04 The d and f-Block Elements

Transition Elements :

Definition :

They are often called 'transition elements' because their position in the periodic table is between s-block and p-block elements and they show transition from highly metallic nature of s-block elements which typically form ionic compounds to the non-metallic nature of p-block elements which form largely covalent compounds.

Typically, the transition elements have incompletely filled d-level. Since Zn group has d^{10} configuration in their ground state as well as in its chemically significant oxidation state, they are not considered as transition elements but they are d-block elements.

1st Series										
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10
2nd Series										
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	2	1	1	0	1	2
4d	1	2	4	5	5	7	8	10	10	10
3rd Series										
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10
4th Series										
	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub
Z	89	104	105	106	107	108	109	110	111	112
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

General Characteristics :

(i) Metallic character : They are all metal and good conductor of heat & electricity

(ii) Electronic configuration : $(n-1)^{1\text{-}10}\ ns^{1\text{-}2}$

in 3d-series

Sc Ti V $\underset{4s^1 3d^5}{Cr}$ Mn Fe Co Ni $\underset{4s^1 3d^{10}}{Cu}$ Zn

others are as usual

(iii) Lattice Structures of Transition Metals

Lattice Structures of Transition Metals

→ Sc, Ti, Fe and Mn* group -hcp structures

→ V and Cr group - bcc structure

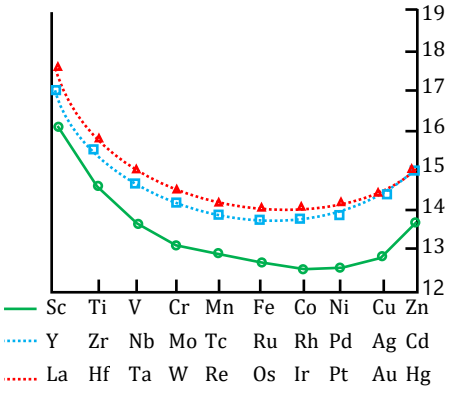
→ Co, Ni, Cu group - CCP structure

Note : Zn, Cd, Hg & Mn have one or more typical metallic structures at normal temp

(iv) Variation in atomic radius :

Sc ⟶ Mn Fe Co Ni Cu Zn

Decreases remains same increases again



Trends in atomic radii of transition elements

Magnetic character

- Metals, which have unpaired electrons show paramagnetism.
- Spin only magnetic moment $\mu = \sqrt{n(n+2)}$

  here n = no. of unpaired electron.
- Diamagnetic substance is one which is slightly repelled by a magnetic field.

Paramagnetism

- A paramagnetic substance is one which is attracted into a magnetic field.
- In paramagnetic substance the magnetic field lines of force travel easier than they travel in vacuum. Thus it can be seen that a paramagnetic material attracts lines of force, if it is free to move, a paramagnetic material will move from a weaker to a stronger part of the field.

Ferromagnetism

- Substances attracted very strongly are said to be ferromagnetic, extreme form of paramagnetism.
- Ferromagnetic materials are ⇒ Fe, Co, Ni.

Formation of coloured ion :

Colour : (aquated)

$Ti^{4\oplus}$	→	colourless	$Sc^{3\oplus}$	→	colourless
$V^{4\oplus}$	→	blue	$Ti^{3\oplus}$	→	purple
$V^{2\oplus}$	→	violet	$V^{3\oplus}$	→	green
$Cr^{3\oplus}$	→	violet	$Cr^{2\oplus}$	→	blue
$Mn^{2\oplus}$	→	light pink	$Mn^{3\oplus}$	→	violet
$Fe^{3\oplus}$	→	yellow	$Fe^{2\oplus}$	→	light green
$Ni^{2\oplus}$	→	green	$Co^{2\oplus}$	→	pink
$Zn^{2\oplus}$	→	colourless	$Cu^{2\oplus}$	→	blue

Formation of Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. The principal physical and chemical characteristics of these compounds are as follows:

(i) They have high melting points, higher than those of pure metals.

(ii) They are very hard, some borides approach diamond in hardness.

(iii) They retain metallic conductivity.

(iv) They are chemically inert.

Alloy Formation :

An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15 percent of each other. Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys so formed are hard and have often high melting points.

The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel. Alloys of transition metals with non transition metals such as brass (copper-zinc) and bronze (copper-tin), are also of considerable industrial importance.

(v) Ionisation energy :

1^{st}, 2^{nd}, 3^{rd} IE's are increasing from left to right for 1^{st} Transition series, but not regularly. Some important orders are :

For 1st I.E. Cr < Mn < Fe and Cu < Zn

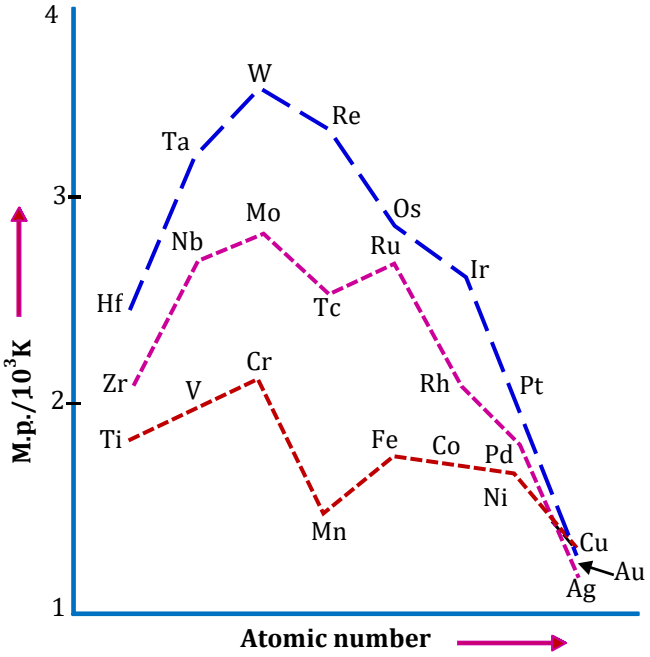
For 2^{nd} IE Cr > Fe > Mn and Cu > Zn

For 3^{rd} IE Mn > Cr > Fe and Zn has highest.

(iii) M.P.

Cr, Mo, W } Maximum 6 no. of unpaired $e^{\ominus}$s are involved in metallic bonding

Zn, Cd, Hg } lowest m.p. due to no unpaired $e^{\ominus}$ for metallic bonding



Trends in melting points of transition elements

→ High melting point and boiling point values of transition elements are due to the involvement of (n-1) d electrons along with ns electrons in the interatomic metallic bonding.

→ In any d-block series M.P-increase upto VI B group (max. unpaired $e^{\ominus}$) and then decreases.

→ Highest M.P. ⇒ Tungsten (W)
lowest M.P. ⇒ Mercury (Hg)

→ Mercury is liquid at room temp.

Variable oxidation states possible :

(1) The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7.

(2) The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or too many d electrons (hence fewer orbitals available in which to share electrons with others) for higher valence (Cu, Zn).

(3) Thus, early in the series scandium(II) is virtually unknown and titanium (IV) is more stable than Ti(III) or Ti(II).

(4) At the other end, the only oxidation state of zinc is +2 (no d electrons are involved).

(5) The maximum oxidation states of reasonable stability correspond in value to the sum of the s and d electrons upto manganese ($Ti^{IV}O_2$,$V^{V}O_2^{\oplus}$,$Cr^{VI}O_4^{2\ominus}$$Mn^{VII}O_4^{\ominus}$) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are $Fe^{II,III}$, $Co^{II,III}$, Ni^{II}, $Cu^{I,II}$, Zn^{II}.

(6) The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of d orbitals in such a way that their oxidation states differ from each other by unity, e.g., V^{II}, V^{III}, V^{IV}, V^{V}.

(7) This is in contrast with the variability of oxidation states of non-transition elements where oxidation states normally differ by a unit of two.

(8) An interesting feature in the variability of oxidation states of the d–block elements is noticed among the groups (groups 4 through 10).

(9) In group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas MoO_3 and WO_3 are not.

(10) Low oxidation states are found when a complex compound has ligands capable of π –acceptor character in addition to the σ-bonding. For example, in $Ni(CO)_4$ and $Fe(CO)_5$, the oxidation state of nickel and iron is zero.

(11) As the oxidation number of a metal increases, ionic character decreases. In the case of Mn, Mn_2O_7 is a covalent green oil. Even CrO_3 and V_2O_5 have low melting points. In these higher oxides, the acidic character is predominant. Thus, Mn_2O_7 gives $HMnO_4$ and CrO_3 gives H_2CrO_4 and $H_2Cr_2O_7$. V_2O_5 is, however, amphoteric though mainly acidic and it gives $VO_4^{3\ominus}$ as well as $VO_2^{\oplus}$ salts. In vanadium there is gradual change from the basic V_2O_3 to less basic V_2O_4 and to amphoteric V_2O_5. V_2O_4 dissolves in acids to give $VO^{2\oplus}$ salts. Similarly, V_2O_5 reacts with alkalis as well as acids to give $VO_4^{3\ominus}$ and $VO_2^{\oplus}$ respectively. The well characterised CrO is basic but Cr_2O_3 is amphoteric.

Oxidation states of the Ist transition series most common ones are in bold types :

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
								+1	
	+2	+2	+2	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**
+3	**+3**	**+3**	**+3**	+3	**+3**	**+3**	+3		
	+4	+4	+4	**+4**	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

Trends in stability of higher oxidation state :

(1) Table shows the stable halides of the 3d series of transition metals. The highest oxidation numbers are achieved in TiX_4 (tetrahalides), VF_5 and CrF_6. The +7 state for Mn is not represented in simple halides but MnO_3F is known, and beyond Mn no metal has a trihalide except FeX_3 and CoF_3.

(2) The ability of fluorine to stabilize the highest oxidation state is due to either higher lattice energy as in the case of CoF_3, or higher bond enthalpy terms for the higher covalent compounds, e.g., VF_5 and CrF_6.

(3) Although V^V is represented only by VF_5, the other halides, however, undergo hydrolysis to give oxohalides, VOX_3.

(4) Another feature of fluorides is their instability in the low oxidation states e.g.,VX_2 (X = CI, Br or I)

Formulas of halides of 3d-metals

Oxidation Number								
+6			CrF_6					
+5		VX_5	CrF_5					
+4	TiX_4	VX_5^{I}	CrF_4	MnF_4				
+3	TiX_3	VX_3	CrF_3	MnF_3	FeX_3^{1}	CoF_3		
+2	TiX_2^{III}	VX_2	CrF_2	MnF_2	FeX_2	CoF_2	XiN_2	CuX_2^{III}
+1								CuX^{III}

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

and the same applies to CuX. On the other hand, all Cu(II) halides are known except the iodide. In this case, $Cu^{2\oplus}$ oxidises $I^{\ominus}$ to I_2:

$$2Cu^{2\oplus} + 4I^{\ominus} \rightarrow Cu_2I_2(s) + I_2$$

(5) However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

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

(6) The stability of $Cu^{2\oplus}$ (aq) rather than $Cu^{\oplus}$ (aq) is due to the much more negative $\Delta_{hyd}H^{\circ}$ of $Cu^{2\oplus}$ (aq) than $Cu^{\oplus}$, which more than compensates for the second ionisation enthalpy of Cu.

(7) The ability of oxygen to stabilize the highest oxidation state is demonstrated in the oxides.

(8) The highest oxidation number in the oxides coincides with the group number and is attained in Sc_2O_3 to Mn_2O_7.

(9) Beyond Group 7, no higher oxides of Fe above Fe_2O_3, are known, although ferrates (VI) $(FeO_4)^{2\ominus}$, are formed in alkaline media but they readily decompose to Fe_2O_3 and O_2.

(10) Besides the oxides, oxocations stabilize V^{V} as $VO_2^{\oplus}$, V_{IV} as $VO^{2\oplus}$ and Ti^{IV} as $TiO^{2\oplus}$

(11) The ability of oxygen to stabilize these high oxidation states exceeds that of fluorine. Thus the highest Mn fluoride is MnF_4 whereas the highest oxide is Mn_2O_7. The ability of oxygen to form multiple bonds to metals explains its superiority.

(12) In the covalent oxide Mn_2O_7, each Mn is tetrahedrally surrounded by O's including a Mn–O–Mn bridge.

(13) The tetrahedral $[MO_4]^{n}$ ions are known for V^{V}, Cr^{VI}, Mn^{V}, Mn^{VI} and Mn^{VII}.

Catalytic Properties :

(1) The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes. Vanadium(V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in Catalytic Hydrogenation) are some of the examples.

(2) Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3d and 4s electrons for bonding).

(3) 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 lowering).

(4) Also because the transition metal ions can change their oxidation states, they become more effective as catalysts. For example, iron(III) catalyses the reaction between iodide and persulphate ions.

$$2I^{\ominus} + S_2O_8^{2\ominus} \rightarrow I_2 + 2SO_4^{2\ominus}$$

An explanation of this catalytic action can be given as:

$$2Fe^{3\oplus} + 2I^{\ominus} \rightarrow 2\,Fe^{2\oplus} + I_2$$

$$2\,Fe^{2\oplus} + S_2O_8^{2\ominus} \rightarrow 2Fe^{3\oplus} + 2SO_4^{2\ominus}$$

Catalyst		Used
$TiCl_3$	→	Used as the Ziegler-Natta catalyst in the production of polythene.
V_2O_5	→	Convert SO_2 to SO_3 in the contact process for making H_2SO_4
MnO_2	→	Used as a catalyst to decompose $KClO_3$ to give O_2
Fe	→	Promoted iron is used in the Haber-Bosch process for making NH_3
$FeCl_3$	→	Used in the production of CCl_4 from CS_2 and Cl_2
$PdCl_2$	→	Wacker process for converting $C_2H_4 + H_2O + PdCl_2$ to $CH_3CHO + 2HCl + Pd$.
Pd	→	Used for hydrogenation (e.g. phenol to cyclohexanone).
Pt/PtO	→	Adams catalyst, used for reductions.
Pt/Rh	→	Formerly used in the Ostwald process for making HNO_3 to oxidize NH_3 to NO
Cu	→	Is used in the direct process for manufacture of $(CH_3)_2SiCl_2$ used to make silicones.
Cu/V	→	Oxidation of cyclohexanol/cyclohexanone mixture to adipic acid which is used to make nylon-66
$CuCl_2$	→	Deacon process of making Cl_2 from HCl
Ni	→	Raney nickel, numerous reduction processes (e.g. manufacture of hexamethylenediamine, production of H_2 from NH_3, reducing anthraquinone to anthraquinol in the production of H_2O_2
$FeSO_4 + H_2O_2$	→	Used as Fenton's reagent for oxidizing alcohols to aldehydes.

Density :

(a) The atomic volume of the transition elements are low, compared with s-block, so their density is comparatively high (D = M/V)

(b) Os (22.57 gm cm^{-3}) and Ir (22.61 gm cm^{-3}) have highest density.

(c) In all the groups (except IIIB) there is normal increase in density from 3d to 4d series, and from 4d to 5d, it increases just double. Due to lanthanide contraction **Ex. :** Ti < Zr << Hf

(d) **In 3d series**

	Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Density/g cm^{-3}	3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

(e) In 3d series highest density – Cu

lowest density – Sc

(f) Some important orders of density

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

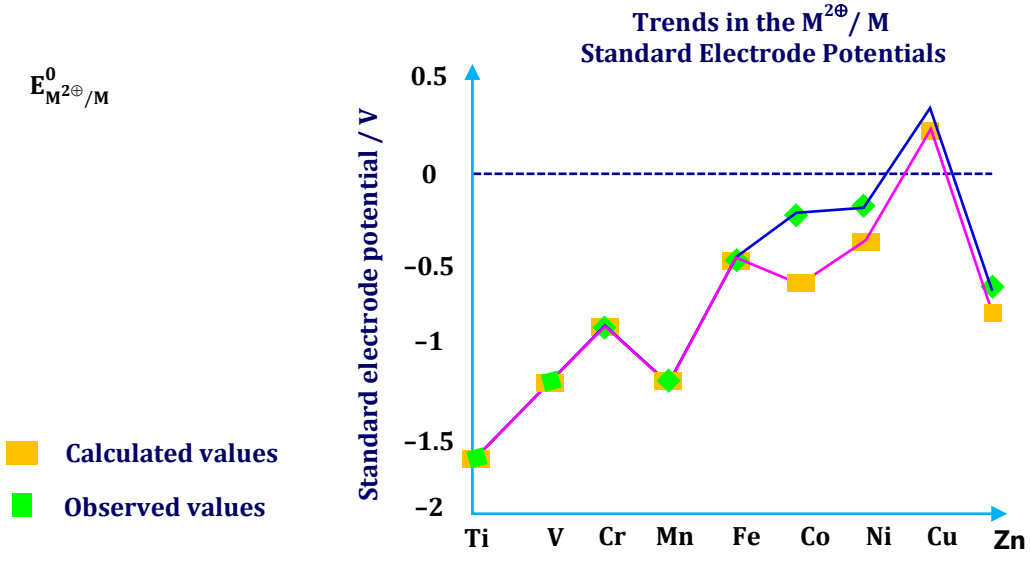
Element		Sc	Ti	v	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number		21	22	23	24	25	26	27	28	29	30
Electronic configuration											
	M	$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^2$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^{10}4s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$
	$M^{\oplus}$	$3d^14s^1$	$3d^24s^1$	$3d^34s^1$	$3d^5$	$3d^54s^1$	$3d^64s^1$	$3d^74s^1$	$3d^84s^1$	$3d^{10}$	$3d^{10}4s^1$
	$M^{2\oplus}$	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
	$M^{3\oplus}$	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	-	-
Enthalpy of atomisation, $\Delta_aH^{\ominus}$/kJ mol^{-1}											
		326	473	515	397	281	416	425	430	339	126
Ionisation Enthalpy, Δ_1H^-/kJ mol^{-1}											
$\Delta_1H°$	I	631	656	650	653	717	762	758	736	745	906
	II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
	III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829
Metallic/Ionic	M	164	147	135	129	137	126	125	125	128	137
radii/pm	$M^{2\oplus}$	-	-	79	82	82	77	74	70	73	75
	$M^{3\oplus}$	73	67	64	62	65	65	61	60	-	-
Standard electrode	$M^{2\oplus}/M$	-	-1.63	-1.18	-0.90	-1.18	-0.44	-0.28	-0.25	+0.34	-0.76
potential $e^{\ominus}$/V	$M^{3\oplus}/M^{2\oplus}$	–2.08	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97	-	-	-
density		3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

Complex Formation :

Complex compounds are those in which the metal ions bind a number of anions or neutral molecules giving complex species with characteristic properties. A few examples are: $[Fe(CN)_6]^{3\ominus}$, $[Fe(CN)_6]^{4\ominus}$, $[Cu(NH_3)_4]^{2\oplus}$ and $[PtCl_4]^{2\ominus}$. The transition metals form a large number of complex compounds. This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of d orbitals for bond formation.

Electrode potential

There is no regular trend in these values. This is attributed to the irregular variation of ionization enthalpies (IE_1+IE_2), hydration energies and the sublimation energies in the period.



Chromate – Dichromate :

Residue (Fe_2O_3)

Filtrate (Na_2CrO_4)

Dissolve in water and filtered

Preparation : $\underset{\text{(chromite ore)}}{4FeCr_2O_4} + 8Na_2CO_3 + 7O_2 \xrightarrow[\text{red hot in presence of air}]{1000°\text{-}1300°C} \overbrace{8Na_2CrO_4 + 2Fe_2O_3} + 8CO_2$

[Lime (CaO) added with Na_2CO_3 which keeps the mass porous so that air has access to all parts and prevents fusion]

Then, $2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2SO_4 + Na_2Cr_2O_7 + H_2O$

conc. It's solubility upto 32°C increases and then decreases } Hence, suitable temp. is to be employed to crystallise out Na_2SO_4 first.

Then $Na_2Cr_2O_7$ is crystallised out as $\underset{\text{(red crystal)}}{Na_2Cr_2O_7 \cdot 2H_2O}$ on evaporation.

How to get $K_2Cr_2O_7$:

$\underset{\text{Hot conc.}}{Na_2Cr_2O_7} + 2KCl \xrightarrow[\text{decomposition}]{\text{double}} K_2Cr_2O_7 + 2NaCl$

NaCl crystallises out first and filtered off. Then $K_2Cr_2O_7$ crystallised out on cooling

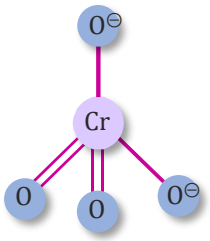
The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

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

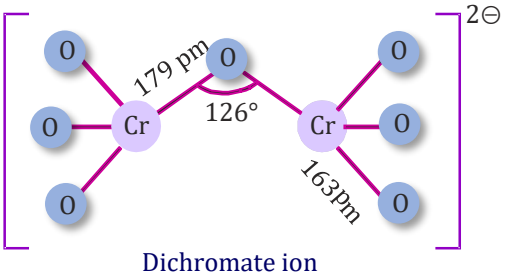
$$Cr_2O_7^{2\ominus} + 2OH^{\ominus} \rightarrow 2CrO_4^{2\ominus} + H_2O$$

The structures of chromate ion, $CrO_4^{2\ominus}$ and the dichromate ion, $Cr_2O_7^{2\ominus}$ are shown below. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Cr–O–Cr bond angle of 126°. Sodium and potassium dichromate are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis. In acidic solution, its oxidising action can be represented as follows:

$$Cr_2O_7^{2\ominus} + 14H^{\oplus} + 6e^{\ominus} \rightarrow 2Cr^{3\oplus} + 7H_2O \ (E^{\ominus} = 1.33V)$$



Chromate ion



Dichromate ion

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

$$6\ I^{\ominus} \rightarrow 3I_2 + 6e^{\ominus};$$

$$3\ Sn^{2\oplus} \rightarrow 3Sn^{4\oplus} + 6e^{\ominus}$$

$$3H_2S \rightarrow 6H^{+} + 3S + 6e^{\ominus}; \qquad 6\ Fe^{2\oplus} \rightarrow 6Fe^{3\oplus} + 6e^{\ominus}$$

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

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

* Similarities between hexavalent Cr & S-compounds :

(i) SO_3 & $CrO_3 \rightarrow$ both acidic.

(ii) $S \rightarrow SO_4^{2\ominus}, S_2O_7^{2\ominus}$, $Cr \rightarrow CrO_4^{2\ominus}, Cr_2O_7^{2\ominus}$

(iii) $CrO_4^{2\ominus}$ & $SO_4^{2\ominus}$ are isomorphous

(iv) SO_2Cl_2 & $CrO_2Cl_2 \xrightarrow{OH^{\ominus}} SO_4^{2\ominus}$ & $CrO_4^{2\ominus}$ respectively.

(v) $SO_3Cl^{\ominus}$ & $CrO_3Cl^{\ominus} \xrightarrow{OH^{\ominus}} SO_4^{2\ominus}$ & $CrO_4^{2\ominus}$

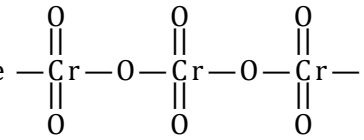
(vi) CrO_3 & b(SO_3) has same structure 

Illustration 1 :

In laboratory $K_2Cr_2O_7$ is used mainly not $Na_2Cr_2O_7$. Why?

Solution:

$Na_2Cr_2O_7$ is deliquescent enough and changes its concentration and can not be taken as primary standard solution whereas $K_2Cr_2O_7$ has no water of crystallisation and not deliquescent.

Illustration 2 :

How to standardise $Na_2S_2O_3$ solution in iodometry?

Solution:

$K_2Cr_2O_7$ is primary standard $\Rightarrow$ strength is known by weighing the salt in chemical balance and dissolving in measured amount of water.

Then in acidic solution add. KI

$$Cr_2O_7^{2\ominus} + 14H^{\oplus} + 6I^{\ominus} \rightarrow 2Cr^{3\oplus} + 3I_2 + 7H_2O$$

This I_2 is liberated can be estimated with $S_2O_3^{2\ominus}$.

Manganate & Permanganate :

Preparation of Manganate ($MnO_4^{2\ominus}$) :-

$MnO_2 \xrightarrow[\text{or NaOH, } \Delta \text{ in presence of air}]{KOH} \underset{\text{green melt}}{MnO_4^{2\ominus}}$

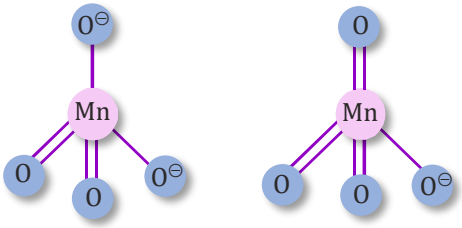
$[2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O]$

$MnO_2 + 2KOH + KNO_3 \longrightarrow K_2MnO_4 + KNO_2 + H_2O$

$3MnO_2 + 6KOH + KClO_3 \longrightarrow 3K_2MnO_4 + KCl + 3H_2O$

$MnO_4^{2\ominus} \xrightarrow[\text{Water +little alkali}]{\text{Cold}}$ Green soln. $\xrightarrow[\text{evaporation}]{\text{On}}$ $\xrightarrow{\text{If KOH used}} K_2MnO_4$(Isomorphous with K_2SO_4)

$\xrightarrow{\text{If NaOH used}} Na_2MnO_4.10H_2O$ isomorphous with $Na_2SO_4.10H_2O$



Tetrahedral manganate (green) ion

Tetrahedral permanganate (purple) ion

In presence of $KClO_3$ & KNO_3 the above reaction is more faster because these two on decomposition provides O_2 easily.

* Manganate is also obtained when $KMnO_4$ is boiled with KOH.

$4KMnO_4 + 4KOH \xrightarrow{\text{boiled}} 4K_2MnO_4 + 2H_2O + O_2$

Properties : The above green solution is quite stable in alkali, but in pure water and in presence of acids, depositing MnO_2 and giving a purple solution of permanganate.

$3K_2MnO_4 + 2H_2O \rightarrow \underset{\text{Purple}}{2KMnO_4} + \underset{\text{dark brown}}{MnO_2} + 4KOH$

Prob. : $E^o_{MnO_4^{2\ominus}/MnO_2} = 2.26\ V$; $E^o_{MnO_4^{2\ominus}/MnO_4^{\ominus}} = -0.56$ V

Prove that $MnO_4^{2\ominus}$ will disproportionate in acidic medium.

Conversion of $MnO_4^{2\ominus}$ to $MnO_4^{\ominus}$

$3K_2MnO_4 + 2H_2SO_4 \rightarrow 2KMnO_4 + MnO_2 + 2K_2SO_4 + 2H_2O$

or $3K_2MnO_4 + 2H_2O + 4CO_2 \rightarrow 2KMnO_4 + MnO_2 + 4KHCO_3$

But in the above method $\frac{1}{3}$ of Mn is lost as MnO_2 but when oxidised either by Cl_2 or by O_3

$2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$ [Unwanted MnO_2 does not form]

OR

$2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + 2KOH + O_2$

OR

$\underset{\text{Manganate}}{MnO_4^{2\ominus}} \xrightarrow[\text{alkaline solution}]{\text{Electrolytic oxidation in}} \underset{\text{permanganate ion}}{MnO_4^{\ominus}}$

Oxidising Prop. of $KMnO_4$: (in acidic medium)

(i) $MnO_4^{\ominus} + Fe^{2\oplus} + H^{\oplus} \rightarrow Fe^{3\oplus} + Mn^{2\oplus} + H_2O$

(ii) $MnO_4^{\ominus} + I^{\ominus} + H^{\oplus} \rightarrow Mn^{2\oplus} + I_2 + H_2O$

(iii) $MnO_4^{\ominus} + H_2O_2 + H^{\oplus} \rightarrow Mn^{2\oplus} + O_2 + H_2O$

(iv) $MnO_4^{\ominus} + SO_2 \xrightarrow{H^{\oplus}} Mn^{2\oplus} + H_2SO_4$

(v) $MnO_4^{\ominus} + NO_2^{\ominus} + H^{\oplus} \rightarrow Mn^{2\oplus} + NO_3^{\ominus} + H_2O$

(vi) $MnO_4^{\ominus} + H_2C_2O_4 + H^{\oplus} \rightarrow Mn^{2\oplus} + CO_2 + H_2O$

(vii) $MnO_4^{\ominus} + H_2S \rightarrow Mn^{2\oplus} + S\downarrow + H_2O$

(viii) $MnO_4^{\ominus} + S_2O_3^{2\ominus} \rightarrow Mn^{2\oplus} + S\downarrow + SO_4^{2\ominus}$

(1)* It is not a primary standard since it is difficult to get it in a high degree of purity and free from traces of MnO_2.

(2)* It is slowly reduced to MnO_2 especially in presence of light or acid

$4MnO_4^{\ominus} + 4H^{\oplus} \longrightarrow 4MnO_2 + 2H_2O + 3O_2$

Hence it should be kept in dark bottles and standardise just before use.

Note: Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.

(ix) $2KMnO_4 + 16HCl \longrightarrow 2KCl + 5Cl_2 + 8H_2O + 2MnCl_2$

Oxidising Prop. of $KMnO_4$ in neutral or faintly alkaline solution.

$2MnO_4^{\ominus} + 2OH^{\ominus} \rightarrow 2MnO_4^{2\ominus} + H_2O + O$. Then $2MnO_4^{2\ominus} + 2H_2O \rightarrow 2MnO_2 + 4OH^{\ominus} + 2O$

(i) $2KMnO_4 + H_2O + KI \rightarrow 2MnO_2 + 2KOH + KIO_3$

(ii) $2KMnO_4 + 3HCO_2K \rightarrow 2MnO_2 + KHCO_3 + 2K_2CO_3 + H_2O$

(iii) $2KMnO_4 + 3H_2O_2 \rightarrow 2KOH + 2MnO_2 + 2H_2O + 3O_2$

(iv) Thiosulphate is oxidised almost quantitatively to sulphate:

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

Oxidising Prop. in neutral or weakly acidic solution:

(i) $2KMnO_4 + 3MnSO_4 + 2H_2O \xrightarrow{\text{in presence } Zn^{2\oplus} \text{ or } ZnO} 5MnO_2 + K_2SO_4 + 2H_2SO_4$

or $2MnO_4^{\ominus} + 3Mn^{2\oplus} + 2H_2O \rightarrow 5MnO_2 + 4H^{\oplus}$

In absence of $Zn^{2\oplus}$ ions, some of the $Mn^{2\oplus}$ ion may escape, oxidation through the formation of insoluble $Mn^{II}[Mn^{IV}O_3]$ manganous permanganite.

Uses of $KMnO_4$:

Besides its use in analytical chemistry, potassium permanganate is used as a favourite oxidant in preparative organic chemistry. Its uses for the bleaching of wool, cotton, silk and other textile fibres and for the decolourisation of oils are also dependent on its strong oxidising power.

** In laboratory conversion of $Mn^{2\oplus}$ to $MnO_4^{\ominus}$ is done by :

(i) PbO_2 (ii) $Pb_3O_4 + HNO_3$ (iii) $Pb_2O_3 + HNO_3$ (iv) $NaBiO_3$ / $H^{\oplus}$

(v) $(NH_4)_2S_2O_8$ / $H^{\oplus}$ (vi) KIO_4 / $H^{\oplus}$

Heating effect : $2KMnO_4 \xrightarrow[200°C]{\Delta} \underset{\text{Green}}{K_2MnO_4} + \underset{\text{Black}}{MnO_2} + O_2$

$2K_2MnO_4 \xrightarrow[\text{hot}]{\text{at red}} 2K_2MnO_3 + O_2$

f- Block Elements

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.**

Position in the periodic table :

The lanthanides resemble with Yttrium in most of their properties. So it became necessary to accommodate 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 – Lr)

Lanthanides (Rare Earths or Lanthanones) :

(i) Lanthanides are reactive elements so do not found in free state in nature.

(ii) Most important minerals for lighter Lanthanides are – Monazite, cerites and for heavier lanthanides – Gadolinite and Xenotime

Electronic configuration :

(i) The general configuration of lanthanides may be given as $4f^{1-14}5s^25p^65d^{0-1}6s^2$.

Atomic Number	Element	Symbol	Outer electronic configuration	
			Atomic	+3 ion
58	**Cerium**	**Ce**	**$4f^1\ 5d^1 6s^2$**	**$4f^1$**
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	**Lutetium**	**Lu**	**$4f^{14}\ 5d^1\ 6s^2$**	**$4f^{14}$**

(ii) It is to be noted 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.

(iii) On the other hand, the filling of f-orbitals is regular in tripositive ions.

(iv) After losing outer electrons, the f-orbitals shrink in size and became more stable.

(v) **Pm** is the only synthetic radioactive lanthanide.

Oxidation states :

Lanthanides	Oxidation	Actinides	Oxidation state
Ce_{58}	+3, +4	Th_{90}	+4
Pr_{59}	+3, (+4)	Pa_{91}	(+4), +5
Nd_{60}	+3	U_{92}	(+3), (+4), (+5), +6
Pm_{61}	+3	Np_{93}	(+3), (+4), +5, (+6), (+7)
Sm_{62}	(+2), +3	Pu_{94}	(+3), +4, (+5), (+6), (+7)
Eu_{63}	+2, +3	Am_{95}	+2,(+3),(+4),(+5),(+6)
Gd_{64}	+3	Cm_{96}	+3, (+4)
Tb_{65}	+3, +4	Bk_{97}	+3, (+4)
Dy_{66}	+3, (+4)	Cf_{98}	+3
Ho_{67}	+3	Es_{99}	+3
Er_{68}	(+2), +3	Fm_{100}	+3
Tm_{69}	(+2), +3	Md_{101}	+3
Yb_{70}	+2, +3	No_{102}	+3
Lu_{71}	+3	Lr_{103}	+3

(Oxidation states in brackets are unstable states)

(i) 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.

(ii) This corresponds to the use of two outermost electrons ($6s^2$) along with 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.

(iii) All the lanthanides attains +3 oxidation state and only **Cerium, Praseodymium,** and **Terbium** exhibit **higher oxidation state (+4). Eu and Yb** exhibit **+2** oxidation state.

(iv) Oxidation states +2 and +4 occur particularly when they lead to –

(a) A noble gas configuration **Ex.** $Ce^{4\oplus}$ (f^0). The formation of Ce^{IV} is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The E° value for $Ce^{4\oplus}/ Ce^{3\oplus}$ is + 1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent.

(b) A half filled 'f ' orbital **Ex.** $Eu^{2\oplus}$, (f^7), Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO_2. $Eu^{2\oplus}$ is formed by losing the two s electrons and its f^7 configuration accounts for the formation of this ion. However, Eu^{2+} is a strong reducing agent changing to the common +3 state. Similarly $Yb^{2\oplus}$ which has f^{14} configuration is a reductant.

(c) A completely filled 'f ' orbital **Ex.** $Yb^{2\oplus}$ (f^{14})

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

Magnetic properties :

(i) 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).

(ii) lanthanum and lutecium ions are diamagnetic, while all other tripositive lanthanide ions are paramagnetic. (Exception – Neodymium is the most paramagnetic lanthanide).

(iii) $Ce^{4\oplus}$ and $Yb^{2\oplus}$ are also diamagnetic ions.

Colour :

(i) 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.

(ii) The colour exhibited depends on the number of unpaired electrons in the 4f orbitals.

(iii) The ions often with $4f^n$ configuration have similar colour to those ions having $4f^{14-n}$ configuration.

(iv) Lanthanide ions having $4f^0$, $4f^{14}$ are colourless.

Other Properties :

- All the lanthanides are silvery white soft metals and tarnish rapidly in air.
- The hardness increases with increasing atomic number, samarium being steel hard. Their melting points range between 1000 to 1200 K but samarium melts at 1623 K.
- They have typical metallic structure and are good conductors of heat and electricity.
- Highly dense metals with high melting points do not show any regular trend.
- **Ionisation Energies :** Lanthanides have fairly low ionisation energies comparable to alkaline earth metals.
- **Electro positive character :** High due to low I.P.
- **Complex formation :** Do not have much tendency to form complexes due to low charge density because of their large size. $Lu^{3\oplus}$ is smallest in size can only form complex.
- **Reducing Agent :** They readily lose electrons so are good reducing agent.
- **Alloy :** Alloys of lanthanides with Fe are called **Misch metals**, which consists of a lanthanide metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al.
- **Basic Nature :** $La(OH)_3$ is most basic in nature while $Lu(OH)_3$ least basic.
- **Carbide :** Lanthanides form MC_2 type carbide with carbon, which on hydrolysis gives C_2H_2.
- The lanthanide elements Eu and Yb dissolve directly in very high concentration in liquid ammonia.

Lanthanide contraction :

(i) In the lanthanide series with increasing atomic number, in general, there is a progressive decrease in the size from Lanthanum to Lutetium and regular decreases in ionic size from $La^{3\oplus}$ to $Lu^{3\oplus}$. This decrease in size is known as lanthanide contraction.

(ii) The general electronic configuration of these elements is $4f^{1-14}\ 5d^{0-1}\ 6s^2$. In these elements the added electron enters the deep-seated f-orbitals.

(iii) Due to very poor shielding effect of (n-2)f electrons, they exert very little screening effect on the outermost $6s^2$ electrons and therefore experiences considerable pull by the nucleus. Hence, with increasing atomic number, the enhanced nuclear charge leads to contraction in the size of atoms and ions.

(iv) The atomic volumes of Europium and Ytterbium are unexpectedly 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 :

Close resemblance 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.

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.

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

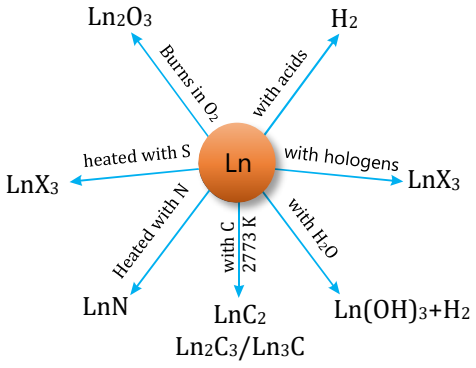
(a) Atomic size : The ionic radii of $Zr^{4\oplus}$ is about 9% more than $Ti^{4\oplus}$. Similar trend is not maintained on passing from the second to third transition series. The ionic radius of $Hf^{4\oplus}$, instead of increasing (because of inclusion of one more electronic shell), decreases (or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

(d) Chemical reactions of the lanthanoids.



Application of lanthanides :

Cerium is most useful element in the lanthanides –

- Ceramic application – CeO_2, La_2O_3, Nd_2O_3 and Pr_2O_3 are used as decolourizing agents for glasses.
- CeS (M.P. – 2000^0C) is used in the manufacture of a special type of crucibles and refractories.
- Lanthanide compounds like cerium molybdate, cerium tungstate are used as paints and dyes.
- In textile and leather industries (Ce salts).
- Misch metal is pyropheric and is used in cigarette & gas lighter.

Actinides (5f - block elements) :

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

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

(iii) Th, Pa and U first three actinides are natural elements.

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**	**$5f^0 6d^2 7s^2$**
91	Protactinium	Pa	$5f^2 6d^1 7s^2$
92	**Uranium**	**U**	**$5f^3 6d^1 7s^2$**
93	**Neptunium**	**Np**	**$5f^4 6d^1 7s^2$**
94	**Plutonium**	**Pu**	**$5f^6 6d^0 7s^2$**
95	Americium	Am	$5f^7 6d^0 7s^2$
96	**Curium**	**Cm**	**$5f^7 6d^1 7s^2$**
97	Berkelium	Bk	$5f^9 6d^0 7s^2$
98	Californium	Cf	$5f^{10} 6d^0 7s^2$
99	Einsteinium	Es	$5f^{11} 6d^0 7s^2$
100	Fermium	Fm	$5f^{12} 6d^0 7s^2$
101	Mendelevium	Md	$5f^{13} 6d^0 7s^2$
102	**Nobelium**	**No**	**$5f^{14} 6d^0 7s^2$**
103	**Lawrencium**	**Lr**	**$5f^{14} 6d^1 7s^2$**

Oxidation states :

(i) In lanthanides and actinides +3 oxidation is the most common for both of the series of elements.

(ii) This oxidation state becomes increasingly more stable as the atomic number increases in the actinide series.

(iii) Highest oxidation states in the actinides is +7 exhibited by Np_{93} & Pu_{94}, it is unstable.

(iv) Highest stable oxidation state is +6 shown by U_{92}.

Other Properties :

- **Physical appearance :** Actinides are silvery white metals. They get tarnished when exposed to the attack of alkalis.
- **Density :** All the actinides except **thorium** and **americium** have high densities.
- **Colour :** Actinide ions are generally coloured. The colour of actinide ions depends upon the number of 5f-electrons. The ions containing no unpaired 5f-electrons (exactly full filled f-subshell) are colourless, as expected.

- **Ionisation energies :** Ionisation energies values of actinides are low.
- **Electropositive character :** All the known actinide metals are **highly electropositive**. They resemble lanthanide series in this respect.
- **Melting Boiling properties :** They have **high melting and boiling points.** They do not follow regular gradation of melting or boiling points with increase in atomic number.
- **Magnetic properties :** The actinide elements are paramagnetic due to the presence of unpaired electrons.
- **Radioactive nature :** All the actinides are radioactive in nature.
- **Actinide contraction :** The size of atom/cation decrease regularly along the actinides series. The steady decrease in ionic radii with increase in atomic number is referred to as **actinide contraction.** This is due to poor shielding of 5f-electrons.

Comparison of lanthanides and Actinides :

Points of Resemblance :

(i) Both lanthanides and actinides show a dominant oxidation state of +3.

(ii) Both are electropositive and act as strong reducing agents.

(iii) Cations with unpaired electrons in both of them are paramagnetic.

(iv) Most of the cations of lanthanides and actinides are coloured.

(v) Both of them show a steady decrease in their ionic radii along the series. Thus, lanthanides show **lanthanide contraction** and actinides show **actinide contraction.**

Difference between lanthanides & Actinides :

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