' series of elements. Their atomic numbers are 57(La), 72(Hf) to 80(Hg)

  4th Series - They are classified in the seventh period and are called as '6d' series of elements. This is an incomplete series. Their atomic numbers are 89(Ac), 104(Ku) to 112 (Uub).
- Electronic configuration of first series of transition elements.

Atomic number	Element	Symbol	Electronic configuration
21.	Scandium	Sc	[Ar) $4s^2 3d^1$
22.	Titanium	Ti	[Ar] $4s^2 3d^2$
23.	Vanadium	V	[Ar) $4s^2 3d^3$
24.	Chromium	Cr	[Ar) $4s^1 3d^5$
25.	Manganese	Mn	[Ar] $4s^2 3d^5$
26.	Iron	Fe	[Ar) $4s^2 3d^6$

27.	Cobalt	Co	[Ar) $4s^2 3d^7$
28.	Nickel	Ni	[Ar) $4s^2 3d^8$
29.	Copper	Cu	[Ar) $4s^1 3d^{10}$
30.	Zinc	Zn	[Ar] $4s^2 3d^{10}$

- Chromium and copper are elements having exceptional electronic configurations of [Ar] $4s^1 3d^5$ and [Ar] $4s^1 3d^{10}$ instead of [Ar] $4s^2 3d^4$ and [Ar] $4s^2 3d^9$
- Zn (30) is [Ar] $4s^2 3d^{10}$

  Cd (48) is [Kr] $5s^2 4d^{10}$

  Hg (80) is [Xe] $6s^2\ 4f^{14}\ 5d^{10}$

  These three elements do not have any unpaired electrons in their 'd' orbitals in atomic as well as in ionic states.Therefore they are only classified as 'd' block elements and not as transition elements. Copper, Silver and Gold, the elements of IB group i.e., coinage metals, have $ns^1\ (n-1)d^{10}$ configuration. They are transition elements as in their higher oxidation state they have an unpaired electron in their 'd' orbitals.

GENERAL PROPERTIES OF D-BLOCK ELEMENTS

- All the elements of '3d' series are good reducing agents except copper.
- In general the reactivity of transition elements is less. Their reactivity decreases with increase in atomic number. The atomic radii of trarsition elements decrease by negligible amounts due to the shielding of valence shell electrons, provided by electrons of 'd' orbitals of penultimate shell.
- The ionisation potential of transition elements increase by negligible amounts due to shielding effect.

1. Metallic Character

- All the d-block elements are metals as the numbers of electrons in the outer most shell are one or two.
- They are hard malleable and ductile. IB group elements Cu, Ag and Au are most ductile and soft.
- These are good conducter of heat and electricity (due to free e-) IB gp. elements are most conductive in nature. Their order of conductivity is

  Ag > Cu > Au > AI.

2. Atomic size

- Atomic and ionic radii of d-block elements is smaller than s-block elements
- Atomic radii depends on effective nuclear charge (Zeff) and screening effect (SE).
- In 3d reries

  Sc → Cr (Zeff > SE) $\therefore$ radius decreases

  Mn → Ni (Zeff = SE) $\therefore$ radius remains constant

  Cu → Zn (Zeff < SE) $\therefore$ radius increases
- In dipositive ions of 3d series Cu^{+2} is the smallest in size.
- The elements of 4d and 5d series belongs to a particular group have almost same atomic radii. This is due to Lanthanide contraction. e.g.

  Zr $\simeq$ Hf, Tc $\simeq$ Re, Nb $\simeq$ Ta, Ru $\simeq$ Os etc.
- In d-block elements

  Largest atomic radii - La

  Smallest atomic radii - Ni
- In IllB group order of atomic radii is

  Sc < Y < La (No lanthanide contraction)

3. Density

- The atomic volume of the transition elements are low compared with s-block, so their density is comparatiely high (D = M/V)
- Except Sc, Y and Ti, all the d-block elements have density greater than 5gm cm^{-3}
- Os (22.57 gm cm^{-3}) and Ir (22.61 gm cm^{-3}) have highest density.
- In all the groups there is normal increase in density from 3d to 4d series, and from 4d to 5d it increases just double it is due to lanthanide contraction.

  Ti < Zr << Hf
- In 3d series

  Sc → Cr density increases

  Mn, Fe, Co, Ni → almost constant

  Cu → Zn decreases
- In 3d series highest density – Cu

  lowest density – Sc
- Some important orders of density

  Fe < Ni < Cu   Fe < Cu < Au   Fe < Hg < Au

4. Melting and boiling points

- M.P. and b. p. of d-block > s-block (the reason is stronger metallic bond and presence of covalent bond formed by unpaired d-electrons.)
- In Zn, Cd, and Hg there is no unpaired electron present in d-orbital, hence due to absence of covalent bond, their m.p. and b.p. are very low. (Volatile metals Zn, Cd, Hg)
- In 3d series

  Sc → Cr m.p. b.p increases

  Mn → Zn m.p. b.p decreases
- Mn and Tc possess comparatively low m.p., it due to stable configuration' (Half filled)
- Lowest mp Hg - 38°C

  Highest mp. W ≃ 3400°C

- **Characteristic properties of transition elements are**

  (a) Variable oxidation state

  (b) Coloured ions

  (c) Paramagnetic properties

  (d) Catalytic properties

  (e) Formation of alloys

  (f) Formation of interstitial compounds and

  (g) Formation of complexes.

(a) Variable valency or variable oxidation states:

They exhibit variable valeney due to involvement of (ns) and (n-1)d electrons in bonding. This is due to less energy difference between these electrons.

- The oxidation states of all transiition elements of '3d' series are as follows

Sc	[Ar] $4s^2 3d^1$		+3				
Ti	[Ar] $4s^2 3d^2$	(+2)	+3	+4			
V	[Ar] $4s^2 3d^3$	+2	+3	+4	+5		
Cr	[Ar] $4s^1 3d^5$	(+1)	+2	+3	(+4)	(+5)	+6
Mn	[Ar] $4s^2 3d^5$	+2	+3	+4	(+5)	(+6)	+7
Fe	[Ar] $4s^2 3d^6$	+2	+3	(+4)	(+5)	(+6)	
Co	[Ar] $4s^2 3d^7$	+2	+3	+4			
Ni	[Ar] $4s^2 3d^8$	+2	(+3)	(+4)			
Cu	[Ar] $4s^1 3d^{10}$	+ 1	+2				

Oxidation
States in brackets
is/are unstable.

- Highest oxidation state of transition elements can be calculated by = n + 2 (n = no. of unpaired e-) (It is not applied for Cr and Cu)
- The transition metal ions having stable configuration are stable

  Metal ions of '3d' series having $3d^o$ configuration Sc^{+3}, Ti^{+4} and V^{+5} etc are stable.

  Transition metal ions having $3d^5$ configuration are stable like Mn^{+2}, Fe^{+3}

  In aqueous medium Cr^{+3} is stable.

  Co^{+2} and Ni^{+2} are stable.
- Transition metal ion with $3d^{10}$ configuration which is stable is Cu^{+1}. In aqueous medium Cu^{+2} is more stable than Cu^{+1}.
- Most common oxidation state among the transition elements is +2.
- Highest oxidation state shown by transition elements of '4d' and '5d' series is +8. The elements showing this oxidation state are Ruthenium (44) and Osmium (76).
- The common oxidation state shown by elements of IIIB i.e., Sc, Y, La and Ac is +3 as their divalent compounds are highly unstable.

- In lower oxidation state transition elements form ionic compounds and in higher oxidation state their compounds are covalent.

  e.g. in chromate ion CrO_4^{-2}, the bonds between Cr and O are covalent.
- Generally higher oxidation states are exhibited in the compounds which are formed with highly electronegative elements like O and F.
- They also shows zero oxidation state in their carbonyl compounds like $Ni(CO)_4$
- Usually transition metal ions in their lower oxidation state act as reducing agents and in higher oxidation state they are oxidising agents.

  e.g. – Ti^{+2}, V^{+2}, Fe^{+2}, Co^{+2} etc are reducing agents Cr^{+6}, Mn^{+7}, Mn^{+4} Mn^{+5}, Mn^{+6} etc are oxidising agents.

5. Colour Property:

- Most of the transition metal ions exhibit colour property. This is due to the presence of unpaired electrons in their 'd' orbitals. They require less amount of energy to undergo excitation of electrons. Hence they absorb visible region of light exhibiting colour.

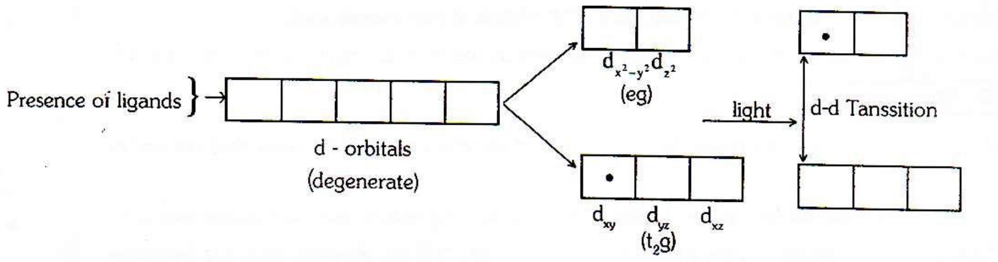
  $Ti^{+2}[Ar]3d^2$, $V^{+2}[Ar]3d^3$ etc.

  These are having unpaired electrons in their 'd' orbitals therefore they are coloured.
- Transition metal ions which do not have any unpaired elctrons in their 'd' orbitals like $3d^0$ and $3d^{10}$ configurations, do not exhibit any colour property.

  e.g., Sc^{+3} $[Ar]3d^0$, $Cu^{+1}[Ar]3d^{10}$, $Ti^{+4}[Ar]3d^0$ etc are colourless ions.
- A transition metal ion absorbs a part of visible region of light and emits rest of the six colours, the combination of which is the colour of emitted light. The colour of metal ion is the colour of the emitted light.
- In transition metal ion the 'd' orbitals split into lower energy set t_2g orbitals and higher energy set eg orbitals. The electrons from t_2g set get excited to higher energy set i.e., eg set. This excitation of electrons is called as 'd-d' transition. As d-d transition requires less amount of energy they absorb visible region of light. Due to this 'd -d' transition the transition metal ions exhibit colour property.

  Lower energy set = t_2g

  Higher energy set = eg.



- $KMnO_4$ (dark pink), $K_2Cr_2O_7$ (orange) having d° onfiguration are coloured due to charge transfer spectrum.

  Some of the coloured metal ions are as follows:

Ti^{+3} -	Purple	Cr^{+3}	Green
Mn^{+2} -	Light pink	Fe^{+2} -	Pale green
Fe^{+3} -	yellow	Co^{+2} -	Blue
Ni^{+2}	green	Cu^{+2} -	Blue

6. Magnetic properties

- Matter, in general is associated with magnetic properties. Majority of substances are either paramagnetic or diamagnetic. A paramagnetic substance is one which is attracted into a magnetic field. Paramagnetism is mainly due to the presence of unpaired electrons in atoms or ions or molecules. Diamagnetic substance is one which is slightly repelled by a magnetic field.

- Ti^{+2} $[Ar]3d^2$, Ti^{+3} $[Ar]3d^1$. $V^{+2}[Ar]3d^3$, $Cr^{+3}[Ar]3d^3$

  As is evident most of the transition metal ions have unpaired electrons in their 'd' orbitals. Hence most of the transition metal ions are paramagnetic in nature. Transition metal ions having $3d^0$ and $3d^{10}$ configuration exhibit diamagnetic nature.
- An unpaired electron spins and as it is a charged particle, magnetic field is created due to its spinning.
- Each electron may, in fact, be considered as a micro magnet having a certain value of magnetic moment. The total magnetic moment of a substance is the resultant of the magnetic moments of all the individual electrons. Thus substances containing unpaired electrons get attracted towards the magnets exhibiting paramagnetic nature.
- The magnetic moment (μ) created due to spinning of unpaired electrons can be calculated by using

  $\mu = \sqrt{n(n+2)}$: Where 'n' is the number of unpaired electrons in the metal ion.

  μ = Magnetic moment in Bohr Magnetons (B.M.)
- The magnetic moment of diamagnetic substances will be zero.
- As the number of unpaired electrons increase the magnetic moment created goes on increasing and hence the paramagnetic nature also increases.
- Transition metal ions having d^5 configuration will have maximum number of unpaired electrons therefore they will be maximum paramagnetic in nature.

7. Catalytic Property

- Transition elements and their compounds exhibit catalytic properties. This is due to their variable valency as well as due to the free valencies on their surface.
- When transition elements and their compounds are in powdered state. their catalytic properties exhibited will be to a greater extent. This is due to greater surface area available in the powdered state.
- Transition metals and their compounds exhibiting catalytic properties in various processes are

(i) Fe is used in Haber's process for manufacture. of NH_3.

(ii) V_2O_5 is used in contact process for H_2SO_4 manufacture

(iii) Pt is used in Ostwald's process of nitric acid

(iv) Ni is used in hydrogenation of oils

(v) $FeSO_4$ is used in oxidation of Benzene with H_2O_2

(vi) Cu is used in dehydrogenation of alcohols

(vii) $TiCI_4$ is used as catalyst in Vinyl polymerisation.

8. Formation of Alloy

- Transition elements have maximum tendency to form alloys.
- The reactivity of transition elements is very less and their sizes are almost similar. Due to this a transition metal atom in the Lattice can be easily replaced by other transition metal atom and hence they have maximum tendency to form alloys.
- In the alloys ratio of component metals is fixed.
- These are extremly hard and have high M.P.

SOME IMPORTANT ALLOY

1. Bronze - Cu (75 - 90 %) +Sn (10 - 25 %)
2. Brass - Cu (60 - 80 %) +Zn (20 - 40 %)
3. Gun metal - (Cu + Zn + Sn) (87 : 3 : 10)
4. German Silver - Cu + Zn + Ni (2 : 1 : 1)
5. Bell metal - Cu (80%) + Sn (20%)
6. Nichrome - (Ni + Cr + Fe)
7. Alnico - (Al, Ni, Co)
8. Type Metal - Pb + Sn + Sb

9. **Alloys of steel**

(a) Vanadium steel - V (0.2 – 1%)
(b) Chromium steet - Cr (2 – 4%)
(c) Nickel steet - Ni (3 – 5%)
(d) Manganese steel - Mn (10 – 18%)
(e) Stainless steel - Cr (12 – 14%) & Ni (2–4%)
(f) Tunguston steel - W (10 – 20%)
(g) Invar - Ni (36%)

10. 14 Carat Gold - 54% Au + Ag (14 to 30%) + Cu (12 – 28%)
11. 24 Carat Gold - 100% Au
12. Solder - Pb + Sn
13. Magnallium - Mg (10%) + Al (90%)
14. Duralumin - (Al + Mn + Cu)
15. Artificial Gold - Cu (90%) + Al (10%)
16. Constantan - Cu (60%) + Ni (40%)

1. **% of Carbon in different type of Iron:**

Name	**% of C**
(i) Wrought Iron	.1 to .25
(ii) Steel	.25 to 2.0
(iii) Cast Iron	2.6 to 4.3
(iv) Pig Iron	2.3 to 4.6

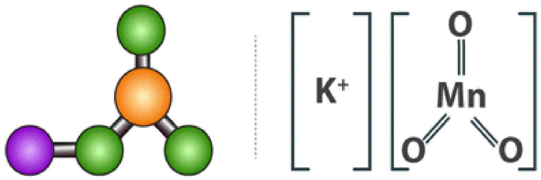
2. **Formation of Interstitial Compounds**

- Transition elements form interstitial compounds with smaller sized non metal elements like hydrogen, carbon, boron, nitrogen etc. The smaller sized atoms get entrapped in between the interstitial spaces of the metal Lattices.
- These interstitial compounds are non stoichiometric in nature and hence cannot be given any definite formula.
- The smaller sized elements are held in interstitial spaces of transition elements by weak Vander Waals forces of attractions.
- The interstitial compounds have essentially the same chemical properties as the parent metals but they differ in physical properties such as density and hardness.

POTASSIUM PERMANGANATE ($KMnO_4$)

- Potassium Permanganate ($KMnO_4$) is an inorganic chemical compound. It is also known as Condy's crystals or permanganate of potash.
- A German-Dutch chemist **Johann Rudolf Glauber** was the first to discover the production of KMnO4 in the year 1659. This compound is water-soluble and consists of two ions: Permanganate ion and potassium ion. It is a dark purple odourless solid in its physical state.
- When potassium permanganate crystals are dissolved in water the solution formed is purple in colour. It is considered as a strong oxidizing agent and does not produce toxic byproducts. It is usually prepared from other minerals such as manganese oxide

Potassium Permanganate Structure - $KMnO_4$



Structure of Potassium Permanganate - $KMnO_4$

Preparation Of Potassium Permanganate - KMnO4

- Potassium permanganate is commercially prepared by mixing solution of KOH and powdered manganese oxide, with oxidizing agents like potassium chlorate. The mixture is boiled evaporated and the residue is heated in iron pans until it has acquired a pasty consistency.

$$6KOH + 3MnO_2 + 6KClO_3 \rightarrow 3K_2MnO_9 + 6KCl + 3H_2O$$

- The potassium manganate (green) so formed is boiled with a large quantity of water and current of chlorine, CO_2 and ozonized air is passed into the liquid until it is converted into permanganate. The MnO_2 formed is removed continuously in order to prevent its breaking down the permanganate.

$$6K_2MnO_4 + 3Cl_2 \rightarrow 6KMnO_4 \text{ (Potassium Permanganate)} + 6KCl$$

The solution of $KMnO_4$ is drawn off from any precipitate of MnO_2 concentrated and crystallized. The crystals are centrifuged and dried.

Physical Properties of Potassium Permanganate - $KMnO_4$

- It is an odourless, purple to magenta crystalline solid.
- It is soluble in water, acetone, acetic acid, methanol, and pyridine.
- It gets dissolved in ethanol and organic solvents.
- Potassium permanganate occurs in the form of monoclinic prisms, almost opaque with a blue metallic luster.
- It is odourless. An aqueous solution has a sweetish astringent taste. It is water-soluble and more soluble in boiling water.

Chemical Properties Of Potassium Permanganate

- Very strong oxidizing agent and used for this reason in many reactions
- It can be seen while performing the redox reaction, in which the dark purple solution turns colourless and then into a brown solution.
- The above reaction can be performed in an acid or a base

Reactions Of Potassium Permanganate ($KMnO_4$)

1. **Thermal decomposition:**

   When solid potassium permanganate is heated it undergoes decomposition. The reaction is as follows:

   $$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2(s) + O_2$$

2. **Reaction with acid:**

   When permanganate reacts with concentrated hydrochloric acid it produces chlorine. In a neutral solution, permanganate is reduced by three electrons to produce manganese dioxide, where the oxidation state of manganese is +4. Potassium permanganate reduces spontaneously in an alkaline solution and turns into green K_2MnO_4.

3. **Effect of Alkalies**

   On heating with alkalies, potassium permanganate changes into manganate and oxygen gas is evolved.

   $$4KMnO_4 + 4KOH \rightarrow 4K_2MnO_4 + 2H_2O + O_2$$

4. **Oxidizing properties**

   $KMnO_4$ acts as a very powerful oxidizing agent in acidic, neutral and alkaline media. The equations representing oxidation in these media are

   In acidic medium

   $$2KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
   $$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

   In neutral or alkaline medium

   $$2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3[O]$$
   $$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

Uses Of Potassium Permanganate ($KMnO_4$)

There are wide applications of $KMnO_4$. Some important uses of potassium permanganate have been discussed below:

- It is used in qualitative analysis to determine the permanganate value
- It is used in as a regeneration chemical in well water treatment to remove hydrogen sulfide and iron
- It is used as a disinfectant to cure skin conditions like foot fungal infections, dermatitis
- It is used in the treatment of bacterial infections
- It is used in tanning leathers, printing fabrics
- It is used as bleach, pesticide, antiseptic
- It is used in industries as an oxidizing agent

POTASSIUM DICHROMATE
$K_2Cr_2O_7$

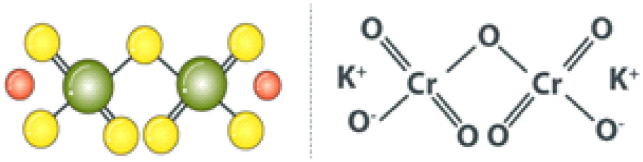
- Potassium compounds are quite common and are extremely useful for a variety of purposes. Potash and other potassium compounds have been used for centuries in the manufacture of glass products. Today 95% of the potassium compounds gathered in the world is used in the manufacture of fertilizers.
- Potassium dichromate is an inorganic chemical compound possess immense industrial and laboratory importance. It is an orange crystalline solid with the chemical formula $K_2Cr_2O_7$. It is a strong oxidising agent and is soluble in water. It is used in the volumetric estimation of ferrous salts, iodides and sulphides for the preparation of chrome alum, chrome yellow and chrome red.

What is Potassium dichromate ($K_2Cr_2O_7$)?

- K_2Cr_2O7 is an inorganic chemical reagent with chemical name Potassium dichromate. It is also called as Potassium bichromate or Dipotassium bichromate. It is crystalline ionic solid, with a bright red-orange colour. It is odourless and insoluble in acetone as well as alcohol but dissolves in water.
- It is widely used as a precursor to potassium chrome alum and leather tanning. It is commonly used as an oxidizing agent in several industries and laboratories. It is highly corrosive and noncombustible. Potassium dichromate is prepared as follows -
- By reacting potassium chloride on sodium dichromate or
- Produced from potassium chromate by the roasting of chromite ore with potassium hydroxide

Potassium dichromate Structure

($K_2Cr_2O_7$ Structure)



Potassium dichromate Structure

Potassium dichromate ($K_2Cr_2O_7$) Uses

- Used in cement to retard the setting of the mixture and to improve its density along with the texture.
- It is used in photographic screen printing.
- It is a common reagent used in analytical chemistry for classical "wet tests".
- It is used to stain certain type of woods to produce deep, rich browns.
- It is used to clean glassware and as an etching material.
- Used in pyrotechnic displays along with iron and tungsten.
- Medically it can be used externally as an antiseptic, caustic, and astringent.

f -Block Elements

They were earlier called as rare earth metals as it was believed that they exist in earth's crust to a very less extent for e.g. : Pm, does not exist in the earth's crust. But this terminology is now not applicable as they exist in earth's crust to a sufficient extent.

INNER TRANSITION ELEMENTS

The elements in which the additional electron enters in (n - 2)f orbitals are called inner **transition elements. or f-block elements.**

1. Position in the periodic table

The lanthanides resemble yttrium in most of their properties. So it became necessary to accomodate all the fifteen elements together at one place. This has been done by placing the first element, lanthanum below yttrium and placing the remaining fourteen elements separately in the lower part of the periodic table.

Lanthanide series	(Z = 58 - 71)	(Ce – Lu)
Actinide series	(Z = 90 - 103)	(Th – Lw)

2. Lanthanides (Lanthanones)

Lanthanides are reactive elements so do not found in free state in nature. Most important minerals for lighter Lanthanides are - Monazite, cerites and orthite and for heavier lanthanides - Gadolinite and Xenotime

3. Electronic configuration

The general configuration of lanthanides may be given as $4f^{2-14}5s^2 5p^6 5d^{0/1} 6s^2$. Lanthamide have outer three shells incomplete.

Atomic Number	Element	Symbol	Outer electronic configuration Atomic	 +3 ion
58	Cerium	Ce	$4f^2\ 6s^2$	$4f^1$
59	Praseodymium	Pr	$4f^3\ 6s^2$	$4f^2$
60.	Neodymium	Nd	$4f^4\ 6s^2$	$4f^3$
61.	Promethium	Pm	$4f^5\ 6s^2$	$4f^4$
62.	Samarium	Sm	$4f^6\ 6s^2$	$4f^5$
63.	Europium	Eu	$4f^7\ 6s^2$	$4f^6$
64.	Gadolinium	Gd	$4f^7\ 5d^1\ 6s^2$	$4f^7$
65.	Terbium	Tb	$4f^9\ 6s^2$	$4f^8$
66.	Dysprosium	Dy	$4f^{10}\ 6s^2$	$4f^9$
67.	Holmium	Ho	$4f^{11}\ 6s^2$	$4f^{10}$
68.	Erbium	Er	$4f^{12}\ 6s^2$	$4f^{11}$
69.	Thulium	Tm	$4f^{13}\ 6s^2$	$4f^{12}$
70.	Ytterbium	Yb	$4f^{14}\ 6s^2$	$4f^{13}$
71.	Lutecium	Lu	$4f^{14}\ 5d^1\ 6s^2$	$4f^{14}$

It is to be noted here that filling of 4f orbitals in the atoms is not regular. A 5d electron appears in gadolinium (z = 64) with an outer electronic configuration of $4f^7 5d^1 6s^2$ (and not $4f^8 6s^2$). This is because the 4f and 5d electrons are at about the same potential energy and that the atoms have a tendency to retain stable half filled configuration.

On the other hand, the filling of f orbitals is regular in tripositive ions.

After losing outer electrons, the f orbitals shrink in size and became more stable. Pm is the only synthetic radioactive lanthanide.

Oxidation states

4.

Lanthanides	**Oxidation States**
Ce_{58}	+3,+4
Pr_{59}	+3, (+4)
Nd_{60}	+3
Pm_{61}	+3
Sm_{62}	(+2), +3
Eu_{63}	+2,+3
Gd_{64}	+3
Tb_{65}	+3,+4
Dy_{66}	+3; (+4)
Ho_{67}	+3
Er_{68}	(+2), +3
Tm_{69}	(+2), +3
Yb_{70}	+2,+3
Lu_{71}	+3

* Oxidation states in brackets are unstable states

* The lanthanides contains two s electrons in the outermost shell, they are therefore expected to exhibit a characteristic oxidation state of +2. But for the lanthanides, the +3 oxidation is common.

* This corresponds to the use of two outermost electrons ($6s^2$) alongwith one inner electron. The inner electron used is a 5d electron (in La, Gd and Lu), or one of the 4f electron if no 5d electrons present.

* All the lanthanides attains +3 oxidation state and only cerium, Praseodymium, and terbium exhibit higher oxidation state (+4).

Oxidation states + 2 and +4 occur particularly when they lead to

(i) A noble gas configuration e.g. Ce^{4+} (f^0)

(ii) A half filled ‘f ‘ orbital e.g. Eu^{2+}, Tb^{4+}, (f^7)

(iii) A completely filled ‘f ‘ orbital e.g. Yb^{2+} (f^{14})

Therefore, in higher oxidation state, they act as oxidising while in lower state as reducing agents.

5. Magnetic properties

In tripositive lanthanide ions the number of unpaired electrons regularly increases from lanthanum to Gadolinium (0 to 7) and then continuously decreases upto lutecium (7 to 0). So lanthanum and lutecium ions which are diamagnetic, all other tripositive lanthanide ions are Paramagnetic.

Colour - The lanthanide ions have unpaired electrons in their 4f orbitals. Thus these ions absorbs visible region of light and undergo f-f transition and hence exhibit colour. The colour exhibited depends on the number of unpaired electrons in the 4f orbitals. The ions often with $4f^n$ configuration have similar colour to those ions having $4f^{14-n}$ configuration.

* Lanthanide ions having $4f^0$, $4f^7$,$4f^{14}$ are colourless. Lanthanide ions $4f^1$ and $4d^{13}$ are also colourless.

6. Other Properties

(a) Highly dense metals with high m.pts. (do not show any regular trend).

(b) Ionisation Energies - Lanthanides have fairly low ionisation energies comparable to alkaline earth metals.

(c) Electro positive Character - High due to low I.P.

(d) Complex formation - Do not have much tendency to form complexes due to low charge density because of their large size.

Lu^{+3} is smallest in size can only form complex.

(e) Reducing Agent - They readily lose electrones so are good reducing agent.

* In +3 oxidation states, nitrates, perchlorates and sulphates of lanthanides and actinides are water soluble, while their hydroxides, fluorides and carbonates are water insoluble.

- Alloys of lanthanides with Fe are called misch metals.
- $La(OH)_3$ is most basic in nature while $Lu(OH)_3$ least basic.
- Lanthanides form MC_2 type carbide with carbon, which on hydrolysis gives C_2H_2.

LANTHANIDE CONTRACTION

- In the lanthanide series with increasing atomic number, there is a progressive decrease in the size from lanthanum to lutecium or from La^{+3} to Lu^{+3}. This contraction in size is known as lanthanide contraction.
- The general electronic configuration of these elements is $4f^{0-14}5s^2p^6d^{0-1}6s^2$. In these elements the added electron enters the deep seated f-orbitals and therefore experiences considerable pull by the nucleus.
- Such an electron cannot add to the size of the element and also because the intervening $5s^2p^6d^1$ electronic shells, it is 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.
- The atomic volumes of europium and ytterbium are unexceptedly large. The large atomic size of Eu and Yb suggest weaker bonding in the solid elements. Both these elements have only two electrons extra than the stable configurations (half filled, f^7, and completely filled, f^{14}), hence they utilise two electrons in metallic bonding as in the case with barium.

EFFECTS OF LANTHANIDE CONTRACTION

(i) Close resembalace of Lanthanides :- The general decrease in the sizes of the lanthanides with an increase in their nuclear charges result in a small increase in their ionisation energies. Hence their basic and ionic nature gradually decreases from La to Lu.

This also explains the variations in properties such as increased tendency for hydrolysis and formation of complex salts and decreased thermal stability. solubility of their salts.

(ii) Similarity of yttrium with lanthanides :-

The properties of yttrium are so similar to the lanthanides that it is considered more a member of the lanthanide series than a congener of scandium.

(iii) Anomalous behaviour of post-lanthanides :-

The following anomalies may be observed in the behaviour of post-lanthanide elements.

(a) Atomic size - The ionic radii of Zr^{+4} is about 9% more than Ti^{+4}. Similar trend is not maintained on passing from the second to third transition series. The ionic radius of Hf^{+4}, instead of increasing (because of inclusion of one more electronic shell). decreases (or is virtually equal to Zr^{+4}) as a consequence of the lanthanide

contraction.

This explains the close similarities between the members of the second and third transition series than between the elements of the first and second series.

(b) lonisation potential and electronegativity :-

The effect of lanthanide contraction is also seen in the increase in the ionisation potential values and electronegativities of the elements of the third transition series, contrary to the general trend.

Because of the lanthanide contraction, the post-lanthanide elements have stronger positive field and thus the electrons are held more tightly.

The greater effective nuclear charge of the former make them more electronegative than the latter.

(c) High density :- Because of lanthanide contraction the atomic sizes of the post lanthanide elements become very small. consequently, the packing of atoms in their metallic crystals become so much compact that their densities are very high.

The densities of the third transition series elements are almost double to those of the second series elements.

APPLICATION OF LANTHANIDES

Cerium is most useful element in the lanthanides

(a) Ceramic application - CeO_2, La_2O_3, Nd_2O_3 and Pr_2P_3 are used as decolourizing agents for glasses.

(b) CeS (m.p. - 2000°C) is used in the manufacture of a special type of crucibles and refractories.

(c) Lanthanide compounds like cerium molybdate, cerium tungstate are used as paints and dyes.

(d) In textile and leather industries (Ce salts).

ACTINIDES (5f - BLOCK ELEMENTS)

* The elements in which the extra electron enters 5f-orbitals of (n - 2)th main shell are known as actinides.

* The man.made eleven elements Np_{93} - Lr_{103} are placed beyond uranium in the periodic table and are collectively called trans-uranic elements.

* Th, Pa and U first three actinides are natural elements.

1. Electronic configuration :-

The general configuration of actinides may be given as $5f^{1-14}\,6d^{0/1}, 7s^2$.

Atomic No.	Elements	Symbol	Electronic Configuration
90	Thorium	Th	$6d^27s^2$
91	Protactinium	Pa	$5f^26d^17s^2$
92	Uranium	U	$5f^36d^17s^2$
93	Neptunium	Np	$5f^46d^17s^2$
94	Plutonium	Pu	$5f^67s^2$
95	Americium	Am	$5f^77s^2$
96	Curium	Cm	$5f^76d^17s^2$
97	Berkellium	Bk	$5f^97s^2$
98	Californium	Cf	$5f^{10}\,7s^2$
99	Einstenium	Es	$5f^{11}7s^2$
100	Fermium	Fm	$5f^{12}\,7s^2$
101	Mandelevnium	Md	$5f^{13}7s^2$
102	Nobellium	No	$5f^{14}7s^2$
103	Lawrencium	Lw	$5f^{14}6d^17s^2$

2. Oxidation states

In lanthanides-and actinides +3 oxidation is the most common for both of the series of elements. This oxidation state becomes increasingly more stable as the atomic number increases in the actinide series.

Actinides	Oxidation state*
Th_{90}	+4
Pa_{91}	(+4), +5
U_{92}	(+3), (+4), (+5), +6
Np_{93}	(+3), (+4), +5, (+6), (+7)
Pu_{94}	(+3), +4, (+5), (+6), (+ 7)
Am_{95}	+2,(+3),(+4),(+5),(+6)
Cm_{96}	+3, (+4)
Bk_{97}	+3, (+4)
Cf_{98}	+3
Es_{99}	+3
Fm_{100}	+3
Md_{101}	+3
No_{102}	+3
Lw_{103}	+3

Difference between Lathanides and Actinides

	Lathanides	Actinides
1	Besides the most common oxidation state of +3 lanthanides show +2 and +4 oxidation states in case of certain elements.	Besides the most common oxidation state of +3, actinides show +4, +5 and +6 oxidation states in case of certain elements.
2	Lanthanides have less tendency towards complex formation.	Actinides have a stronger tendency towards complex formation.
3	Except promethium, they are non radioactive	All the actinides are radioactive.
4	Oxides and hydroxide of lanthanides are less basic.	Oxides and hydroxides of actinides are more basic

Some important uses of actinides are as follows –

Thorium : Thorium is used in atomic reactors as fuel rods and in the treatment of cancer.

Uranium : Uranium is used as nuclear fuel. Its salts are used in glass industry (for imparting green colour). textile industry and also in medicines.

Plutonium : Plutonium is used as fuel for atomic reactors as well as in atomic bombs.