THE d & f BLOCK ELEMENTS

THE TRANSITION ELEMENTS (d-BLOCK)

- The elements belonging to groups 3-12 are known as d block elements or transition elements.
- Transition elements are placed in between s block and p block elements.
- In transition elements, a transition from metallic to non-metallic character takes place.
- They have incompletely filled d-orbitals in its ground state or in any one of its oxidation states.
- Zinc, cadmium and mercury are not regarded as transition metals.
- It is due to the completely filled d^{10} configuration in their ground state as well as in their common oxidation states.

ELECTRONIC CONFIGURATION OF d-BLOCK ELEMENTS

- The general outer electronic configuration of d-block elements is $(n-1)d^{1-10}ns^{1-2}$.
- The $(n-1)$ stands for the inner d orbitals which may have one to ten electrons.
- The outermost ns orbitals may have one or two electrons.
- The d block elements consist of four rows of elements.
- These rows are called first, second, third and fourth transition series.
- They involve the filling of 3d, 4d, 5d and 6d orbitals respectively.

3d series	Sc (21) to Zn (30)
4d series	Y (39) to Cd (48)
5d series	La (57) and Hf (72) to Hg (80)
6d series	Ac (89) and elements 104 to 112

FIRST TRANSITION SERIES (3d series)

Scandium, Titanium, Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel, Copper and Zinc.

SECOND TRANSITION SERIES (4d series)

Yttrium, Zirconium, Niobium, Molybdenum, Technetium, Ruthenium, Rhodium, Palladium, Silver, Cadmium

THIRD TRANSITION SERIES (5d series)

Lanthanum, Hafnium, Tantalum, Tungsten, Rhenium, Osmium, Iridium, Platinum, Gold, Mercury

FOURTH TRANSITION SERIES (6d series)

Actinium, Rutherfordium, Dubnium, Seaborgium, Bohrium, Hassium, Meitnerium, Darmstadtium, Roentgenium, Copernicium

ELECTRONIC CONFIGURATIONS OF ELEMENTS BELONGING TO 3d Series

3d series		4d series		5d series		6d series	
E	E.C	E	E.C	E	E.C	E	E.C
$_{21}$Sc	[Ar]$3d^{1}4S^{2}$	$_{39}$Y	[Kr]$4d^{1}5S^{2}$	$_{57}$La	[Xe]$5d^{1}6S^{2}$	$_{89}$Ac	[Rn]$5f^{0}$ $6d^{1}7S^{2}$
$_{22}$Ti	[Ar]$3d^{2}4S^{2}$	$_{40}$Zr	[Kr]$4d^{2}5S^{2}$	$_{72}$Hf	[Xe]$5d^{2}6S^{2}$	$_{104}$Rf	[Rn]$5f^{14}$ $6d^{1}7S^{2}$
$_{23}$V	[Ar]$3d^{3}4S^{2}$	$_{41}$Nb	[Kr]$4d^{4}5S^{1}$	$_{73}$Ta	[Xe]$5d^{3}6S^{2}$	$_{105}$Db	[Rn]$5f^{14}$ $6d^{2}7S^{2}$
$_{24}$Cr	[Ar]$3d^{5}4S^{1}$	$_{42}$Mo	[Kr]$4d^{5}5S^{1}$	$_{74}$W	[Xe]$5d^{4}6S^{2}$	$_{106}$Sg	[Rn]$5f$ $^{14}6d^{3}7S^{2}$
$_{25}$Mn	[Ar]$3d^{5}4S^{2}$	$_{43}$Tc	[Kr]$4d^{5}5S^{2}$	$_{75}$Re	[Xe]$5d^{5}6S^{2}$	$_{107}$Bh	[Rn]$5f^{14}$ $6d^{4}7S^{2}$
$_{26}$Fe	[Ar]$3d^{6}4S^{2}$	$_{44}$Ru	[Kr]$4d^{7}5S^{1}$	$_{76}$Os	[Xe]$5d^{6}6S^{2}$	$_{108}$Hs	[Rn]$5f^{14}$ $6d^{5}7S^{2}$
$_{27}$Co	[Ar]$3d^{7}4S^{2}$	$_{45}$Rh	[Kr]$4d^{8}5S^{1}$	$_{77}$Ir	[Xe]$5d^{7}6S^{2}$	$_{109}$Mt	[Rn]$5f^{14}$ $6d^{6}7S^{2}$
$_{28}$Ni	[Ar]$3d^{8}4S^{2}$	$_{46}$Pd	[Kr]$4d^{10}5S^{0}$	$_{78}$Pt	[Xe]$5d^{9}6S^{1}$	$_{110}$DS	[Rn]$5f^{14}$ $6d^{7}7S^{2}$
$_{29}$Cu	[Ar]$3d^{10}4S^{1}$	$_{47}$Ag	[Kr]$4d^{10}5S^{1}$	$_{79}$Au	[Xe]$5d^{10}6S^{1}$	$_{111}$Rg	[Rn]$5f^{14}$ $6d^{10}7S^{1}$
$_{30}$Zn	[Ar]$3d^{10}4S^{2}$	$_{48}$Cd	[Kr]$4d^{10}5S^{2}$	$_{80}$Hg	[Xe]$5d^{10}6S^{2}$	$_{112}$Cn	[Rn]$5f^{14}$ $6d^{10}7S^{2}$

ELECTRONIC CONFIGURATIONS OF CHROMIUM AND COPPER

- Cr: $1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}\ 4s^{1}\ 3d^{5}$

- Cu: $1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}\ 4s^{1}\ 3d^{10}$

GENERAL PROPERTIES OF TRANSITION ELEMENTS

1. METALLIC CHARACTER

- All the transition elements are metals.
- This is due to their low ionisation energy and also due to the incompletely filled d orbitals.
- They are good conductors of heat and electricity, since the valence electrons are highly mobile.
- They have high tensile strength, ductility, malleability, lustre and relatively high densities.

2. MELTING AND BOILING POINTS

- The melting and boiling points of transition metals are high.
- This is due to the strong metallic bonds between the atoms of these elements.
- Greater the number of unpaired electrons, stronger the bonding and consequently melting points are high.

3. OXIDATION STATES

- Most of the transition elements show variable oxidation states.

- This is due to the participation of penultimate (n–1) d electrons as well as ultimate ns electrons in chemical combination.
- The highest oxidation states are found in compounds of fluorine and oxygen.
- This is due to the high electronegativity values and small size of F and O.
- The highest oxidation state shown by any transition metal is eight.

PROMINENT FEATURES OF OXIDATION STATES

- For the elements of the first transition series (except Sc), the most common oxidation state is +2.
- In each transition series, the oxidation state reaches a maximum value near the centre of the series and then decreases as we move towards the right of the series.
- Within a group, the highest oxidation state increases with increase in atomic number.
- In lower oxidation states, +2 and +3, the transition metal form ionic bonds.
- But in higher oxidation states, the bonds formed are essentially covalent.

4. CATALYTIC PROPERTIES

- Many transition metals and their compounds are good catalysts.
- Finely divided Iron (Spongy Iron) is used as a catalyst in the manufacture of ammonia by Haber process.
- V_2O_5 or Pt is used in contact process for the manufacture of H_2SO_4.
- The catalytic activity of transition metal is due to the following reasons.
- (i) Variable valencies enable transition metals to form unstable intermediate compounds readily.
- (ii) This provides a new path with lower activation energy for the reaction.
- (iii) Transition metals can provide a large surface area for the reactants to be adsorbed.

5. FORMATION OF COLOURED IONS

- Most of the transition metal compounds are coloured both in the solid state and in aqueous solution.
- The unpaired d electrons of transition metal ions can undergo d–d transition.
- An electron from a lower energy d orbital is excited to a higher energy d orbital.
- The energy of excitation corresponds to the frequency of light absorbed.
- This frequency generally lies in the visible region.
- The colour observed corresponds to the complementary colour of the light absorbed.
- Eg: Hydrated cupric compounds absorb red light and the transmitted colour is greenish blue.

E	Valence E.C.	E.C Box diagram	Metal ion	Valence EC of ion	E.C Box diagram	Colour
$_{21}$Sc	$3d^1 4s^2$	[↑][ ][ ][ ][ ] [↑↓]	Sc^{3+}	$3d^0 4s^0$	[ ][ ][ ][ ][ ] [ ]	Colourless
$_{22}$Ti	$3d^2 4s^2$	[↑][↑][ ][ ][ ] [↑↓]	Ti^{4+}	$3d^0 4s^0$	[ ][ ][ ][ ][ ] [ ]	Colourless
$_{22}$Ti	$3d^2 4s^2$	[↑][↑][ ][ ][ ] [↑↓]	Ti^{3+}	$3d^1 4s^0$	[↑][ ][ ][ ][ ] [ ]	Purple
$_{23}$V	$3d^3 4s^2$	[↑][↑][↑][ ][ ] [↑↓]	V^{4+}	$3d^1 4s^0$	[↑][ ][ ][ ][ ] [ ]	Blue
$_{23}$V	$3d^3 4s^2$	[↑][↑][↑][ ][ ] [↑↓]	V^{3+}	$3d^2 4s^0$	[↑][↑][ ][ ][ ] [ ]	Green
$_{24}$Cr	$3d^5 4s^2$	[↑][↑][↑][↑][↑] [↑]	Cr^{3+}	$3d^3 4s^0$	[↑][↑][↑][ ][ ] [ ]	Violet
$_{25}$Mn	$3d^5 4s^2$	[↑][↑][↑][↑][↑] [↑↓]	Mn^{3+}	$3d^4\ 4s^0$	[↑][↑][↑][↑][ ] [ ]	Violet
$_{25}$Mn	$3d^5 4s^2$	[↑][↑][↑][↑][↑] [↑↓]	Mn^{2+}	$3d^5\ 4s^0$	[↑][↑][↑][↑][↑] [ ]	Pink
$_{26}$Fe	$3d^6 4s^2$	[↑↓][↑][↑][↑][↑] [↑↓]	Fe^{3+}	$3d^5 4s^0$	[↑][↑][↑][↑][↑] [ ]	Yellow
$_{26}$Fe	$3d^6 4s^2$	[↑↓][↑][↑][↑][↑] [↑↓]	Fe^{2+}	$3d^6 4s^0$	[↑↓][↑][↑][↑][↑] [ ]	Green
$_{27}$Co	$3d^7 4s^2$	[↑↓][↑↓][↑][↑][↑] [↑↓]	Co^{2+}	$3d^7 4s^0$	[↑↓][↑↓][↑][↑][↑] [ ]	pink
$_{28}$Ni	$3d^8 4s^2$	[↑↓][↑↓][↑↓][↑][↑] [↑↓]	Ni^{2+}	$3d^8 4s^0$	[↑↓][↑↓][↑↓][↑][↑] [ ]	green
$_{29}$Cu	$3d^{10} 4s^2$	[↑↓][↑↓][↑↓][↑↓][↑↓] [↑]	Cu^{2+}	$3d^9\ 4s^0$	[↑↓][↑↓][↑↓][↑↓][↑] [ ]	blue
$_{30}$Zn	$3d^{10} 4s^2$	[↑↓][↑↓][↑↓][↑↓][↑↓] [↑↓]	Zn^{2+}	$3d^{10}\ 4s^0$	[↑↓][↑↓][↑↓][↑↓][↑↓] [ ]	Colourless

6. COMPLEX FORMATION

- Transition metal forms a large number of complexes.
- It is due to
- (i) their small size
- (ii) high effective nuclear charge and
- (iii) availability of vacant d orbitals of suitable energy for bonding with molecules or ions containing pairs of electrons.
- In complexes, the transition metal ions bind to a number of anions or neutral molecules by coordinate bonds.
- Eg: $[Fe(CN)_6]^{3-}$, $[Cu(NH_3)_4]^+$, $[PtCl_4]^{2-}$, $[Ag(NH_3)_2]^+$

7. MAGNETIC PROPERTIES

- Many transition metals and their compounds exhibit magnetic properties.
- Paramagnetism, diamagnetism and ferromagnetism are found in transition metal compounds.
- The substances which are weakly attracted by a magnetic field are called paramagnetic

substances.

- Paramagnetism is caused by the presence of unpaired electrons.
- Transition metals contain unpaired electrons, and are paramagnetic.
- The paramagnetism is expressed in terms of **magnetic moment**.

Magnetic Moment, $\mu = \sqrt{n(n+2)}$ Where n is the number of unpaired electrons.

Ion	EC	No of unpaired electron	Magnetic moment	
			observed	calculated $\mu = \sqrt{n(n+2)}$
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.75	1.73
V^{3+}	$3d^2$	2	2.76	2.83
Cr^{3+}	$3d^3$	3	3.80	3.87
Mn^{2+}	$3d^5$	5	5.96	5.92
Fe^{2+}	$3d^6$	4	5.3-5.5	4.90
Co^{2+}	$3d^7$	3	4.4-5.2	3.87
Ni^{2+}	$3d^8$	2	2.9-3.4	2.84
Cu^{2+}	$3d^9$	1	1.8-2.2	1.73
Zn^{2+}	$3d^{10}$	0	0	0

- The substances which are weakly repelled by a magnetic field are called diamagnetic substances.
- Diamagnetism is due to the presence of pairs of electrons with opposite spin.
- Ferromagnetism is a special type of paramagnetism in which permanent magnetic moment is acquired by substances.
- They can retain magnetism even after they are removed from the applied magnetic field.

8. INTERSTITIAL COMPOUNDS

- When small atoms like H, C or N are trapped inside the crystal lattices of metals, Interstitial compounds are formed
- They are prepared by heating together the transition metal and the non-metal.
- The non-metallic atoms occupy the voids between the larger metal atoms in the metallic lattice and also form bonds with them.
- The interstitial compounds are non-stoichiometric compounds.

9. ALLOY FORMATION

- The transition metals have almost similar atomic sizes.
- Metals can mutually substitute their positions in the crystal lattice, giving solid solutions called alloys.

- Transition metals are miscible with each other in the molten state.
- On cooling, transition metal alloys are formed.
- The alloys so formed are harder and more resistant to corrosion than the parent metals.

SOME IMPORTANT COMPOUNDS OF TRANSITION ELEMENTS

1. POTASSIUM DICHROMATE [$K_2Cr_2O_7$]

- Potassium dichromate is a very important chemical used in leather industry.
- It is used as an oxidant for the preparation of many azo compounds.

PREPARATION

- $K_2Cr_2O_7$ is prepared from chromite ore ($FeCr_2O_4$).

a) Conversion of chromite ore to sodium chromate

- The chromite ore is fused with Na_2CO_3 or K_2CO_3 in presence of air.

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

b) Conversion of sodium chromate to sodium dichromate

- The yellow solution of sodium chromate is filtered and acidified with dilute H_2SO_4.

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

c) Conversion of sodium dichromate to potassium dichromate

- A hot concentrated solution of dichromate is treated with KCl.
- NaCl being less soluble, precipitates out from the hot solution.
- It is removed by filtration.
- On cooling the mother liquor, orange crystals of $K_2Cr_2O_7$ separate out.

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

COLOUR OF CHROMATE AND DICHROMATE IN ACIDIC AND BASIC MEDIUM

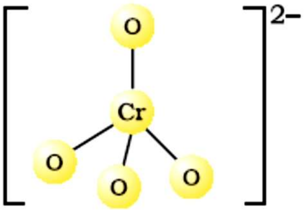
- The chromates and dichromates are inter convertible in aqueous solution depending upon the pH of the solution.
- In acid medium, potassium dichromate is orange in colour
- In basic medium it is yellow in colour.

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

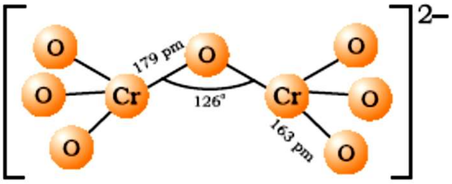
$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$

STRUCTURE OF CHROMATE ION AND DICHROMATE ION

- The chromate ion is tetrahedral.
- The dichromate ion consists of two tetrahedron sharing an oxygen atom at the common corner.



Chromate ion



Dichromate ion

REACTIONS OF POTASSIUM DICHROMATE

1. On heating, $K_2Cr_2O_7$ decomposes to give potassium chromate, chromic oxide and oxygen.

$$4K_2Cr_2O_7 \longrightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

2. It act as a powerful oxidising agent in acidic medium.

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

3. Typical Oxidation reactions of acidified potassium dichromate

a) It oxidises Iodide to Iodine. $6I^- \longrightarrow 3I_2 + 6e^-$

b) It oxidises ferrous salts to ferric salts. $6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^-$

c) It oxidises Hydrogen sulphide to Sulphur. $3H_2S \longrightarrow 6H^+ + 3S + 6e^-$

d) It oxidises tin(II) to tin(IV). $3Sn^{2+} \longrightarrow 3Sn^{4+} + 6e^-$

USES OF POTASSIUM DICHROMATE

- $K_2Cr_2O_7$ is used as a powerful oxidising agent.
- It is used as a laboratory reagent in volumetric analysis.
- It is used in leather industry.
- It is used as an oxidant for the preparation of many azo compounds.

2. POTASSIUM PERMANGANATE [$KMnO_4$]

- Potassium permanganate is a purple coloured crystalline solid.
- It is used as a disinfectant.
- It is used to treat a variety of skin conditions including fungal infections.

PREPARATION

A) From Pyrolusite Ore

- Potassium permanganate is prepared from Pyrolusite ore (MnO_2).
- Pyrolusite is fused with KOH and an oxidising agent like KNO_3.
- This produces the dark green coloured potassium manganate, K_2MnO_4.
- It disproportionates in a neutral or acidic solutions to give permanganate.

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

$$3K_2MnO_4 + 4H^+ \longrightarrow 2KMnO_4 + MnO_2 + 2H_2O$$

B) Commercial Preparation

- Commercially $KMnO_4$ is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (VI).

$$MnO_2 \xrightarrow[\text{Oxidised with air or } KNO_3]{\text{Fused with KOH}} K_2MnO_4$$

$$K_2MnO_4 \xrightarrow[\text{in alkaline medium}]{\text{Electrolytic oxidation}} KMnO_4$$

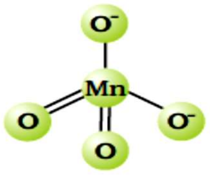
PROPERTIES

- $KMnO_4$ is a purple coloured crystalline solid.
- It is fairly soluble in water.
- It is a very powerful oxidising agent in acidic, alkaline and neutral media.
- On heating, $KMnO_4$ decomposes at 513K.

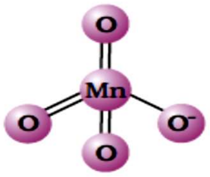
$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$

STRUCTURES OF MANGANATE AND PERMANGANATE IONS

- The manganate and permanganate ions are tetrahedral.
- Manganate ion is paramagnetic with one unpaired electron.
- The permanganate ion is diamagnetic.



Tetrahedral manganate (green) ion



Tetrahedral permanganate (purple) ion

- Acidified $KMnO_4$ oxidises
- Oxalates to Carbon dioxide.

$$5C_2O_4^{2-} \longrightarrow 10CO_2 + 10e^-$$

- Ferrous iron to Ferric iron. $5Fe^{2+} \longrightarrow 5Fe^{3+} + 5e^-$
- Nitrites to Nitrates. $5NO_2^- + 5H_2O \longrightarrow 5NO_3^- + 10H^+ + 10e^-$
- Iodides to free Iodine. $10I^- \longrightarrow 5I_2 + 10e^-$

IMPORTANT OXIDATION REACTIONS OF $KMnO_4$

1. In Acid Solutions

a) Iodine is liberated from potassium iodide.

$$10I^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

b) Fe^{2+} ion (green) is converted to Fe^{3+} (yellow)

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

c) Oxalate ion or Oxalic acid is oxidized at 333K.

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

d) H_2S is oxidised, sulphur being precipitated.

$$H_2S \longrightarrow 2H^+ + S^{2-}$$

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

e) Sulphurous acid or sulphite is oxidised to a sulphate or sulphuric acid.

$5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$

f) Nitrite ion is oxidised to nitrate.

$5NO_2^- + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

2. In neutral or faintly alkaline solutions

a) Oxidation of Iodide to Iodate.

$2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$

b) Thiosulphate is oxidized almost quantitatively to sulphate.

$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

c) Manganous salt is oxidized to MnO_2.

The presence of Zinc Sulphate or ZnO catalysis the oxidation.

$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$

USES OF $KMnO_4$

- $KMnO_4$ is used as a powerful oxidising agent.
- It is used as a laboratory reagent in volumetric analysis.
- It is used for bleaching wool, cotton, silk and other textile fibres and
- It is for the decolourisation of oils.

THE INNER TRANSITION ELEMENTS (f BLOCK)

- The elements in which the last electron enters the f orbitals of their atoms are called f block elements.
- In these elements, the last electron is added to the f-orbital of the antipenultimate shell. i.e., (n–2)f.
- These elements are also called inner transition elements.
- They consist of two series of elements namely lanthanides and actinides.

ELECTRONIC CONFIGURATION

- The general electronic configuration is $(n-2)f^{1-14}\ (n-1)d^{0-1}ns^2$.
- Inner 4f and 5f orbitals are progressively filled.
- The extra stability of half-filled orbitals is seen in the elements Europium ($4f^7\ 6s^2$) and Gadolinium ($4f^7 5d^1 6s^2$).

- Ytterbium ($4f^{14}6s^2$) and Lutetium ($4f^{14}5d^16s^2$) show the stability of completely filled f orbitals.
- Lanthanum, Gadolinium and Lutetium have a single electron in 5d orbitals.
- The other lanthanides do not have electrons in the 5d orbitals.

OXIDATION STATES

- The most common and the most stable oxidation state of the lanthanides is +3.
- Cerium and Terbium also exhibit +4 oxidation states.
- An aqueous solution of Ce^{4+} is a good oxidising agent.

$$Ce^{4+} + Fe^{2+} \longrightarrow Ce^{3+} + Fe^{3+}$$

- Some of the elements exhibit +2 oxidation states also.
- Aqueous solutions of Sm^{2+}, Eu^{2+} and Yb^{2+} are good reducing agents.

$$2Sm^{2+} + 2H_2O \longrightarrow 2Sm^{3} + +2OH^{-} + H_2$$

- The actinides exhibit several oxidation states.
- +3 oxidation state is most common in actinides.
- Actinoids exhibit higher oxidation states from +4 to +7
- This is because 5f, 6d, and 7s subshells have nearly equal energies.

Atomic No.	**Element**	**Symbol**	**Oxidation states**	**Electronic Configuration**	
				Lanthanoid (Ln)	**Lanthanoid ion (Ln^{3+})**
57	Lanthanum	La	+3	[Xe] $5d^1\,6S^2$	[Xe]$4f^0$
58	Cerium	Ce	+3,+4	[Xe] $4f^2\,6S^2$	[Xe] $4f^1$
59	Praseodymium	Pr	+3,+4	[Xe] $4f^3\,6S^2$	[Xe] $4f^2$
60	Neodymium	Nd	+2,+3,+4	[Xe] $4f^4\,6S^2$	[Xe] $4f^3$
61	Promethium	Pm	+3	[Xe] $4f^5\,6S^2$	[Xe] $4f^4$
62	Samarium	Sm	+2,+3	[Xe] $4f^6\,6S^2$	[Xe] $4f^5$
63	Europium	Eu	+2,+3	[Xe] $4f^7\,6S^2$	[Xe] $4f^6$
64	Gadolinium	Gd	+3	[Xe] $4f^7\,5d^1\,6S^2$	[Xe] $4f^7$
65	Terbium	Tb	+3,+4	[Xe] $4f^9\,6S^2$	[Xe] $4f^8$
66	Dysprosium	Dy	+3,+4	[Xe] $4f^{10}\,6S^2$	[Xe] $4f^9$
67	Holmium	Ho	+3	[Xe] $4f^{11}\,6S^2$	[Xe] $4f^{10}$
68	Erbium	Er	+3	[Xe] $4f^{12}\,6S^2$	[Xe] $4f^{11}$
69	Thulium	Tm	+2,+3	[Xe] $4f^{13}\,6S^2$	[Xe] $4f^{12}$
70	Ytterbium	Yb	+2,+3	[Xe] $4f^{14}\,6S^2$	[Xe] $4f^{13}$
71	Lutetium	Lu	+3	[Xe] $4f^{14}\,5d^16S^2$	[Xe] $4f^{14}$

Atomic No.	Element	Symbol	Oxidation States	Electronic Configuration	
				Actinoid	Actinoid ion (M^{3+} ion)
89	Actinium	Ac	+3	[Rn] $6d^1 7S^2$	[Rn] $5f^0$
90	Thorium	Th	+3, +4	[Rn] $6d^2 7S^2$	[Rn] $5f^1$
91	Protactinium	Pa	+3, +4, +5	[Rn] $5f^2 6d^1 7S^2$	[Rn] $5f^2$
92	Uranium	U	+3, +4, +5, +6	[Rn] $5f^3 6d^1 7S^2$	[Rn] $5f^3$
93	Neptunium	Np	+3, +4, +5, +6, +7	[Rn] $5f^4 6d^1 7S^2$	[Rn] $5f^4$
94	Plutonium	Pu	+3, +4, +5, +6, +7	[Rn] $5f^6 7S^2$	[Rn] $5f^5$
95	Americium	Am	+3, +4, +5, +6	[Rn] $5f^7 7S^2$	[Rn] $5f^6$
96	Curium	Cm	+3, +4	[Rn] $5f^7 6d^1 7S^2$	[Rn] $5f^7$
97	Berkelium	Bk	+3, +4	[Rn] $5f^8 6d^1 7S^2$	[Rn] $5f^8$
98	Californium	Cf	+2, +3	[Rn] $5f^{10} 7S^2$	[Rn] $5f^9$
99	Einsteinium	Es	+2, +3	[Rn] $5f^{11} 7S^2$	[Rn] $5f^{10}$
100	Fermium	Fm	+2, +3	[Rn] $5f^{12} 7S^2$	[Rn] $5f^{11}$
101	Mendelivium	Md	+2, +3	[Rn] $5f^{13} 7S^2$	[Rn] $5f^{12}$
102	Nobelium	No	+2, +3	[Rn] $5f^{14} 7S^2$	[Rn] $5f^{13}$
103	Lawrencium	Lr	+3	[Rn] $5f^{14} 6d^1 7S^2$	[Rn] $5f^{14}$

COLOUR OF LANTHANIDES

- Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions.
- Colour of these ions is due to the presence of ‘f’ electrons.
- Neither La^{3+} nor Lu^{3+} ion shows any colour.

MAGNETIC PROPERTIES

- The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic.
- The paramagnetism rises to maximum in neodymium.

PHYSICAL PROPERTIES

- The lanthanides and actinides have high density and high melting points.
- A well-known alloy of lanthanides and actinides is **‘Misch Metal’**.
- It consists of a rare earth element (94-95%), Iron (upto 5%) and traces of sulphur, carbon, calcium and aluminium.
- It is pyrophoric (ignites spontaneously in air) and used in cigarette & gas lighters, tracer bullets, shells etc.
- 3% misch metal is added to magnesium for making jet engine parts with an increased strength.

ATOMIC AND IONIC SIZES

LANTHANIDE CONTRACTION

- In the lanthanide series, with the increase in atomic number, there is a regular decrease in the size of the atoms and ions from lanthanum to lutetium.
- The contraction of atomic and ionic size along the period of lanthanide elements is known as lanthanide contraction.

CAUSE OF LANTHANIDE CONTRACTION

- Along the lanthanide series, the nuclear charge increases by one unit at each successive element.
- The new electron is added to the 4f orbitals.
- The shape of the f orbitals is much diffused.
- So the electrons in them cannot effectively shield the nuclear charge from the valence electrons.
- This ineffective shielding is unable to counter balance the effect of increased nuclear charge.
- Hence the net result is a contraction in size, though the decrease is very small.

CONSEQUENCE OF LANTHANIDE CONTRACTION

- Difficulty in the separation of lanthanides.
- Similarity in size of elements belonging to the second and third transition
- series.
- Eg: Zr (160 pm) and Hf (159 pm) have almost the same size.
- Due to this Zr and Hf have almost same chemical properties and hence their separation is difficult.

ACTINIDE CONTRACTION

- There is a gradual decrease in the size of atom or M^{3+} ions across the actinide series.
- This is called Actinide contraction.
- This results from the poor shielding by 5f electrons.

GENERAL CHATRACTERISTICS OF LANTHANIDES

- All the lanthanides are silvery white soft metals and tarnish rapidly in air.
- The hardness increases with increasing atomic number.
- They are good conductors of heat and electricity.
- Many trivalent lanthanide ions are coloured both in solid state and in aqueous solutions.
- Colour of these ions may be due to the presence of f electrons.
- The lanthanide ions other than f^0 type and f^{14} type are all paramagnetic.

APPLICATIONS OF d-BLOCK ELEMENTS

- Iron and steels are the most important construction materials.

- TiO is used in pigment industry.
- MnO_2 is used in dry cells.
- Zn, Ni and Cd are used in battery industry.
- The elements of group II are used as coinage metals.
- Many of the d block elements are used as catalysts.

APPLICATIONS OF f-BLOCK ELEMENTS

USES OF LANTHANIDES

- Lanthanide oxides are used for polishing glass.
- Cerium salts are used in dyeing cotton. They are also used as catalysts.
- Lanthanide compounds are sued as catalysts for hydrogenation, oxidation, petroleum cracking etc.
- Misch metal is used in Mg-based alloy to produce bullets and shell.
- Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking.
- Some individual Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.

USES OF ACTINIDES

- Thorium oxide is used for making incandescent mantles.
- Thorium salts are used in medicines in the treatment of cancer.
- Uranium is used in the production of nuclear energy by the process of nuclear fission.
- Uranium salts are used in textile industry, ceramic industry as well as in medicines.
- Plutonium is used as a fuel in atomic reactors.

PREVIOUS YEARS QUESTIONS

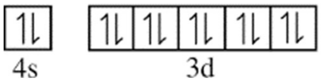
1. Suggest a reason why a transition metal exhibits higher oxidation states in oxides and Fluorides?

- Transition metal combines with oxygen in its metal oxide
- Transition metal combines with Fluorine in its metal Fluorides.
- Oxygen and Fluorine are the most electronegative elements.
- Shifting of electron density from electropositive transition metal is readily done.
- In transition metals the penultimate d orbitals facilitate this and metals show variable oxidation states.

2. Give example and suggest reasons for the lowest oxide of transition metal is basic, the highest is acidic.

Transition metal oxide	Oxidation Number	Nature of solution of the metal oxide in suitable solvent
MnO	+2	Basic
Mn_2O_3	+3	Basic
Mn_3O_4	+8/3	Amphoteric
MnO_2	+4	Amphoteric
Mn_2O_7	+7	Acidic

- $_{25}$Mn: 3d^{5}4s^2



- Oxidation number means number of electrons involved in bonding or reaction.
- In MnO the oxidation state of Mn is +2.
- It means 5 unpaired electrons are not involved in bonding.
- That is, its effective nuclear charge is not very high.
- MnO can donate these electrons and therefore base.
- In Mn_2O_7, manganese is in +7 oxidation state.
- Effective nuclear charge is very high.
- Hence it has a tendency to gain electrons and behaves as Lewis acid.

3. Suggest a reason why a transition metal exhibits higher oxidation states in oxides and Fluorides

- Transition metal combines with oxygen in its metal oxide
- Transition metal combines with Fluorine in its metal Fluorides.
- Oxygen and Fluorine are the most electronegative elements.
- Shifting of electron density from electropositive transition metal is readily done.

- In transition metals the penultimate d orbitals facilitate this and metals show variable oxidation states.

4.The highest Oxidation state is exhibited in oxoanions of a metal. Why?

- The highest oxidation state of transition element is seen in oxides.
- These oxides dissolve in acids and bases to form oxoanions.
- This is why, the highest oxidation state is exhibited in oxoanions of a metal.
- Eg: The highest oxidation state of Mn is +7
- Its oxoanion is MnO_4^-, $KMnO_4 \longrightarrow K^+ + MnO_4^-$
- The highest oxidation state of Cr is +6
- Oxoanion is CrO_4^{2-}(Chromate ion) and Dichromate anion ($Cr_2O_7^{2-}$)

5. Ce^{4+} is a good oxidizing agent, whereas Sm^{+2} is a good reducing agent. Why?

- Among lanthanoids +3 state is most stable.
- Ce^{+4} tends to go over to +3 state by undergoing reduction and hence it acts as oxidising agent.
- But Sm^{+2} tends to go over to +3 state by undergoing oxidation.
- Hence it acts as reducing agent.

6. $La(OH)_3$ is stronger base than $Lu(OH)_3$. Why?

- Lu^{3+} is smaller in size than La^{3+} due to Lanthanoid contraction.
- Due to smaller size of Lu^{3+}, Lu—O bond is stronger than La—O bond in respective hydroxides.
- Due to weaker La—O bond, $La(OH)_3$ behaves as stronger base.

7. Explain why Cu^+ ion is not stable in aqueous solutions?

Cu^+ ion is less stable than Cu^{2+} ion in aqueous solution and hence undergoes disproportionation, $2Cu^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$

Cu^{2+}(aq) is more stable than Cu^+(aq) due to more negative enthalpy of hydration which more than compensates for the second ionisation enthalpy of Cu.

8. Ni^{2+}compounds are thermodynamically more stable than Pt^{2+} but Pt^{4+} compounds are relatively more stable than Ni^{4+} compounds?

The sum of first two ionisation enthalpies (IE_1+IE_2) is less for Ni than Pt whereas sum of first four ionisation energies is less for Pt than for Ni.

Ionisation energy is the amount of energy required to release the most loosely bound electron from an isolated gaseous atom.

Last electron is removed is IE_1, next electron removed is IE_2, 3rd electron removed is IE_3 and fourth electron removed is IE_4

Element	(IE_1 + IE_2) (KJ/mol)	(IE_1 + IE_2 + IE_3 + IE_4) KJ/mol
Nickel (Ni -$3d^8 4s^2$)	2490 (Ni^{2+}- $3d^8$ $4s^0$)	11290
Platinum (Pt – $4f^{14}5d^9 6s^1$)	2660 (Pt^{2+} -$4f^{14}5d^8$ $6s^0$)	8360