

31. d AND f-BLOCK ELEMENTS

d-BLOCK ELEMENTS

1. INTRODUCTION

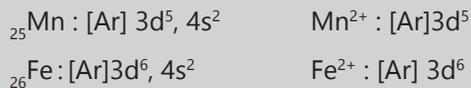
The elements in which the last electron enters $(n - 1)d$ orbitals of the atom are called d-block elements. Also, these elements lie in between s and p block elements in the long form of the periodic table. So, they are also called transition elements.

2. ELECTRONIC CONFIGURATION AND IRREGULARITIES

The valence shell configurations of these elements can be represented by $(n - 1)d^{1-10}ns^{0,1,2}$. All the d-block elements are classified into four series viz 3d, 4d, 5d and 6d orbitals of $(n - 1)^{\text{th}}$ main shell. Each series has 10 elements. Cr($3d^5, 4s^1$), Cu($3d^{10}, 4s^1$), Mo($4d^5, 5s^1$), Pd($4d^{10}, 5s^0$), Ag($4d^{10}, 5s^1$) and Au($5d^{10}, 6s^1$) clearly show irregularities in the configurations. These are explained on the basis of the concept that half-filled and completely filled d-orbitals are relatively more stable than other d-orbitals.

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It should be noted here that when atoms of these elements form cations, electrons are removed from the outermost s-subshell instead of the penultimate d-subshell, although the former was filled earlier.



Vaibhav Krishnan (JEE 2009 AIR 22)

Illustration 1: To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with example. **(JEE MAIN)**

Sol: Empty, Half-filled and completely filled orbitals have extra stability

E.g. $\text{Mn}^{2+} = [\text{Ar}]3d^5$, $\text{Sc}^{3+} = [\text{Ar}]3d^0$, $\text{Zn}^{2+} = [\text{Ar}] 3d^{10}$

Illustration 2: What may be the stable oxidation state of the transition element with the following d-electron configurations in the ground state of their atoms: $3d^3$, $3d^5$, $3d^8$ and $3d^4$? **(JEE ADVANCED)**

Sol: Ground state configuration	Stable oxidation state
$3d^3$	+5
$3d^5$	+2, +7
$3d^8$	+2
$3d^4$	$3d^4$ does not exist

3. GENERAL PROPERTIES OF THE TRANSITION METALS

3.1 Atomic and Ionic Radii

- (a) The atomic and ionic radii for transition elements are smaller than their corresponding s-block elements and are greater than their corresponding p-block elements.
- (b) The atomic and ionic radii for transition elements for a given series show a decreasing trend for the first five elements and then becomes almost constant for next five elements of the series. For example, in 3d-series atomic radius decreases from $_{21}\text{Sc}$ to $_{25}\text{Mn}$ and then becomes constant for next five i.e. $_{26}\text{Fe}$ to $_{30}\text{Zn}$

Explanation: This is due to the combined effect of the increasing effective nuclear charge, (ENC) and increasing screening effect along the period. An increase in ENC favors a decrease in atomic radii, whereas increase in number of d-elements increases the screening effect and thus increases the atomic radii. Thus both ENC and screening effect act opposite to each other and therefore the atomic size is governed by the net influence of these two.

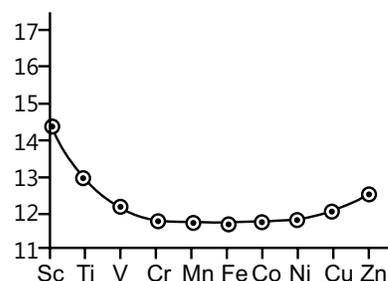
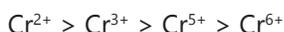
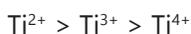


Figure 31.1: Atomic radii of element of 3d-series

- (c) The atomic and ionic radii of the elements of 4d-series are higher than 3d-series as the number of shells increases down the group. However, the elements of 4d-series and 5d-series on moving down the group reveal almost constant value. For example, Zirconium and Hafnium, the members of 4d and 5d-series, respectively have the almost same size i.e. 145 pm. Similarly, Zr^{4+} and Hf^{4+} have their atomic radii as 80 pm and 81 pm respectively. This is due to the Lanthanoid contraction.

- (d) The ionic radii decreases as charge on the cation increases (i.e., higher oxidation state). e.g.



- (e) For ions having same oxidation states, the ionic radii decreases with increase in atomic number e.g.

For 3d-series

	Sc^{2+}	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
Ionic radii (in Å)	0.95	0.90	0.88	0.84	0.80	0.76	0.74	0.72	0.69

Illustration 3: In a transition series, with an increase in atomic number, the atomic radius does not change very much. Why is it so? **(JEE MAIN)**

Sol: With increase in atomic number along a transition series, the nuclear charge increases which tends to decrease the size of the atom. But, the addition of electrons in the d-subshell increases the screening effect which counterbalances the increased nuclear charge. Hence, along a transition series the atomic radius does not change very much.

3.2 Atomic Volume and Density

- (a) The size decreases along the period and, therefore, atomic volume also decreases along the period.
- (b) Atomic volumes are smaller than group 1 and 2 members i.e. s-block elements.
- (c) The density, however, increases along the period.

3.3 Melting and Boiling Points

- (a) All the transition elements have a higher melting point as compared to s-block elements due to strong metallic bonding as well as unpaired d-electrons leading to covalence.
- (b) It is evident from that the melting point of transition metals or a given series increases on moving left to right in a period and attains a maximum value and after that the m.p. goes on decreasing towards the end of period. This is due to the fact that the strength of inter particle bonds in transition elements is also directly related to the number of half-filled d-orbitals. In the beginning, the number of unpaired electrons in d-orbitals increases till the middle of the period (d^1 to d^5). After this, the pairing of electrons occurs in d-orbitals (d^6 to d^{10}). An increase in inter atomic bonds due to the increase in number of unpaired electron results in higher m.p.

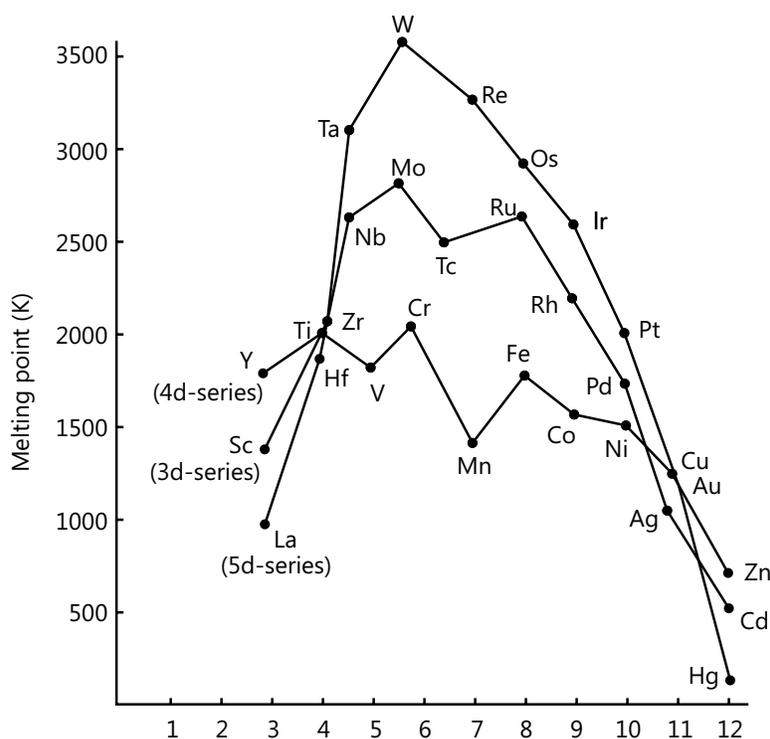


Figure 31.2: Trends in melting points of different group

3.4 Metallic Character

- (a) All the transition metals possess one or two electrons in their outermost shell and thus exhibit metallic nature.
- (b) All are hard, ductile and malleable solids with strong metallic bonding (except mercury which is liquid) and possess hcp, bcc or ccp crystal lattices.
- (c) Transition metals show a gradual decrease in electropositive character on moving along the period.
- (d) Strong metallic bonding in transition metals is due to greater effective nuclear charge and a large number of valence electrons (inner d-subshell and outermost s-subshell).
- (e) Due to strong metallic bonding, transition metals are hard, possess high densities and high enthalpies for atomization.

- (f) Due to metallic bonding, these are good conductors of heat and electricity.
- (g) Transition metals form numerous useful alloys with other metals.

3.5 Enthalpies of Atomisation

Transition elements have a high enthalpy of atomization due to strong interatomic attraction. Greater the number of valency electrons, stronger is the resultant bonding and higher is the enthalpy of atomization. The members of 4d and 5d-series have greater enthalpy of atomization than those of 3d-series. Thus, they form metal-metal bonding frequently in their compounds.

3.6 Ionization Energy

- (a) The ionization energy (IE) of d-block elements lies in between s- and p-block elements showing less electropositive character than s-block.
- (b) Smaller atomic size and a fairly high IE is noticed for transition metals.
- (c) IE values first increase up to $_{25}\text{Mn}$ and then become irregular or constant values due to irregular trend of atomic size after $_{25}\text{Mn}$ in 3d-series. Similar trend is noticed in 5d- and 6d-series.
- (d) The magnitude of ionization energies give an idea about the relative stabilities of various oxidation states of transition elements.

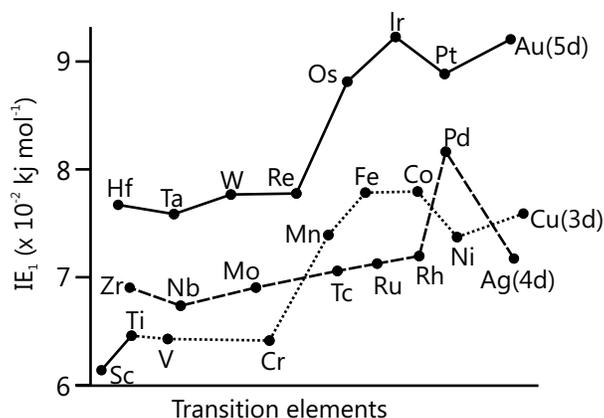


Figure 31.3: Ionization energies of transition elements

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The ionization energy of 5-d series are higher than that of 3-d and 4-d series due to the poor shielding effect of 4-f electrons present in 3-d series

Ionization energy of Zn, Cd and Hg are abnormally higher on account of greater stability of s-subshell

Nikhil Khandelwal (JEE 2010 AIR 443)

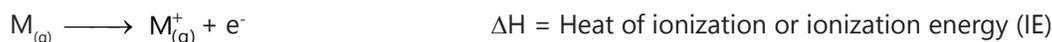
Illustration 4: In the series Sc(Z = 21) to Zn(Z = 30), the enthalpy of atomization of zinc is the lowest, i.e. 125 kJ mol⁻¹. Why? **(JEE ADVANCED)**

Sol: In the formation of metallic bonds, no electrons from 3d-orbitals are involved in case of zinc, while in all other metals of the 3d series, electrons from the d-orbitals are always involved in the formation of metallic bond. This is why the enthalpy of atomization of zinc is the lowest in the series.

3.7 Reactivity

(a) Transition metals are less reactive than s-block elements. Their low reactivity is due to:

- (i) High ionization energy.
- (ii) Existence of metallic bonding among atoms which gives rise to higher heat of sublimation.



More negative the value of ΔH for the change, lesser is the energy level for $M_{(aq)}^+$ and greater will be the stability of that oxidation state in aqueous solution.

3.8 Variable Valency and Oxidation State

(a) Most of the transition elements show variable valencies or different oxidation states because of incomplete d-subshell. The variable oxidation states of transition elements are due to the participation of ns and (n - 1) d electrons in bonding.

(b) It is thus evident that for the first five transition elements, the minimum oxidation state is given by the electrons in outermost s-subshell and the maximum oxidation state by the total number of ns and (n - 1) d-subshell electrons.

- (i) ${}_{21}\text{Sc}$ shows +2 and +3 (due to $4s^2$ and $3d^1$ electrons)
- (ii) ${}_{22}\text{Ti}$ shows + 2, +3 and +4 (due to $4s^2$ and $3d^2$ electrons)
- (iii) ${}_{23}\text{V}$ shows +2, +3, +4, +5 (due to $4s^2$ and $3d^3$ electrons)
- (iv) ${}_{24}\text{Cr}$ shows +2, +3, +4, +5, +6 (due to $4s^1$ and $3d^5$ electrons)
- (v) ${}_{25}\text{Mn}$ shows +2 to +7 (due to $4s^2$ and $3d^5$ electrons)

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- The transition elements in their lower oxidation states (+2 and +3) usually form ionic compounds. In higher oxidation state, compounds are normally covalent. For example, Mn in MnCl_2 has Mn^{2+} ion whereas in KMnO_4 , Mn exists in +7 state of covalent nature.
- Some transition metals also exhibit zero oxidation state in their compounds such as carbonyls. Ni and Fe in $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$ have zero oxidation state.
- The highest oxidation states of transition metals are found in their compounds with fluorine and oxygen. This is due to higher electronegativity and small atomic size of fluorine and oxygen. Eg. MnO_4^-

Neeraj Toshniwal (JEE 2009 AIR 21)

Illustration 5: Which metal in the first series of transition metal exhibits +1 oxidation state most frequently and why? **(JEE ADVANCED)**

Sol: Copper, because it will achieve a completely filled d-orbital and a stable configuration on losing an electron.

3.9 Colour

Substances appear coloured when they absorb light of a particular wavelength in the visible region of the spectrum and transmit light of other wavelengths. The colour which we see is the colour of the transmitted wavelengths. In other words, the colour of the compound observed by us is the complementary colour of the colour absorbed by the compound.

In the s- and p-block elements, there cannot be any d-d transitions and the energy needed to promote the s or p electrons to a higher level is much greater and may correspond to ultraviolet region, in which case the compound will not appear coloured to the eye.

Table 31.1: Color spectrum

Wavelength absorbed in nm	Colour absorbed	Colour observed
< 400	UV region	White/colourless
400–435	Violet	Yellow-green
435–480	Indigo	Yellow
480–490	Green-blue	Orange
490–500	Blue-green	Red
500–560	Green	Purple
560–580	Yellow-green	Violet
580–595	Yellow	Indigo
595–605	Orange	Green-blue
605–750	Red	Blue-green
> 750	Infra-red	White/colourless

Illustration 6: Transition metal ions like Cu^+ , Ag^+ , Zn^{2+} , Hg^{2+} and Cd^{2+} are colourless. Explain. **(JEE ADVANCED)**

Sol: Due to forbidden transition some metal ions are colourless. All the ions reported above have no unpaired electrons in them and the d-orbital $[(n-1)d^{10}]$ is also completely filled. Thus, due to d-d transition above mentioned metal ions are colourless.

3.10 Magnetic Properties

Magnetic Properties: When a substance is placed in a magnetic field of strength H , the intensity of the magnetic field on the substance may be greater than or less than H .

Diamagnetic: The substances which are weakly repelled by a magnetic field; absence of unpaired electrons.

Paramagnetic: The substances which are weakly attracted by the magnetic field and lose their magnetism when removed from the field; presence of unpaired electrons.

Paramagnetism is expressed by magnetic moment,

$$\mu = \sqrt{n(n+2)} \text{ B.M.}$$

n = Number of unpaired electrons

B.M. = Bohr Magneton, unit of magnetic moment

Illustration 7: The paramagnetic character in 3d transition series increases up to Cr and then decreases. Explain (JEE MAIN)

Sol: As number of unpaired electron increases paramagnetic nature increases. The number of unpaired electrons increases from ${}_{21}\text{Sc}$: $[\text{Ar}]3d^1, 4s^2$ to ${}_{24}\text{Cr}$: $[\text{Ar}] 3d^5, 4s^1$ and after chromium, the pairing of electrons takes place and thus number of unpaired electrons goes on decreasing continuously to ${}_{30}\text{Zn}$: $[\text{Ar}] 3d^{10}, 4s^2$.

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The magnetic properties of d-block elements are due to the only spin value of the unpaired electrons present in d-orbital while in the case of f-block elements, it is due to both the orbital motion as well as spin contribution.

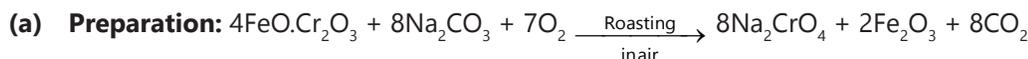
Magnetic moment for d-block elements: $\mu = \sqrt{n(n+2)}$ B.M. (where n is the number of unpaired electrons)

Magnetic moment of f-block elements: $\mu = \sqrt{4s(s+1) + \ell(\ell+1)}$. (where s is sum of spin quantum number and ℓ , the angular momentum quantum number)

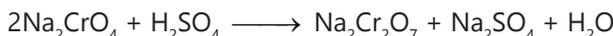
Aman Gour (JEE 2012 AIR 230)

4. SOME IMPORTANT COMPOUNDS OF d-BLOCK ELEMENTS

4.1 Chromate and Dichromate



The roasted mass is extracted with water when Na_2CrO_4 goes into the solution leaving behind insoluble Fe_2O_3 . The solution is treated with calculated amount of H_2SO_4 .



The solution is concentrated when less soluble Na_2SO_4 crystallizes out. The solution is further concentrated when crystals of $\text{Na}_2\text{Cr}_2\text{O}_7$ are obtained. Then a hot saturated solution of $\text{Na}_2\text{Cr}_2\text{O}_7$ is treated with KCl, then reddish orange crystals of $\text{K}_2\text{Cr}_2\text{O}_7$ are obtained on crystallization

(b) $\text{K}_2\text{Cr}_2\text{O}_7$ is preferred to $\text{Na}_2\text{Cr}_2\text{O}_7$ because $\text{Na}_2\text{Cr}_2\text{O}_7$ is hygroscopic but $\text{K}_2\text{Cr}_2\text{O}_7$ is not.

(c) Similarities between hexavalent Cr & S-compounds:

(i) SO_3 & $\text{CrO}_3 \rightarrow$ Both acidic

(ii) CrO_4^{2-} & SO_4^{2-} Isomorphous

(iii) SO_2Cl_2 & $\text{CrO}_2\text{Cl}_2 \xrightarrow{\text{OH}^-} \text{SO}_4^{2-}$ & CrO_4^{2-} respectively

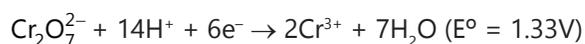
(iv) $\text{SO}_3\text{Cl}^- + \text{CrO}_3\text{Cl}^- \xrightarrow{\text{OH}^-} \text{SO}_4^{2-}$ & CrO_4^{2-}

(v) CrO_3 & $\text{B}(\text{SO}_3)$ has same structure $\begin{array}{c} \text{O} \quad \text{O} \quad \text{O} \\ \parallel \quad \parallel \quad \parallel \\ -\text{Cr}-\text{O}-\text{Cr}-\text{O}-\text{Cr}- \\ \parallel \quad \parallel \quad \parallel \\ \text{O} \quad \text{O} \quad \text{O} \end{array}$

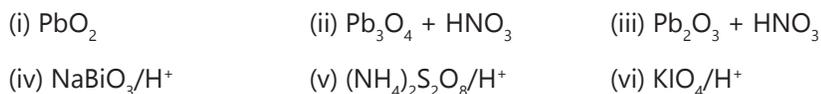
(vi) Potassium dichromate reacts with hydrochloric acid and evolves chlorine.



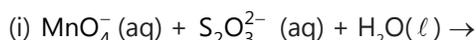
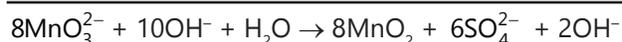
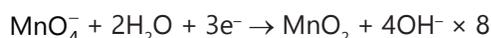
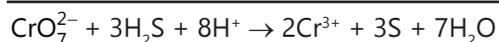
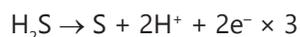
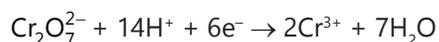
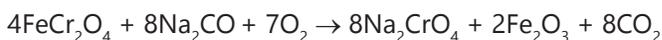
(vii) It acts as a powerful oxidizing agent in an acidic medium (dilute H_2SO_4)



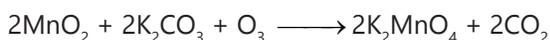
The oxidation state of Cr changes from +6 to +3

In neutral or weakly acidic solution:Conversion of Mn^{+2} to MnO_4^- :**MASTERJEE CONCEPTS**

In the oxidation reactions of KMnO_4 in acidic medium, only H_2SO_4 is used to produce an acidic medium and not HCl or HNO_3 because HCl reacts with KMnO_4 and produce Cl_2 while HNO_3 , itself acts as an oxidising agent.

B Rajiv Reddy (JEE 2012 AIR 11)**Illustration 8:** Complete the equation of following chemical reactions:**(JEE MAIN)****Sol:****(i)** In neutral or faintly alkaline solutions**(ii)** In acidic solutions**Illustration 9:** Write steps involved in the preparation of**(JEE ADVANCED)****(i)** Mn_2CrO_4 from chromite ore and**(ii)** K_2MnO_4 from pyrolusite ore.**Sol:** **(i)** Chromite ore is fused with sodium carbonate in excess of air.

Chromite ion Sod. Chromites

(ii) K_2MnO_4 from pyrolusite ore

4.3 Silver Nitrate

Properties:

(i) It is called lunar caustic because in contact with skin it produces a burning sensation that of caustic soda with the formation of finely divided silver (black colour).

(ii) Thermal decomposition



(iii) $6\text{AgNO}_3 + 3\text{I}_2 + 3\text{H}_2\text{O} \rightarrow 5\text{AgI} + \text{AgIO}_3 + 6\text{HNO}_3$ (excess)

(iv) $\text{Ag}_2\text{SO}_4 \xrightarrow{\Delta} 2\text{Ag} + \text{SO}_2 + \text{O}_2$

(v) A - $(\text{AgNO}_3) \xrightarrow[\text{added}]{\text{B}}$ white ppt appears quickly

B - $(\text{Na}_2\text{S}_2\text{O}_3) \xrightarrow[\text{added}]{\text{A}}$ It takes time to give white ppt.

(vi) $\text{Ag}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \xrightarrow{\Delta} \text{Ag}_2\text{S} + \text{H}_2\text{SO}_4$

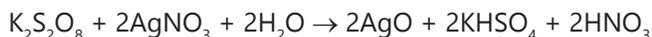
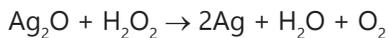
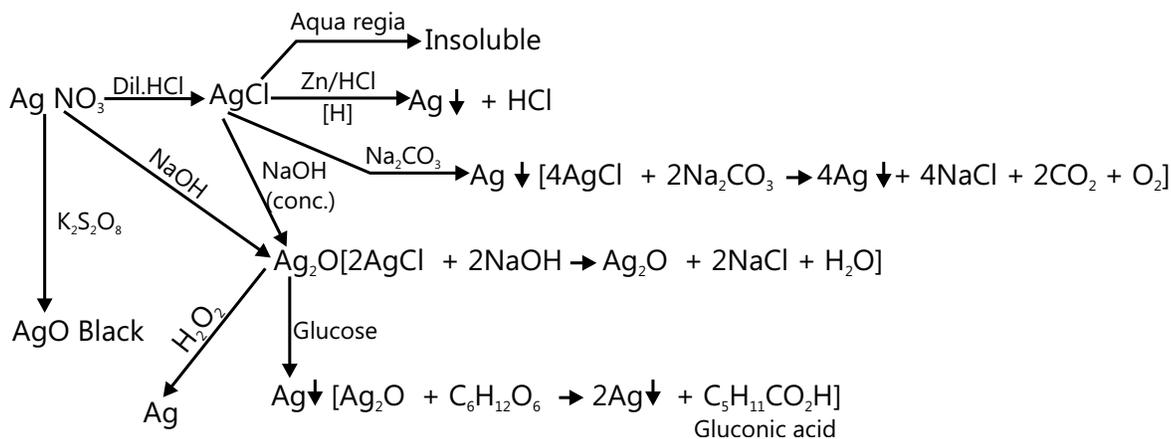
AgCl , AgBr , AgI (but not Ag_2S) are soluble in $\text{Na}_2\text{S}_2\text{O}_3$ forming $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{-3}$ complexes

(vii) $\text{AgBr} + \text{AgNO}_3 \xrightarrow{\text{KBr}} \underset{\text{Pale yellow ppt.}}{\text{AgBr}} \downarrow + \text{KNO}_3$

Heating effect: $2\text{AgNO}_3 \xrightarrow{212^\circ\text{C}} 2\text{AgNO}_2 + \text{O}_2$



(viii)



MASTERJEE CONCEPTS

AgO is supposed to be paramagnetic due to d^9 configuration. But actually it is diamagnetic and exists as $Ag^I[Ag^{III}O_2]$

Silvering of mirror: The process of depositing a thin and uniform layer of silver on a clean glass surface is known as **silvering of mirrors**. It is employed for making looking glasses, concave mirrors and reflecting surfaces. The process is based on the reduction of ammoniacal silver nitrate solution by some reducing agent like formaldehyde, glucose, etc. The silver film deposited on the glass is first coated with a varnish and finally painted with red lead to prevent its loss due to scrap.

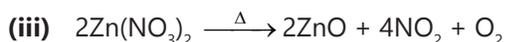
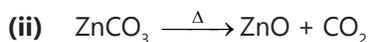
Rohit Kumar (JEE 2012 AIR 79)

4.4 Zinc Compounds

1. Zinc oxide, ZnO (Chinese white or philosopher's wool)

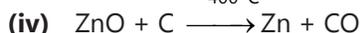
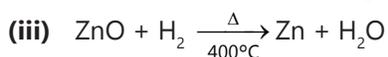
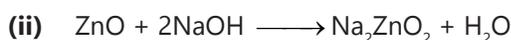
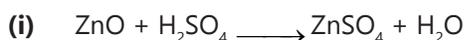
It found in nature as zincite or red zinc ore.

(a) Preparation:



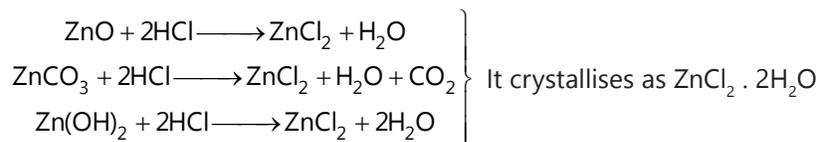
(b) Physical Properties: It is a white powder, which becomes yellow on heating and again turns white on cooling, is insoluble in water, and sublimes at $400^\circ C$.

(c) Chemical Properties:

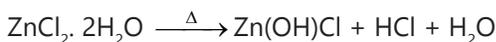


2. ZnCl₂ (Zinc Chloride)

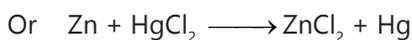
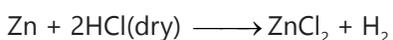
(a) Preparation:



Anhydrous $ZnCl_2$ cannot be made by heating $ZnCl_2 \cdot 2H_2O$ because



To get anh. $ZnCl_2$:

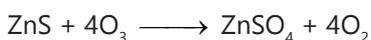
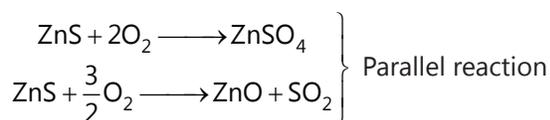
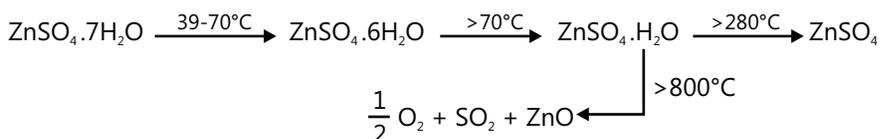


(b) Properties:

- (i) It is deliquescent white solid (when anhydrous)
- (ii) $\text{ZnCl}_2 + \text{H}_2\text{S} \longrightarrow \text{ZnS}$
- (iii) $\text{ZnCl}_2 + \text{NaOH} \longrightarrow \text{Zn(OH)}_2 \xrightarrow{\text{excess}} \text{Na}_2[\text{Zn(OH)}_4]$
- (iv) $\text{ZnCl}_2 + \text{NH}_4\text{OH} \longrightarrow \text{Zn(OH)}_2 \xrightarrow{\text{excess}} [\text{Zn(NH}_3)_4]^{2+}$

(c) Uses:

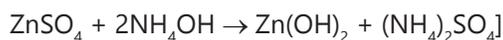
- (i) Used for impregnating timber to prevent destruction by insects
- (ii) As a dehydrating agent when anhydrous
- (iii) ZnO, ZnCl₂ used in dental filling

3. ZnSO₄ (Zinc Sulphate)**(a) Preparation:****(b) Properties****(c) Uses:**

- (i) In eye lotion
- (ii) Lithopone making ($\text{ZnS} + \text{BaSO}_4$) as white pigment

Illustration 10: The addition of NH_4OH to ZnSO_4 solution produces white precipitate but no precipitate is formed if it contains NH_4Cl . Why? **(JEE ADVANCED)**

Sol: NH_4OH is a weak hydroxide. It ionizes slightly, furnishing OH^- ions. However, the OH^- ions are sufficient to cause the precipitation of Zn(OH)_2 as its ionic product exceeds the K_{sp} .



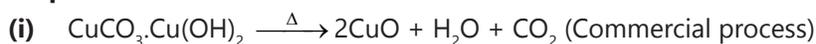
White ppt

In the presence of NH_4Cl , the ionization of NH_4OH is further suppressed and sufficient OH^- ions are not available to cause precipitation as the ionic product does not exceed the K_{sp} .

MASTERJEE CONCEPTS

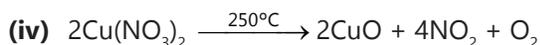
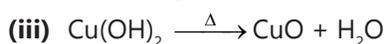
Zinc oxide is white at room temperature but turns yellow on heating

Krishan Mittal (JEE 2012, AIR 199)

4.5 Copper Compounds**1. CuO:****(a) Preparation:**

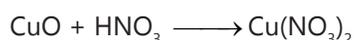
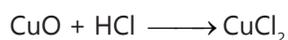
Malachite green

(Native Cu-carbonate)

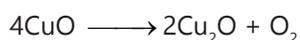
**(b) Properties:**

(i) CuO is insoluble in water

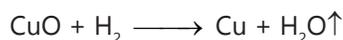
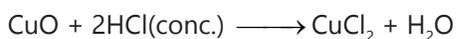
(ii) Readily dissolves in dil. acids



(iii) It decomposes when, heated above 1100°C



(iv) CuO is reduced to Cu by H₂ or C under hot condition

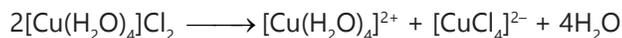
**2. CuCl₂:****(a) Preparation:****(b) Properties:**

(i) It is crystallized as CuCl₂·2H₂O of Emerald green colour

(ii) Dilute solution in water is blue in colour due to the formation of [Cu(H₂O)₄]²⁺ complex.

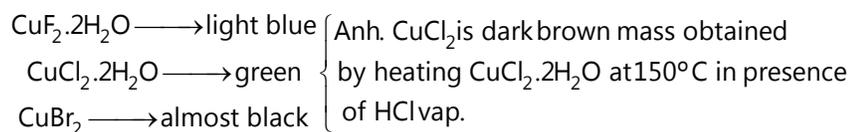
(iii) conc. HCl or KCl added to dil. solution of CuCl₂, the colour changes into yellow, owing to the formation of [CuCl₄]²⁻

(iv) The conc. aq. solution is green in colour having the two complex ions in equilibrium

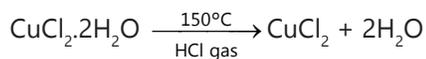


(v) $\text{CuCl}_2 \longrightarrow \text{CuCl}$

- $\text{CuCl}_2 + \text{Cu-turning} \xrightarrow{\Delta} 2\text{CuCl}$
- $2\text{CuCl}_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \longrightarrow 2\text{CuCl} + 2\text{HCl} + 2\text{H}_2\text{SO}_4$
- $2\text{CuCl}_2 + \text{Zn/HCl} \longrightarrow 2\text{CuCl} + \text{ZnCl}_2$
- $\text{CuCl}_2 + \text{SnCl}_2 \longrightarrow \text{CuCl} + \text{SnCl}_4$

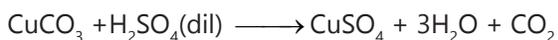
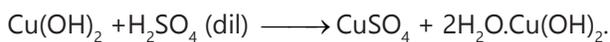


CuI_2 does not exist

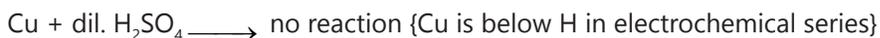


3. CuSO_4 :

(a) Preparation:

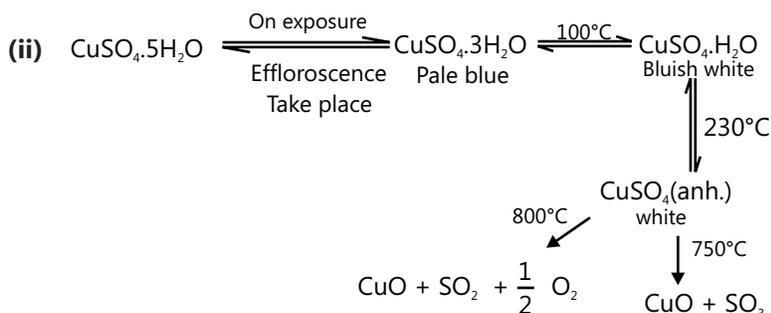


(Scrap)



(b) Properties:

(i) It is crystallized as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$



MASTERJEE CONCEPTS

Anhydrous copper sulphate (white) regains its blue colour when moistened with a drop of water (it is a test of water).

T P Varun (JEE 2012, AIR 640)

Illustration 11: Blue copper sulphate turns white on heating. Why ?

(JEE MAIN)

Sol: Hydrated copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) is blue which on heating loses its water of crystallization to form anhydrous CuSO_4 a white compound. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \xrightarrow{\text{Heat}} \text{CuSO}_4 + 5\text{H}_2\text{O}$

Illustration 12: Cu^+ ion is not stable in an aqueous solution. Why ?

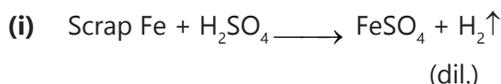
(JEE ADVANCED)

Sol: $\text{Cu}^{2+}(\text{aq})$ is much more stable than $\text{Cu}^+(\text{aq})$. This is because although the second ionization enthalpy of copper is large but $\Delta_{\text{hyd}} H$ for $\text{Cu}^{2+}(\text{aq})$ is much more negative than that for $\text{Cu}^+(\text{aq})$ and therefore it more than compensates for the second ionization enthalpy of copper. Thus many copper (I) compounds are unstable in aqueous solution and undergoes disproportionation as follows $2\text{Cu}^+(\text{aq}) \longrightarrow \text{Cu}^{2+}(\text{aq}) + \text{Cu}(\text{s})$

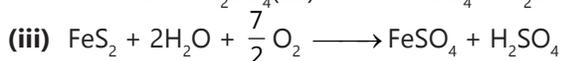
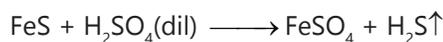
4.6 Iron Compounds

1. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$:

(a) Preparation:

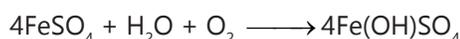


(ii) From Kipp's waste

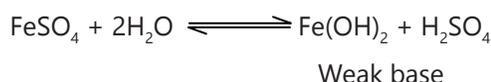


(b) Properties:

(i) It undergoes aerial oxidation forming basic ferric sulphate



(iii) Aq. Solution is acidic due to hydrolysis



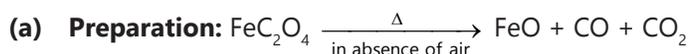
(iv) It is a reducing agent

- $\text{Fe}^{2+} + \text{MnO}_4^- + \text{H}^+ \longrightarrow \text{Fe}^{3+} + \text{Mn}^{2+} + \text{H}_2\text{O}$
- $\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + \text{H}^+ \longrightarrow \text{Fe}^{3+} + \text{Cr}^{3+} + \text{H}_2\text{O}$
- $\text{Au}^{3+} + \text{Fe}^{2+} \longrightarrow \text{Au} + \text{Fe}^{3+}$
- $\text{Fe}^{2+} + \text{HgCl}_2 \longrightarrow \text{Hg}_2\text{Cl}_2 \downarrow + \text{Fe}^{3+}$

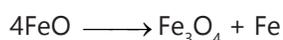
White ppt.

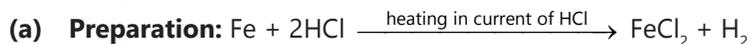
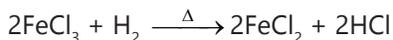
(v) It forms double salt. Example $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$

2. FeO (Black):

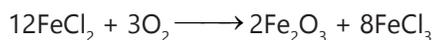


(b) **Properties:** It is stable at high temperature and on cooling slowly disintegrates into Fe_3O_4 and iron

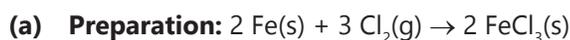


3. FeCl₂:**OR****(b) Properties:**

- (i) It is deliquescent in air like FeCl₃
- (ii) It is soluble in water, alcohol and ether also because it is sufficiently covalent in nature
- (iii) It volatilizes at about 1000°C and vapour density indicates the presence of Fe₂Cl₄. Above 1300°C density becomes normal
- (iv) It oxidizes on heating in air



- (vi) It can exist as a different hydrated form

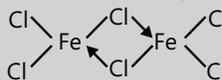
**4. FeCl₃:**

(b) **Properties:** Anhydrous ferric chloride is prepared by heating metallic iron in a stream of dry chlorine gas.

- (i) FeCl₃ solid is almost black. It sublimes at about 300°C, giving a dimeric gas.
- (ii) FeCl₃ dissolves in both ether and water, giving solvated monomeric species.
- (iii) Iron (III) chloride is usually obtained as yellow-brown lumps of the hydrate FeCl₃·6H₂O.
- (iv) This is very soluble in water and is used both as an oxidizing agent, and as a mordant in dyeing.

MASTERJEE CONCEPTS

Anhydrous ferric chloride is soluble in non-polar solvents like ether, alcohol, etc as it possesses covalent bonds and has a chlorine bridge structure.

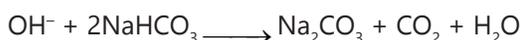
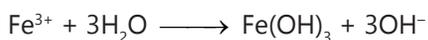


Saurabh Chatterjee (JEE Advanced 2013, AIR)

Illustration 13: FeCl₃(aq) gives CO₂ with NaHCO₃(aq) Explain.

(JEE ADVANCED)

Sol: Fe³⁺ ions hydrolyse to form alkaline solution which reacts with NaHCO₃ to liberate CO₂.



f-BLOCK ELEMENTS

1. INTRODUCTION

1.1 Inner transition elements/f-block elements

The elements in which the additional electrons enter $(n - 2)f$ orbitals are called inner transition elements. The valence shell electronic configuration of these elements can be represented as $(n-2) f^{0,2,\dots,14}(n-1)d^{0,1,2}ns^2$. These are also called as f-block elements because the extra electrons go to f-orbitals which belong to $(n-2)$ th main shell. 4f-block elements are also called Lanthanides or rare earths. Similarly, 5f-block elements are called actinides or actinones. The name Lanthanides and Actinides have been given due to close resemblance with Lanthanum and Actinium respectively. Lanthanides constitute the first inner transition series while actinides constitute the second inner transition series.

General Characteristics:

- 1. Electronic Configuration :** $[\text{Xe}] 4f^{n+1}5d^06s^2$ or $[\text{Xe}] 4f^n5d^16s^2$
- 2. Oxidation state:** They readily form M^{+3} ions. Some of them also exhibit oxidation states of +2 and +4.
- 3. Colouration:** Ions of Lanthanides and Actinides are coloured in the solid state as well as in aqueous solution because of absorption of light due to f-f-transition, since they have partly filled f-orbitals.

Magnetic properties: $\text{La}^{3+}(4f^0)$ and $\text{Lu}^{3+}(4f^{14})$ having no unpaired electrons do not show paramagnetism while all other tri-positive ions of lanthanides are paramagnetic

Illustration 14: What is the basic difference between the electronic configuration of transition and inner transition elements. **(JEE MAIN)**

Sol: General electronic configuration of transition elements = $[\text{Noble gas}] (n - 1) d^{1-10}ns^{1-2}$ and for inner transition elements = $(n - 2) f^{1-14}(n - 1)d^{0-1}ns^{0-2}$. Thus, in transition elements, the last electron enters d-orbitals of the penultimate shell while in inner transition elements, it enters f-orbital of the penultimate shell.

Illustration 15: What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements: 29, 59, 74, 95, 102, 104. **(JEE MAIN)**

Sol: Inner transition elements are those which have incomplete 4f or 5f orbitals. Thus 59, 95 and 102 are inner transition elements.

2. LANTHANIDES AND THEIR PROPERTIES

The lanthanide series of chemical elements comprises the fifteen metallic chemical elements with atomic numbers 57 through 71, from lanthanum through lutetium. These fifteen lanthanide elements, along with the chemically similar elements, scandium and yttrium, are often collectively known as the rare earth elements.

2.1 Lanthanide Contraction

In lanthanides, the additional electron enters the 4f-sub shell but not in the valence-shell i.e. sixth shell. The shielding effect of one electron in 4f-sub-shell by another in the same sub-shell is very little, being even smaller than that of d-electrons, because the shape of f-sub shell is very much diffused, while there is no comparable increase in the mutual shielding effect of 4f-electrons. This results in outermost shell electrons experiencing increasing nuclear attraction from the growing nucleus. Consequently, the atomic and ionic radii go on decreasing as we move from La_{57} to Lu_{71} .

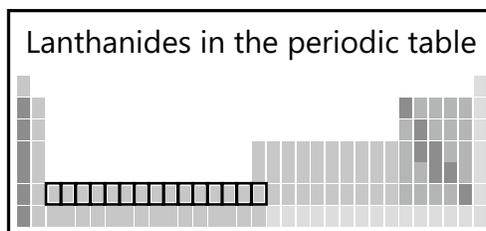


Figure 31.4: Position of lanthanides in the periodic table

Consequence of Lanthanide contraction

- 1. Atomic and ionic radii of post-Lanthanide elements:** The atomic radii of second row transition elements are almost similar to those of the third row transition elements because the increase in size on moving down the group from second to third transition elements is cancelled by the decrease in size due to lanthanide contraction.
- 2. High density of post Lanthanide elements:** It is because of a very small size due to lanthanide contraction and increase in molar mass.
- 3. Basic strength of oxides and hydroxides:** Due to lanthanide contraction, the decrease in size of lanthanides ions, from La^{3+} to Lu^{3+} increases the covalent character (i.e. decreases the ionic character) between Ln^{+3} and OH^- ions in $\text{Ln}(\text{III})$ hydroxides (Fajan's rules). Thus $\text{La}(\text{OH})_3$ is the most basic while $\text{Lu}(\text{OH})_3$ is the least basic. Similarly, there is a decrease in the basic strength of the oxides.
- 4. Separation of Lanthanides:** Due to the similar size (lanthanide contraction) of the lanthanides, it is difficult to separate them. But a slight variation in their properties is utilized to separate.

MASTERJEE CONCEPTS

The existence of lanthanoids in oxidation state of +2 and +4 is due to the fact that empty, half-filled or completely filled f-subshells provide lower energy levels and the ions get stabilized. For example, Ce and Tb show +4 oxidation state by attaining stable f^0 and f^7 configuration respectively whereas Eu and Yb show +2 oxidation state by attaining stable f^7 and f^{14} configuration, respectively.

Mredul Sharda (JEE Advanced 2013)

Illustration 16: Why is the separation of lanthanoids difficult? Explain.

(JEE MAIN)

Sol: All the Lanthanoid ions are of almost the same size, so they have almost similar chemical and physical properties and thus their separation becomes difficult.

Illustration 17: Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behavior with the electronic configuration of these elements.

(JEE MAIN)

Sol: +4 = Ce, Pr, Nd, Tb, Dy. +2 = Eu, Yb. These states are accounted by the extra stability of half-filled and completely filled f-orbitals.

2.2 Chemical Reactivity

These are very reactive metals like alkaline earth metals, however, they show very little difference in their chemical reactivity. On strong heating with H_2 and carbon, these form salt like non-stoichiometric hydrides and carbides. They burn in oxygen to give sesquioxides M_2O_3 (except Ce which gives CeO_2). Their ionic oxides react with water to form

insoluble hydroxides. The oxides and hydroxides being strong base react with CO_2 to form carbonates (M_2CO_3). On burning in sulphur these form sulphides (M_2S_3).

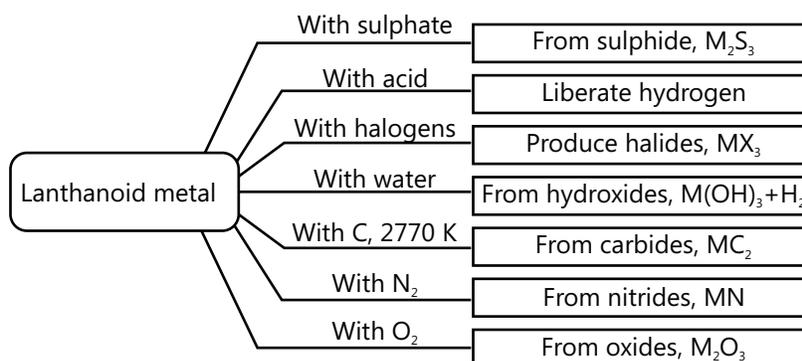


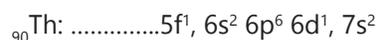
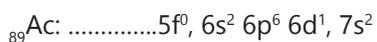
Figure 31.5: Chemical reactivity of lanthanoid metal

2.3 Uses of Lanthanoids

- (i) Pyrophoric alloys, known as **Misch metals**, contain lanthanoids about 90-95% (Ce 40.5%, lanthanum and neodymium 44%), iron 4.5%, calcium, carbon and silicon about 10.5% are used in cigarette and gas lighters, flame throwing tanks, toys, tank and tracer bullets as well as in shells.
- (ii) Any alloy containing 30% Misch metals and 1% Zr are used for making parts of jet engines.
- (iii) Cerium salts are commonly used as catalyst in petroleum cracking (cerium phosphate), volumetric analysis and as oxidizing agent (ceric sulphate), in dyeing cotton, in lead accumulators etc,
- (iv) Oxides of praseodymium (Pr_2O_3) and neodymium (Nd_2O_3) are used in the preparation of coloured glasses and standard filters.
- (v) Oxides of cerium and thorium are used in the preparation of gas lamp mantles.
- (vi) Cerium oxide is used to prepare sunglasses as cerium cuts off heat and ultraviolet light.

3. ACTINIDES AND THEIR PROPERTIES

- (i) The differentiating electron occupies 5f-subshell and thus these elements also have three outermost shells not filled to their capacity. These are called actinoids or actinones.



- (ii) The electronic configuration of actinoids is $[\text{Rn}] 5f^{0-14}, 6d^{0-2}, 7s^2$ where [Rn] stands for radon core. Like lanthanoids, they are placed together because of similar chemical nature.
- (iii) Like lanthanoids contraction, these too show actinoid contraction due to poor shielding effect of 5f-subshells. Thus, atomic size of actinoids too decreases gradually from Ac to Lw.
- (iv) Actinoids show a range of oxidation states, which is due to comparable energies of 5f, 6d and 7s-orbitals. The general oxidation state of actinoids is +3; the elements in the first half of the series show higher oxidation states.
- (v) All these elements are strong reducing agents and are very reactive metals. Actinoids are radioactive and, therefore, it is difficult to study their chemical nature. However, relatively more stable isotopes of these elements beyond uranium have been discovered and the chemistry of these elements has been studied to an extent by using radiotracer techniques.

Like lanthanoids, they react with oxygen, halogens, hydrogen, sulphur and acids.

Uses of Actinoids: Only U, Th have found applications in nuclear reactions undergoing nuclear fission to produce nuclear power and nuclear bombs.

MASTERJEE CONCEPTS

The 5f orbitals extend in space beyond 6s and 6p orbitals and participate in bonding.

Vaibhav Krishnan (JEE 2009, AIR 22)

Illustration 18: The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. **(JEE MAIN)**

Sol: This difference is due to occurrence of a wide range of oxidation states in actinoids. Also, their radioactivity causes a hindrance in their study.

POINTS TO REMEMBER

- General electronic configuration of d-block elements is $(n-1)d^{1-10}ns^{0,1,2}$ and that of f-block element is $(n-2)f^{0,2,....,14}(n-1)d^{0,1,2}ns^2$
- Their melting and boiling points are high which are attributed to the involvement of $(n-1)d$ electrons resulting in strong metallic bonds.
- Successive ionisation enthalpies do not increase as steeply as in the main group elements with increasing atomic number. Hence, the loss of variable number of electrons from $(n-1)d$ orbitals is not energetically unfavourable.
- Ionisation energies where the electron is removed from half-filled or completely filled orbitals are especially large. Hence, Zn^{3+} is not formed.
- The metals, in addition to variable oxidation states, they exhibit paramagnetic behaviour, catalytic properties and tendency for the formation of coloured ions, interstitial compounds and complexes.
- Reactivity of these elements is calculated as a sum of heat of sublimation, ionization enthalpy as well as heat of hydration.
- The transition elements are sufficiently electropositive to dissolve in mineral acids. Of the first series, with the exception of copper, all the metals are relatively reactive.
- The transition metals react with a number of non-metals like oxygen, nitrogen, sulphur and halogens to form binary compounds. The first series transition metal oxides are generally formed from the reaction of metals with oxygen at high temperatures.
- These oxides dissolve in acids and bases to form oxometallic salts.
- The two series of inner transition elements, lanthanoids and actinoids constitute the f-block of the periodic table. With the successive filling of the inner orbitals, 4f, there is a gradual decrease in the atomic and ionic sizes of these metals along the series (lanthanoid contraction). This has far reaching consequences in the chemistry of the elements succeeding them.
- Lanthanum and all the lanthanoids are rather soft white metals. They react easily with water to give solutions giving +3 ions. The principal oxidation state is +3, although +4 and +2 oxidation states are also exhibited by some occasionally.