

# d & f-Block Elements

## d-Block Elements

- The d-block of the periodic table contains the elements of the group 3-12 in which the d-orbitals are progressively filled in each of the four long periods.
- In these elements, the last electron enters  $(n - 1)$  d-subshell (d-orbitals of the penultimate orbit), i.e.,  $(n - 1)$  d-subshell is gradually filled up. The configuration varies from  $(n - 1)d^1ns^2$  to  $(n - 1)d^{10}ns^2$ .
- These are present between s-block and p-block elements. The properties of these elements are intermediate between the properties of s-block and p-block elements.
- Forty elements belong to d-block. Fourth, fifth, sixth and seventh periods consists of ten elements each.
- There are mainly three series of the transition metals.
  - (i) 3d series (Sc — Zn)
  - (ii) 4d series (Y — Cd)
  - (iii) 5d series (La — Hg)
  - (iv) 6d series (Ac — Uub)

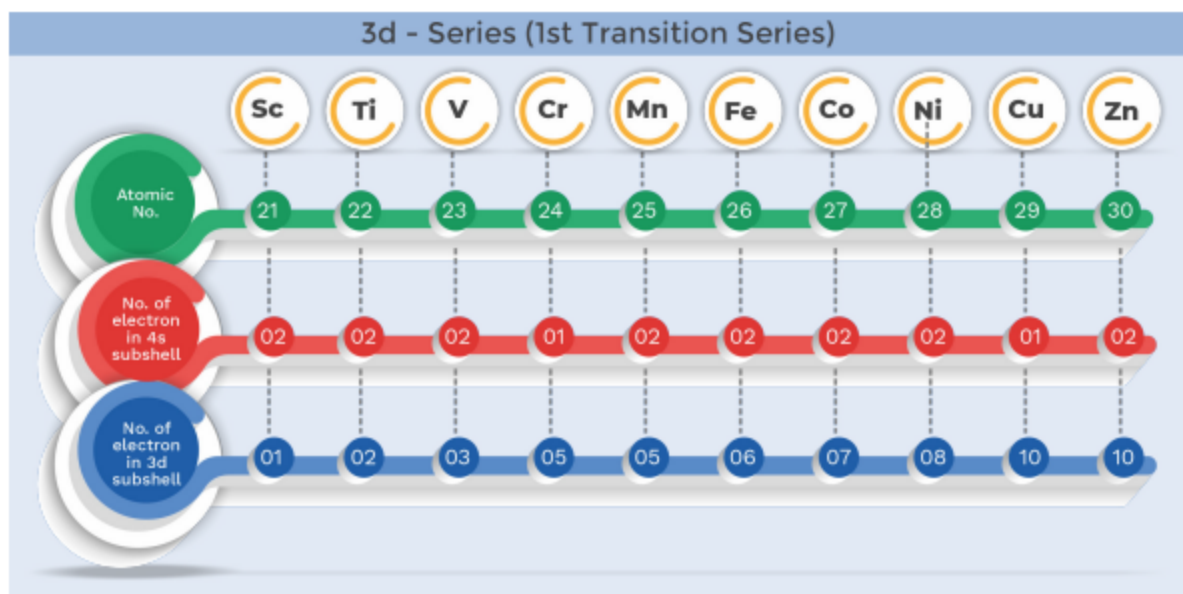
## Definitions

Elements in which last electron enters into d-subshell are known as d-block elements.

## Concept Ladder

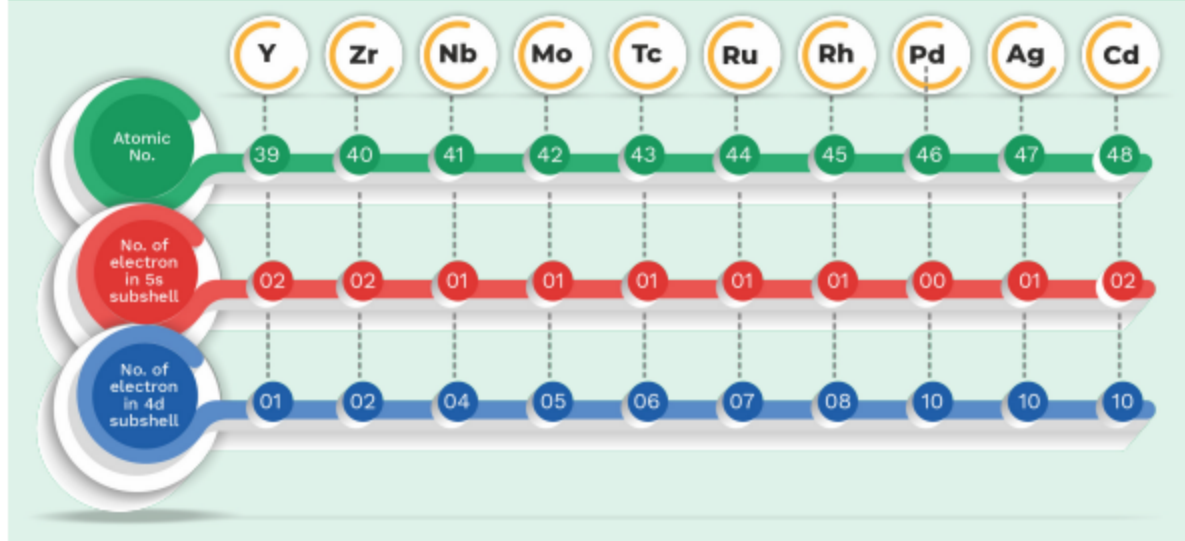


Vertical relationship is due to similar outer electronic configuration while horizontal relationship is due to combined effect of  $s$  and  $z_{eff}$ .

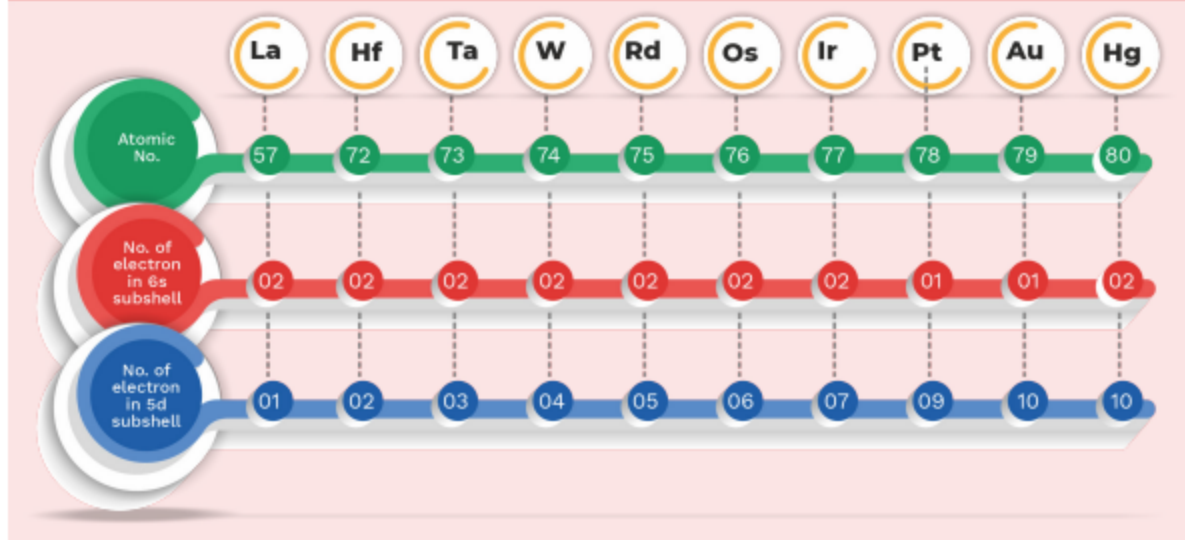




### 4d - Series (2nd Transition Series)



### 5d - Series (3rd Transition Series)







**Q.1** Why chromium is a transition element but zinc is not ?

**A.1** Transition elements have incomplete d-orbitals chromium has  $[\text{Ar}]4s^13d^5$  i.e. Partially filled d-orbitals but in case zinc having  $[\text{Ar}]4s^23d^{10}$  i.e. fully filled d-orbitals.

Hence, chromium is a transition element whereas zinc is not.

### Electronic Configuration :

#### General E.C. of d-block $(n-1)d^{1-10}ns^{0-2}$

For 3d series  $3d^{1-10}4s^{1-2}$

For 4d series  $4d^{1-10}5s^{0-2}$

For 5d series  $5d^{1-10}6s^{1-2}$

For 6d series  $6d^{1-10}7s^{1-2}$

- Most of the elements possess two electrons in the outermost orbital, i.e.,  $ns^2$ . However, some of the elements such as Cr, Cu, Nb, Mo, Ru, Rh, Ag, Pt, Au and Rg have one electron in the outermost orbital, i.e.,  $ns^1$  while one element palladium has no electron on ns orbital.

### Concept Ladder



The d-orbitals of the transition element project to the periphery of an atom more than the other orbitals (s and p). Hence, they are more influenced by the surrounding as well as affecting the atoms or molecules surrounding them.

**Q.2** Write the electronic configuration of following species.

(i) Cr (ii) Zn

**A.2** (i) Cr – Atomic number ( $Z = 24$ )

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

(ii) Zn – Atomic number ( $Z = 30$ )

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

- The irregularities in the observed configuration of Cr  $[\text{Ar}]3d^54s^1$  instead of  $[\text{Ar}]3d^44s^2$ , Cu  $[\text{Ar}]3d^{10}4s^1$ , Mo  $[\text{Kr}]4d^55s^1$ , Pd  $[\text{Kr}]4d^{10}5s^0$ , Au  $[\text{Xe}]4f^{14}5d^{10}6s^1$ , Ag  $[\text{Kr}]4d^{10}5s^1$  are explained on the basis of the concept that half-filled and completely filled d-orbitals is relatively more stable than partially filled d-orbitals.

### Rack your Brain



Why copper is considered to be transition element even its atom has completely filled d-orbital in its ground state.



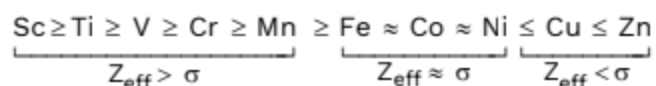
## General Properties of d-Block Elements (Transition elements) :

### (1) Variation in atomic and ionic sizes of transition metals :

- On moving left to right in the period, generally atomic and ionic radius value decreases.
- The atomic radii decrease from Sc to Cr because the effective nuclear charge (ENC) increases.
- The atomic size of Fe, Co, Ni is almost same due to increase in nuclear charge is cancelled by the repulsion between the electrons and increase in shielding effect.
- Cu and Zn have bigger size because the shielding effect decreases and electron-electron repulsion increases.

#### Order of size of 3d series :

(i) Covalent radius :



(ii) Metallic radius :



- The variation in covalent and metallic radius of Cr and Mn is due to the fact that in case of Mn two electrons participate in metallic bond formation whereas in case of Cr three electrons participate in formation of metallic bond, therefore metallic bond strength of Cr is high and its metallic radius is low.

#### Ionic Radii :

- The ionic radii follow the same trend as the atomic radii. For the same oxidation state, the ionic radii generally decreases as the atomic number increases in a particular transition series
- The ionic radii decreases with increase of charge on the ion.



### Concept Ladder



There is hardly increase in atomic size with increase in atomic number, in a series of transition metals.



### Rack your Brain

Why metallic bond strength of Cr is high, and its metallic radius is low?

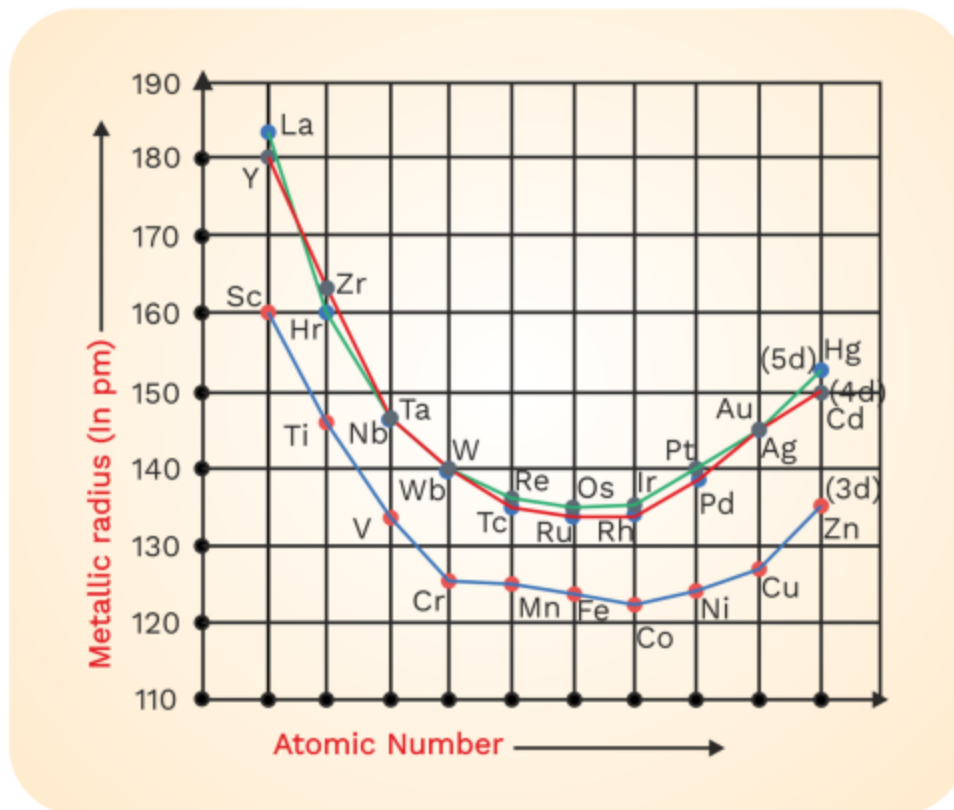


### Previous Year's Question

Which of the following pairs has the same size

[AIPMT-2010]

- (1)  $\text{Zn}^{2+}$ ,  $\text{Hf}^{4+}$       (2)  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$   
 (3)  $\text{Zr}^{4+}$ ,  $\text{Ti}^{4+}$       (4)  $\text{Zr}^{4+}$ ,  $\text{Hf}^{4+}$



### Lanthanoid Contraction

- There is regular decrease in the atomic and ionic radii of the transition metals as the atomic number increases. This is because of filling of 4f orbitals before the 5d orbitals. This contraction in size is quite regular. This is called lanthanoid contraction.
- The conclusion of the **Lanthanoid contraction** is that the 4d and 5d series exhibit similar radii and have very similar physical and chemical properties much more than the expected on the usual family relationship.
- 14 lanthanides between La and Hf, [there is continuous decrease in size from Ce(58) to Lu(71)] Hf size becomes nearly equal to the size of Zr.

### Previous Year's Question



Reason of lanthanoid contraction is

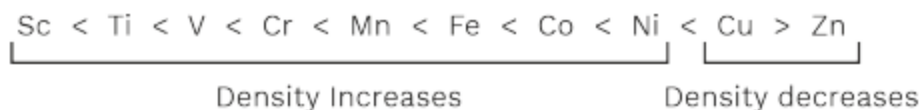
[NEET-2014]

- (1) Decreasing nuclear charge
- (2) Decreasing screening effect
- (3) Negligible screening effect of 'f' orbitals
- (4) Increasing nuclear charge



## (2) Density :

- Density of these elements generally increases with decrease in metallic radius coupled with increase in mass. Thus, from Ti to Cu the significant increase in density may be noted.
- Order of density (3d series) :



- In d-block Os and Ir have highest density and in 3d-series Cu have highest density.

### Order of Density

(Due to Lanthanide Contraction)



## (3) Ionisation Enthalpy :

- There is slight and irregular variation in ionization energies of transition metals due to irregular variation of atomic size. The I.E. of 5d transition series is higher than 3d and 4d transition series because of lanthanoid contraction.
- Order of IP of d-block Elements is  $3d < 5d > 4d$
- There are various exceptions in the IP of d-block elements which is due to the following reasons.
  - Exceptional electronic configuration.
  - Irregular variation in size and  $Z_{\text{eff}}$
  - When  $e^-$  is removed from ns orbital then remaining  $e^-$  is shifted to (n-1) orbital due to which the no. of exchanges are changed and IP also changes.
- On moving from top to bottom in d-block  $Z_{\text{eff}}$  is dominating factor.
- Order of IP of 3d series will be:-  
 $\text{Sc} < \text{Ti} > \text{V} < \text{Cr} < \text{Mn} < \text{Fe} > \text{Co} > \text{Ni} < \text{Cu} < \text{Zn}$

### Rack your Brain



Why are d-block elements dense?

### Concept Ladder



The density of transition element is high as compared to s-block element due to its low atomic volume.

### Previous Year's Question



The correct order of decreasing second ionisation enthalpy of Ti(22), V(23), Cr(24) and Mn(25) is  
**[AIPMT]**

- $\text{Mn} > \text{Cr} > \text{Ti} > \text{V}$
- $\text{Ti} > \text{V} > \text{Cr} > \text{Mn}$
- $\text{Cr} > \text{Mn} > \text{V} > \text{Ti}$
- $\text{V} > \text{Mn} > \text{Cr} > \text{Ti}$



#### (4) Oxidation States :

- d-Block elements show variable oxidation states due to tendency of  $(n-1)d$  as well as  $ns$  electrons to take part in bond formation (except 3<sup>rd</sup> and 12<sup>th</sup> group elements).

#### Absorption of Energy



#### Characteristics features of oxidation state :

- Sc[III B] and Zn[II B] don't show variable oxidation state.
- Most common oxidation state of d-block metals is +2.
- Highest oxidation state of 3d-series element is +7, while those of d-block element is +8.
- Highest oxidation state of d-block element is found in mid of the series [Stability of highest oxidation state is increases upto mid of the series and then start decreasing]
- d-block metals can also show zero oxidation state (low oxidation state) when a complex compound has ligands capable of  $\pi$ -acceptor character in addition to the  $\sigma$ -bonding. For example :  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{Fe}(\text{CO})_5]$
- Highest oxidation state of d-block metals is found in their compounds with oxygen and fluorine.
- The high value of oxidation state of above elements is due to very small size and very high electronegativity of oxygen and fluorine.
- Highest oxidation state of d-block metals with respect to halogen is found to be +6.

#### Concept Ladder



$\text{Cr}^{2+}$  is good reducing agent than  $\text{Fe}^{2+}$  due to low crystal field stabilizing energy (CFSE).

#### Rack your Brain



Why d-block metals have high oxidation state, when compounds are formed with oxygen rather than fluorine.

#### Previous Year's Question



For the four successive transition elements (Cr, Mn, Fe and Co), the stability of +2 oxidation state will be there in which of the following order

[AIPMT-2011]

- (1)  $\text{Cr} > \text{Mn} > \text{Co} > \text{Fe}$
- (2)  $\text{Mn} > \text{Fe} > \text{Cr} > \text{Co}$
- (3)  $\text{Fe} > \text{Mn} > \text{Co} > \text{Cr}$
- (4)  $\text{Co} > \text{Mn} > \text{Fe} > \text{Cr}$

#### Rack your Brain

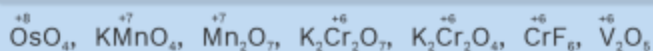


Which transition element does not show the variable oxidation state?





### Higher Oxidation states of some d-block elements



- Moving from left to right the elements having high oxidation state are less stable.  
**Ex :** Fe(+2, +3), Ni(+2) Cu(+1, +2).
- The relative stability of various oxidation states of a given element can be explained on the basis of stability of  $d^0$ ,  $d^5$  and  $d^{10}$  configurations. For example,  $\text{Ti}^{4+}$  ( $3d^04s^0$ ) is more stable than  $\text{Ti}^{3+}$  ( $3d^14s^0$ );  $\text{Mn}^{2+}$  ( $3d^54s^0$ ) is more stable than  $\text{Mn}^{3+}$  ( $3d^44s^0$ );  $\text{Fe}^{3+}$  ( $3d^54s^0$ ) is more stable than  $\text{Fe}^{2+}$  ( $3d^64s^0$ ), etc.

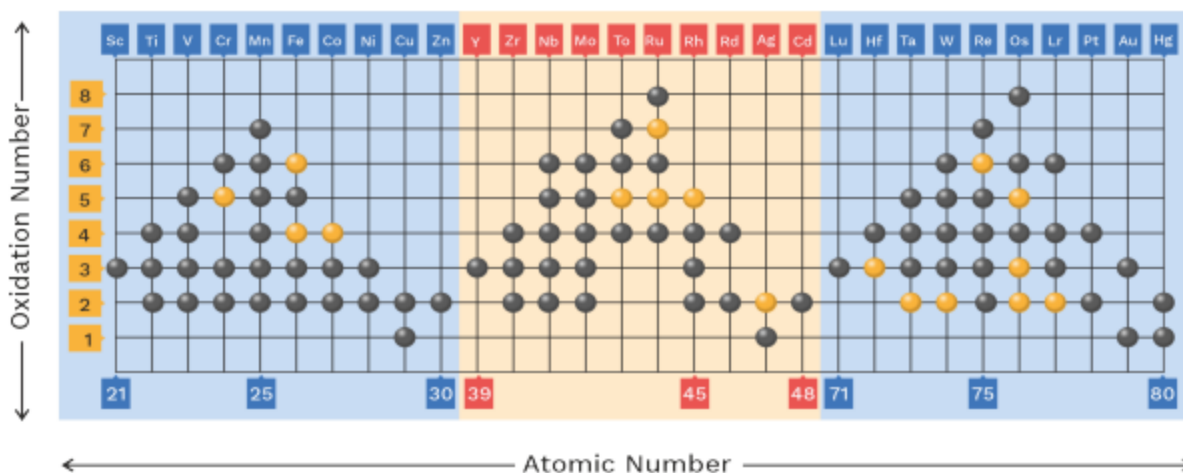
### Concept Ladder



Compounds of d-block metal in their lowest oxidation state are ionic in nature while those of highest oxidation state are covalent in nature.

**Q.3** Why halides lowest oxidation state of d-block metal is quite unstable with fluoride ?

**A.3** Fluorine is a powerful oxidising agent which oxidise the lowest oxidation state into highest.



**Q.4** Which ion is more stable in aqueous medium?  
 (1)  $Ti^{3+}$  (2)  $V^{3+}$  (3)  $Cr^{3+}$  (4)  $Mn^{3+}$

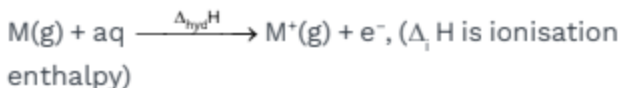
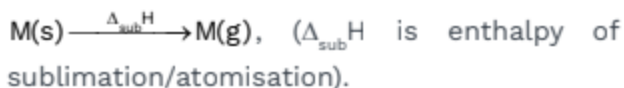
**A.4** (3)  
 $Cr^{3+}$  ion have half-filled electronic configuration ( $t_{2g}^3, e_g^0$ ).

**Q.5** d-Block elements exhibit more oxidation states than f-block elements. Give Reason.

**A.5** d-Block elements exhibit more oxidation states because of less energy gap between d and s subshell whereas f-block elements have large energy gap between f and d subshell.

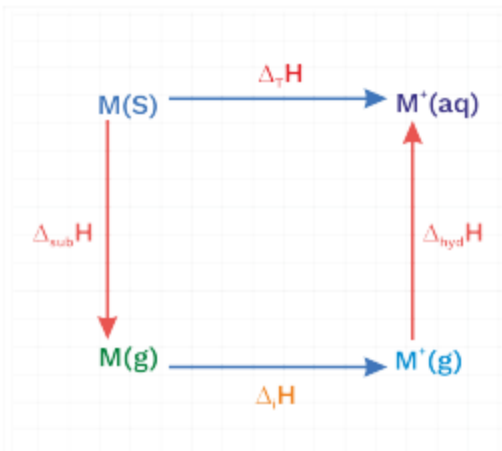
**(5) Standard electrode potential ( $E^\circ$ ) and chemical reactivity :**

- The stability of the compounds in solution depends upon standard electrode potentials rather than I.E.
- Electrode potential values depend upon factors such as enthalpy of sublimation (or atomisation) of the metal, the ionisation enthalpy and the hydration enthalpy, i.e.,



of hydration)

- For the process,  $M(s) \rightarrow M^+(aq) + e^-$ , will be the sum of the three types of enthalpies, i.e.,  $\Delta_r H = \Delta_{sub}H + \Delta_i H + \Delta_{hyd}H$ .
- Thus,  $\Delta_r H$ , is the total enthalpy change when solid metal, M is brought in the aqueous medium in the form of monovalent ion,  $M^+(aq)$ .
- The low value of electrode potential, implies more negative the standard reduction potential of the electrode, more stable is the oxidation state of the transition metal in the aqueous medium.



**Concept Ladder**



Copper having positive  $E^\circ$  values, does not liberate hydrogen from acids. It reacts only with oxidising acids such as  $HNO_3$  and conc.  $H_2SO_4$ .





- The standard reduction potential values,  $E^\circ(M^{2+}/M)$  and  $(M^{3+}/M^{2+})$  of the members of first transition series are given ahead:

Element	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$E^\circ(M^{2+}/M)V$	-1.63	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34	-0.76
$E^\circ(M^{3+}/M^{2+})V$	0.37	0.26	-0.41	+1.57	+0.77	+1.97	—	—	—

### Trends in $M^{2+}/M$

#### Standard Electrode Potentials

- There is irregular trend in the  $E^\circ(M^{2+}/M)$  values, due to irregular variation of I.E. and sublimation energies of the atoms of the members of the transition series.
- Except copper, all other elements have negative reduction potential values, i.e., these elements except copper should have the capacity to liberate hydrogen from dilute acids.  

$$M + 2H^+ (\text{from acid}) \longrightarrow M^{2+} + H_2 \uparrow$$
- In actual practice, the rate of liberation of hydrogen is very slow some of the metals, in fact, get protected by the formation of a thin film of an inert oxide on the surface. Chromium, for example, in spite of its high negative reduction potential value is an unreactive metal as it does not liberate hydrogen due to a thin coating of  $Cr_2O_3$  on its surface.
- Less negative of  $E^\circ$  values along the series is due to increase in the first and second ionisation energies.

### Trends in $M^{3+}/M^{2+}$

#### Standard Electrode Potentials

- $E^\circ$  value for  $Sc^{3+}/Sc^{2+}$  is very low. Hence,  $Sc^{3+}$  is stable. This is due to its noble gas configuration.
- $E^\circ$  values for the redox couple  $M^{3+}/M^{2+}$  indicate that  $Mn^{3+}$  and  $Co^{3+}$  ions are strong oxidising agents.

#### Concept Ladder



The values of  $E^\circ$  for Mn, Zn and Ni are more negative than expected. This is due to extra stability of half-filled d-subshell ( $d^5$ ) in ( $Mn^{2+}$ ) and completely filled ( $d^{10}$ ) in  $Zn^{2+}$ .

#### Previous Year's Question



Four successive members of the first series of the transition metals are listed below. For which one of them the standard potential ( $E^\circ_{M^{2+}/M}$ ) value has a positive sign?

[AIPMT-2012]

- (1) Co (Z = 27)    (2) Ni (Z = 28)  
 (3) Cu (Z = 29)    (4) Fe (Z = 26)



### (6) Magnetic Property :

- On applying magnetic field to substances, mainly two types of magnetic behaviour are observed :

(i) **Diamagnetism :**

Diamagnetic substance is one which is slightly repelled by a magnetic field.

(ii) **Paramagnetism :**

Paramagnetic substance is one which is attracted by a magnetic field.

- Due to presence of unpaired electrons Paramagnetism occurs, each such electron having a magnetic moment associated with its spin angular momentum.
- The magnetic moment is determined by the number of unpaired electrons.

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

Where,  $n$  = number of unpaired electrons.

If all electrons are paired, substance will be diamagnetic and magnetic moment will be zero.

- As it is evident most of the transition metal ions have unpaired electrons in their 'd' orbitals. Hence most of the transition metal ions are paramagnetic in nature. Transition metal ions having  $3d^0$  and  $3d^{10}$  configuration exhibit diamagnetic nature.
- An unpaired electron spins and as it is a charged particle, magnetic field is created due to its spinning.
- The magnetic moment of diamagnetic substance will be zero.
- As the number of unpaired electrons increase the magnetic moment created goes on increasing and hence the paramagnetic nature also increases.
- Transition metal ions having  $d^5$  configuration will have maximum number of unpaired electrons therefore they will be maximum paramagnetic in nature.

### Concept Ladder



Along the 3d-series paramagnetism increases upto the middle and then decreases. (Pairing start)

### Rack your Brain



Among  $V^{3+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$  which one have maximum unpaired electron?

### Concept Ladder



Behaviour of paramagnetic species in solid state is known as ferromagnetism.

### Previous Year's Question



The calculated spin only magnetic moment of  $Cr^{2+}$  ion is :

[NEET-2020]

- (1) 2.84 BM      (2) 3.87 BM  
(3) 4.90 BM      (4) 5.92 BM



Ion	Configuration	Unpaired electrons	Magnetic moment(BM)
Sc <sup>3+</sup>	3d <sup>0</sup>	0	0
Ti <sup>3+</sup>	3d <sup>1</sup>	1	1.73
Ti <sup>2+</sup>	3d <sup>2</sup>	2	2.84
V <sup>2+</sup>	3d <sup>3</sup>	3	3.87
Cr <sup>2+</sup>	3d <sup>4</sup>	4	4.90
Mn <sup>2+</sup>	3d <sup>5</sup>	5	5.92
Fe <sup>2+</sup>	3d <sup>6</sup>	4	4.90
Co <sup>2+</sup>	3d <sup>7</sup>	3	3.87
Ni <sup>2+</sup>	3d <sup>8</sup>	2	2.84
Cu <sup>2+</sup>	3d <sup>9</sup>	1	1.73
Zn <sup>2+</sup>	3d <sup>10</sup>	0	0

**Q.6** Which divalent 3d ion contain maximum unpaired electron.  
(1) Cr<sup>2+</sup>                      (2) Mn<sup>2+</sup>                      (3) Fe<sup>2+</sup>                      (4) Co<sup>2+</sup>

**A.6** (2)  
Mn — 3d<sup>5</sup>, 4s<sup>2</sup> ; Mn<sup>2+</sup> — 3d<sup>5</sup>, 4s<sup>0</sup>.  
So, Mn<sup>2+</sup> have maximum 5 unpaired electrons.



**Q.7** Calculate the magnetic moment of  $\text{Cr}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$  is :

**A.7** Magnetic moment =  $\sqrt{n(n+2)}$  BM (n = unpaired electron)

- (1)  $\text{Cr}^{2+}$  ; E.C. =  $[\text{Ar}]4s^0 3d^4 \Rightarrow n = 4$   
Magnetic moment =  $\sqrt{4(4+2)} = \sqrt{24}$  BM
- (2)  $\text{Mn}^{2+}$  ; E.C. =  $[\text{Ar}]4s^0 3d^5 \Rightarrow n = 5$   
Magnetic moment =  $\sqrt{5(5+2)} = \sqrt{35}$  BM
- (3)  $\text{Fe}^{2+}$  ; E.C. =  $[\text{Ar}]4s^0 3d^6 \Rightarrow n = 4$   
Magnetic moment =  $\sqrt{4(4+2)} = \sqrt{24}$  BM
- (4)  $\text{Co}^{2+}$  ; E.C. =  $[\text{Ar}]4s^0 3d^7 \Rightarrow n = 3$   
Magnetic moment =  $\sqrt{3(3+2)} = \sqrt{15}$  BM

**(7) Formation of coloured ion :**

- d-block compounds are generally coloured due to :
  - (i) Unpaired electron result in d-d transition.
  - (ii) Charge transfer spectrum.
  - (iii) Polarisation.
- A substance appears coloured because it absorbs light at specific wavelengths in the visible part of the electromagnetic spectrum (4000-7000 Å) and transmits or reflects the rest of the wavelengths.
- The frequency of light i.e. absorbed by :
  - (i) Nature of ligand.
  - (ii) Oxidation states of metal.
  - (iii) Size of metal ion.
- d-block metal cation having paired electronic configurations are colourless, whereas those have unpaired electrons are coloured in nature.
- Transition metal compounds are mostly coloured in their solid or in solution states.

**Definitions**

When an electron from a lower energy d-orbital is excited to higher energy d-orbital, the energy of excitation corresponds to the frequency of light absorbed.

**Previous Year's Question**



**Assertion :** Cuprous ion ( $\text{Cu}^+$ ) has unpaired electrons while cupric ion ( $\text{Cu}^{2+}$ ) does not.

**Reason :** Cuprous ion ( $\text{Cu}^+$ ) is colourless where as cupric ion ( $\text{Cu}^{2+}$ ) is blue in the aqueous solution.

[AIIMS]



Colours of some of the first row transition metal ions in aqueous solutions. From left to right

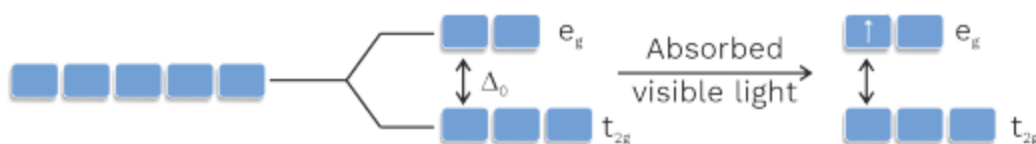


## Formation of Coloured Ions

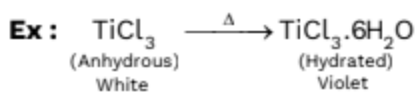
### d-d transition :

- Excitation of unpaired electron from  $t_{2g}$  to  $e_g$  after absorption of visible light.

**Example :**  $Ti^{3+}(3d^1)$



Colour of a complex ion depend on nature of ligand (Strong and weak field ligand) and number of ligands.



### Rack your Brain



Why anhydrous  $CuSO_4$  is colourless but hydrated  $CuSO_4$  is blue in colour?







### (8) Formation of complexes compounds :

- By virtue of their small size, comparatively high nuclear or ionic charge and availability of vacant d-orbitals of suitable energy, these metals exert strong electrostatic attraction on the ligands. The species formed on interaction of metal ions form complexes because of the following reasons :
  - Their size of cation is small.
  - High effective nuclear charge.
  - Availability of vacant (n-1)d-orbitals of appropriate energy.
  - The structure commonly found in such complex are linear (i.e. co-ordination number, C.N. = 2), square.
  - Cobalt form more complex than any other elements.



Metal ion	Ligand	C.N.	Complex ion
$\text{Ag}^+$	$\text{NH}_3$	2	$[\text{Ag}(\text{NH}_3)_2]^+$
$\text{Fe}^{2+}$	$\text{CN}^-$	6	$[\text{Fe}(\text{CN})_6]^{4-}$
$\text{Cu}^{2+}$	$\text{NH}_3$	4	$[\text{Cu}(\text{NH}_3)_4]^{2+}$
$\text{Ni}^{2+}$	$\text{CN}^-$	4	$[\text{Ni}(\text{CN})_4]^{4-}$

### (9) Catalytic Properties :

- d-block elements and their compounds are known to act as good catalyst as they have variable oxidation state. They provide a new path with lower activation energy for the reaction and form unstable intermediate compounds (intermediate compounds theory).

### Concept Ladder



Anhydrous  $\text{CuSO}_4$  is paramagnetic and white but hydrated  $\text{CuSO}_4$  is blue in colour because in presence of  $\text{H}_2\text{O}$  ligand, d-d transition possible.

### Rack your Brain



What is the difference between complexes  $[\text{Cr}(\text{H}_2\text{O})_5(\text{NO}_2)]^{+2}$  and  $[\text{Cr}(\text{H}_2\text{O})_5(\text{ONO})]^{+2}$ ?

### Rack your Brain



Which catalyst is used in the given process?



- The adsorbed reactants provide a large surface area for adsorption, which are finely divided metals or their compounds react faster due to the closer contact (Adsorption theory).
- Catalytic property is probably due to the utilisation of  $(n-1)d$ -orbitals or formation of interstitial compounds.

### Previous Year's Question



Which of the following transition metal is used as a catalyst

[AIPMT]

- (1) Nickel      (2) Cobalt  
(3) Gold        (4) Both (1) and (2)

Catalysts	Uses
$\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$	Ziegler-Natta catalyst, used in polymerisation of ethylene.
$\text{V}_2\text{O}_5$	Contact process $\text{SO}_2 \longrightarrow \text{SO}_3$
Fe	Haber Bosch process
$\text{PdCl}_2$	Wacker's process for $\text{CH}_3\text{CHO}$ manufacturing
Pd	Hydrogenation of alkane, alkyne etc.
Pt/PtO	Adam's catalyst for selective reduction
Pt	Catalytic convertor, for cleaning
Pt/Rh	Ostwald's process $\text{NH}_3 \longrightarrow \text{NO}$
Cu	Oxidation of alcohols

### Example :



### Mechanism



### Concept Ladder



Alkali metals are highly soft and ductile due to very weak metallic bond that's why it cannot form interstitial compound.

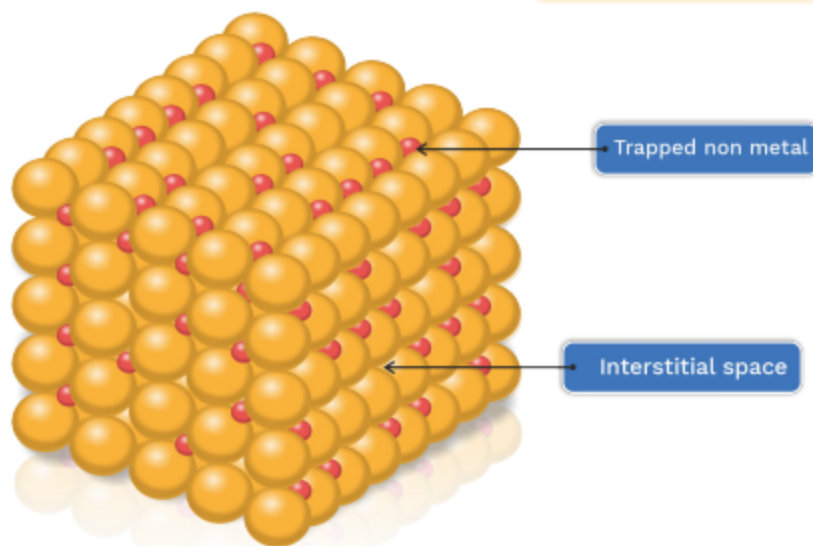
### (10) Formation of interstitial compounds :

- Interstitial compounds have similar chemical property as the parent metal but have different physical properties such as density, conductivity and hardness.
- Interstitial compounds are neither ionic nor covalent these are nonstoichiometric.

**Ex.**  $\text{VH}_{0.56}$ ,  $\text{TiH}_{1.5}$

### Definitions

Small non metallic atom such as H, B, C, N etc are able to occupy interstitial space of the lattice of the d-block elements to form combinations which are termed interstitial compounds.



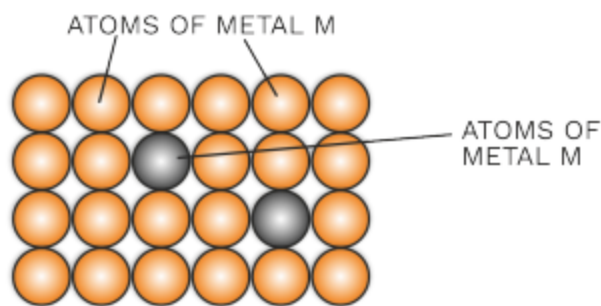
**Interstitial compound**

- Characteristics feature of interstitial compounds:
- They have high melting points, higher than those of pure metals.
- They are chemically inert.
- They are less malleable and ductile.
- These are non-stoichiometry in nature and do not follow the common rule of valency.
- Interstitial compounds are neither ionic nor covalent.
- Cementite ( $\text{Fe}_3\text{C}$ ) is an interstitial carbide. Cementite used for making railway track.

#### (11) Alloy Formation :

- Alloy is a mixture two or more than two different metals.
- d-block metals readily form alloy due to almost same metallic radii.  
(Size difference less than 50%)

**Ex :** Brass (copper-zinc) and bronze (copper-tin) etc.



Formation of alloys

- The purpose of making alloy is develop some useful properties which are absent in constituent elements.
- Alloy containing mercury as one of the constituents element are called Amalgams.  
**Ex :** Sodium amalgam (Na-Hg).

#### Previous Year's Question



Which of the following statements about the interstitial compounds is incorrect? **[NEET-2013]**

- (1) They have higher melting points than the pure metal
- (2) They retain metallic conductivity
- (3) They are chemically reactive
- (4) They are much harder than the pure metal

#### Definitions

Alloy is a homogenous solid solution of two or more than two different metals in which atom of one metal can randomly distributed among atoms of other metal.

#### Concept Ladder



The purpose of making alloys is to develop some useful properties which are absent in the constituent elements.

### Properties of alloy :

- Alloy are resistive towards rusting.
- Melting point of alloy is more than pure metal.
- Alloys of transition metal like brass and bronze have industrial importance. Also ferrous alloys, Cr, W, Mo and Mn are used for the production of a variety of steels and stainless steel.

**Ex :** Some important alloys of transition metals.

1. Brass  $\longrightarrow$  Cu + Zn
2. Bronze  $\longrightarrow$  Cu + Sn
3. Rolled gold  $\longrightarrow$  Cu + Al
4. Invar  $\longrightarrow$  Fe + Ni
5. Alnico  $\longrightarrow$  Fe + Al + Ni + Co (Use for making permanent magnet)
6. Stainless steel  $\longrightarrow$  Fe + Ni + Cr
7. Tungsten steel  $\longrightarrow$  Fe + Ni + W
8. German silver  $\longrightarrow$  Ni + Cu + Zn  
(Percentage of silver = 0)
9. 20 ct. gold  $\longrightarrow$  Au + Cu
10. 24 ct. gold  $\longrightarrow$  100% Au

### (12) Melting and Boiling Point :

- As the number of d-electron increases the number of covalent bond between the atoms are expected to increase up to Cr-Mo-W family where each of the d-orbital has only unpaired electrons and the opportunity for covalent sharing is greatest.
- In spite of presence of five unpaired electrons in Mn, the unexpected low melting and boiling points is due to its complex structure, it is unable to form metallic and covalent bonds.
- The absence of unpaired electron  $[(n-1) d^{10} 4s^2]$  in Zn, Cd & Hg is responsible for its low melting and boiling point.
- Tungsten (W) and Mercury (Hg) have highest

### Previous Year's Question



Bell metals is an alloy of

[AIPMT]

- (1) Cu, Zn and Sn
- (2) Cu, Zn and Ni
- (3) Cu and Zn
- (4) Cu and Sn

### Rack your Brain



Why do we use alloys?

### Previous Year's Question



Percentage of silver in German silver is

[AIPMT]

- (1) 0%
- (2) 1%
- (3) 5%
- (4) 4%

### Concept Ladder



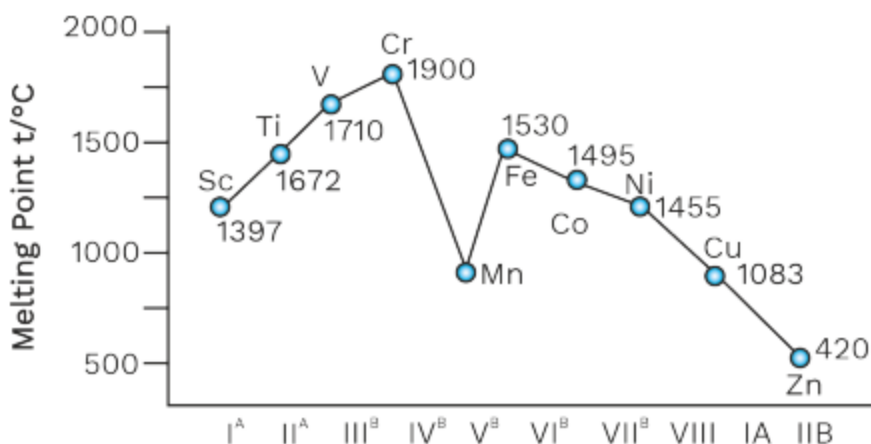
Fe, CO, Ni does not combine with Hg, so Hg liquid store in iron container.

and lowest melting points respectively.

- Along the 3d-series melting point increases upto the middle (Cr) and then decreases

**Order of Melting point (3d-series)**

Sc < Ti < V < Cr < Mn < Fe > Co > Ni > Cu > Zn



Graphic representation m.p. of 3d-series elements

**Q.8** Why Mn has very low melting point.

**A.8** Mn has very low melting point because it has :

- (i) Stable electronic configuration ( $4s^2 3d^5$ )
- (ii) High ionisation energy.
- (iii) Less delocalisation of electron.
- (iv) Weak metallic bond.

**(13) Metallic Character :**

- Transition elements have relatively low ionization energies and have one or two electrons in their outermost energy level ( $ns^1$  or  $ns^2$ ). As a result, metallic bonds are formed. Hence, they behave as metals.
- Greater the number of unpaired d-electrons, stronger is the bonding due to the overlapping of unpaired electrons between different metal atoms.

**Definitions**

Minimum energy required to break the metallic lattice of crystalline metals into atoms is known as enthalpy of atomisation.

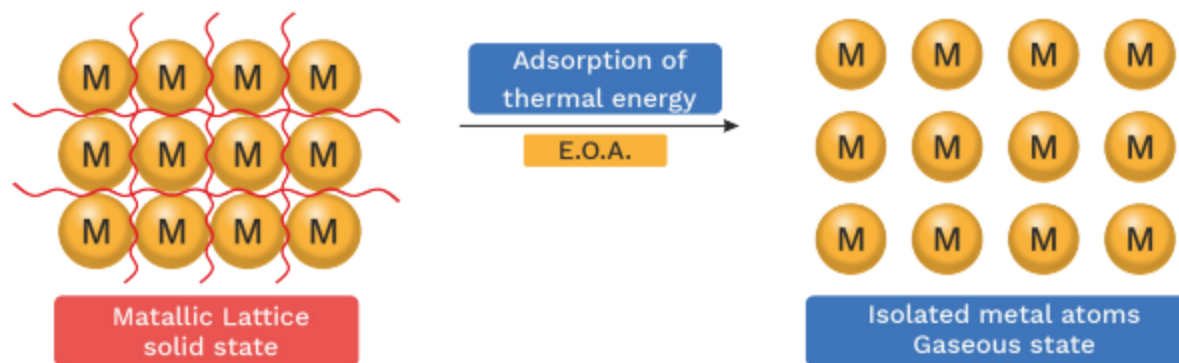
- Transition metals are good conductors of electricity and heat.
- They exhibit all the 3 types of structures: fcc, hcp, bcc.
- Melting point and boiling points of metal increases then metallic bond strength increases.
- Strength of these bonds increases, as there are more number of unpaired electrons, hence greater the number of covalent bonds.
- Zn, Cd and Hg are soft in nature as they have fully filled d-orbitals whereas Cr, Mo and W are hardest metals as they have max. no. of unpaired d-orbitals.

#### (14) Enthalpy of atomisation:

- d-block metals have very high enthalpy of atomisation (E.O.A.) due to presence of strong metallic bond.
- In a series when we move from left to right E.O.A. is first increases then start decreases.
- Enthalpy of atomisation is depend upon interatomic interaction.

#### Metallic bond strength

$$\Delta_{\text{atom}} H^{\circ} \propto \text{Interatomic interaction}$$



#### Rack your Brain



Why last element of each period in d-block have low melting point and low enthalpy of atomization.

#### Concept Ladder



All d-block elements are hard, malleable and ductile except Hg which is liquid and soft at room temperature.

## Some important compounds of transition elements :

### Oxide and Oxoanions of Metals :

- The oxides of transition elements are generally formed by the reaction of metals with  $O_2$  at high temperature. All the metals except Sc form metal oxide which are ionic.
- For Mn with increase in oxidation number, ionic character decreases.  $Mn_2O_7$  is a covalent green oil. Even  $CrO_3$  and  $V_2O_5$  as well as  $VO_2^+$  salt.  $V_2O_5$  react with alkalis as well as acids to give  $VO_4^{3-}$  and  $VO_4^{+3}$  respectively. The well characterised  $CrO$  is basic but  $Cr_2O_3$  is amphoteric.

### $K_2Cr_2O_7$ Potassium dichromate :

- It is important chemical used in leather industry and an oxidant for preparation of many azo compounds. It is prepared from chromite ore ( $FeCr_2O_4$ ).

**Step 1 :** Chromite ore is fused with  $Na_2CO_3$  or  $K_2CO_3$  in excess air.



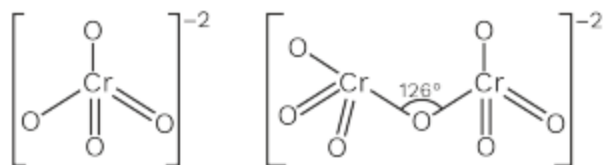
- Yellow solution of  $Na_2CrO_4$  is filtered and acidified with  $H_2SO_4$  to give a solution from which orange sodium dichromate  $Na_2Cr_2O_7 \cdot 2H_2O$  is crystallised.

**Note :**  $Na_2Cr_2O_7$  is more soluble than  $K_2Cr_2O_7$



$2NaCl$

### Structure of $CrO_4^{2-}$ and $Cr_2O_7^{2-}$



### Concept Ladder



Cr and Zn has very high and low enthalpy of atomization respectively among d-block elements.

### Rack your Brain



Why I-A group metal have very low enthalpy of atomization.

### Previous Year's Question

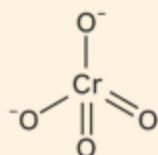


$K_2Cr_2O_7$  on heating with aqueous NaOH gives

[AIPMT]

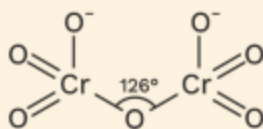
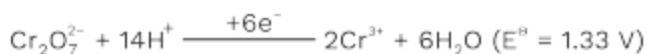
- (1)  $Cr_2O_7^{2-}$       (2)  $Cr(OH)_2$   
 (3)  $CrO_4^{2-}$       (4)  $Cr(OH)_3$





Electronic Configuration of  $\text{Cr}^{+6} \rightarrow 3d^0$   
 Unpaired electron (n)  $\rightarrow 0$   
 Magnetic nature  $\rightarrow$  Diamagnetic  
 Colour  $\rightarrow$  Yellow  
 All M—O Bond Length  $\rightarrow$  Equal  
 Hybridization  $\rightarrow d^2s$   
 Geometry  $\rightarrow$  Tetrahedral

- Sodium and potassium dichromate are good oxidising agent. But potassium dichromate is used as primary standard in volumetric analysis.

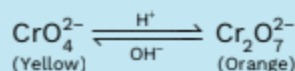


Electronic Configuration of  $\text{Cr}^{+6} \rightarrow 3d^0$   
 Unpaired electron (n)  $\rightarrow 0$   
 Magnetic nature  $\rightarrow$  Diamagnetic  
 Colour  $\rightarrow$  Orange  
 All M—O Bond Length  $\rightarrow$  Equal  
 Hybridization  $\rightarrow d^2s$   
 Geometry  $\rightarrow$  Tetrahedral

### Concept Ladder



$\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  exist in equilibrium (pH = 4).



### Previous Year's Question



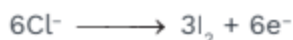
Identify the incorrect statement :

[NEET-2020]

- The oxidation state of Cr in  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  are not the same
- $\text{Cr}^{2+}$  ( $d^4$ ) is a stronger reducing agent than  $\text{Fe}^{2+}$  ( $d^6$ ) in water
- The transition metals and their compounds are known for their catalytic activity due to their ability to adopt multiple oxidation states and to form complexes.
- Interstitial compounds are those that are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals.



Example of reaction involving oxidation by  $\text{Cr}_2\text{O}_7^{2-}$ .

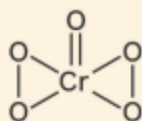


### Rack your Brain



When acidic  $\text{K}_2\text{Cr}_2\text{O}_7$  react with  $\text{Na}_2\text{SO}_3$ , green colour appear due to formation of?

$\text{CrO}_5$   
Chromium Peroxide



Butterfly Structure  
One — oxo ligand  
Two — Peroxo ligand

Electronic Configuration of  $\text{Cr}^{+6} \rightarrow 3d^0$

Unpaired electron (n)  $\rightarrow 0$

Magnetic nature  $\rightarrow$  Diamagnetic

Colour  $\rightarrow$  Blue

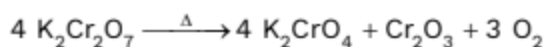
All M—O Bond Length  $\rightarrow$  Unequal

Hybridization  $\rightarrow sp^3d$

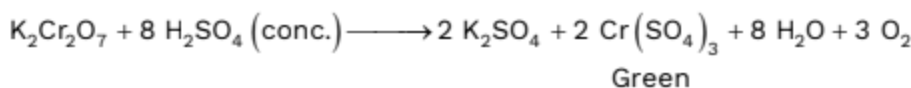
Geometry  $\rightarrow$  Trigonal bipyramidal

### Chemical Properties of $\text{K}_2\text{Cr}_2\text{O}_7$

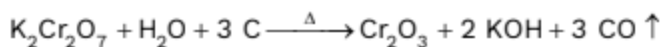
#### (1) Heating Effect



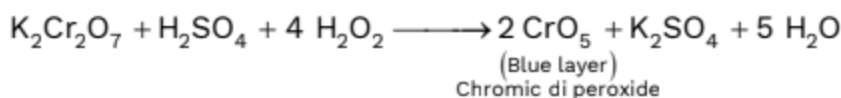
#### (2) Reaction with $\text{H}_2\text{SO}_4$



#### (3) Reduction with $\text{H}_2\text{O}$



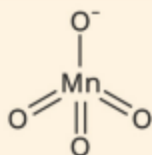
#### (4) Reduction with $\text{H}_2\text{O}_2$



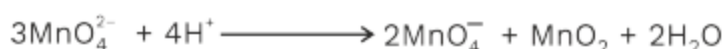
$\text{CrO}_5$  contains 5 oxygen atoms. In these 5 oxygen atoms four atoms participate in the formation of two peroxide linkages. So, in  $\text{CrO}_5$  the oxidation state of Cr is +6.

### Potassium Permanganate $\text{KMnO}_4$ :

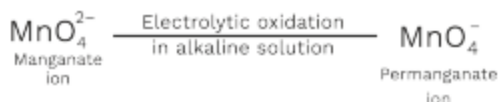
- Preparation :**  $\text{KMnO}_4$  is prepared by fusion of  $\text{MnO}_2$  with an alkali metal hydroxides and an oxidising agent like  $\text{KNO}_3$ . This produces dark green  $\text{K}_2\text{MnO}_4$  which disproportionates in a neutral or acidic solution to give permanganate.



Electronic Configuration of  $\text{Mn}^{7+} \rightarrow 3d^0$   
 Unpaired electron (n)  $\rightarrow 0$   
 Magnetic nature  $\rightarrow$  Diamagnetic  
 Colour  $\rightarrow$  Purple  
 All M—O Bond Length  $\rightarrow$  Equal  
 Hybridization  $\rightarrow d^3s$   
 Geometry  $\rightarrow$  Tetrahedral



- Commercially it is prepared by the alkaline oxidative fusion of  $\text{MnO}_2$  followed by the electrolytic oxidation of manganate (VI).



### Concept Ladder



$\text{NaNO}_3$  cannot react with  $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$  because of its resamble maximum oxidation state (+5). Hence, it cannot be oxidised ( $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ ).

### Previous Year's Question



The manganate and permanganate ions are tetrahedral, due to

[NEET 2019]

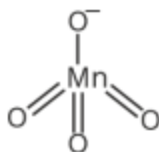
- (1) the  $\pi$ -bonding involves overlap of d-orbitals of oxygen with d-orbitals of manganese
- (2) the  $\pi$ -bonding involves overlap of p-orbitals of oxygen with d-orbitals of manganese
- (3) there is no  $\pi$ -bonding
- (4) the  $\pi$ -bonding involves overlap of p-orbitals of oxygen with p-orbitals of manganese

- **Laboratory preparation :** In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.

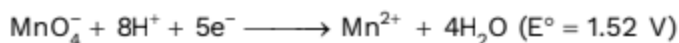
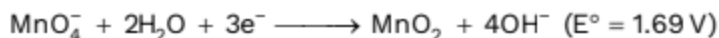


**Characteristic properties :**

1.  $\text{KMnO}_4$  forms dark purple (almost black) crystals which have same structure as those of  $\text{KClO}_4$ . The salt is not soluble in  $\text{H}_2\text{O}$ . (6.4 g/100 g of  $\text{H}_2\text{O}$  at 293 K).
2. It has intense colour and weak temperature dependent paramagnetism.
3. Green manganate ion is paramagnetic while permanganate ion is diamagnetic.
4.  $\pi$ -bonding takes place by overlap of p-orbital of oxygen with d-orbitals of manganese.
5. **Structure :**



6.  $\text{KMnO}_4$  is a good oxidising agent in acidic, basic or neutral medium.
7. Half cell reaction of  $\text{KMnO}_4$  in different medium.



**Concept Ladder**



Potassium permanganate act as an oxidising agent in alkaline, neutral and acidic solution.

**Rack your Brain**



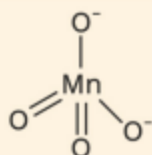
Why is  $\text{KMnO}_4$  an oxidising agent?

**Previous Year's Question**



Which one of the following statements is correct when  $\text{SO}_2$  is passed through acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution ? **[NEET-2016 Phase-I]**

- (1) The solution turns blue
- (2) The solution is decolourized
- (3)  $\text{SO}_2$  is reduced
- (4) Green  $\text{Cr}_2(\text{SO}_4)_3$  is formed



Electronic Configuration of  $\text{Mn}^{+6} \rightarrow 3d^1$   
Unpaired electron (n)  $\rightarrow 1$   
Magnetic nature  $\rightarrow$  Paramagnetic  
Colour  $\rightarrow$  Green  
All M—O Bond Length  $\rightarrow$  Equal  
Hybridization  $\rightarrow d^2s$   
Geometry  $\rightarrow$  Tetrahedral

- The hydrogen ion concentration of the solution plays an important part in influencing the reaction. Although reactions can be understood by consideration of redox potential, kinetics of the reaction is also an important factor.

#### Important oxidising reactions of $\text{KMnO}_4$ :

##### 1. In acidic medium :

- $10\text{I}^- + 2\text{MnO}_4^- + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{I}_2$
- $5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$   
(Green) (Yellow)
- $5\text{C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$
- $5\text{S}^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{S}$
- $5\text{SO}_3^{2-} + 2\text{MnO}_4^- + 6\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + 5\text{SO}_4^{2-}$
- $5\text{NO}_2^- + 2\text{MnO}_4^- + 6\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + 5\text{NO}_3^-$

##### 2. In neutral or faintly alkaline solutions :

- $2\text{MnO}_4^- + \text{H}_2\text{O} + \text{I}^- \longrightarrow 2\text{MnO}_2 + 2\text{OH}^- + \text{IO}_3^-$
- $8\text{MnO}_4^- + \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \longrightarrow 8\text{MnO}_2 + 6\text{SO}_4^{2-} + 2\text{OH}^-$
- $2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \xrightarrow{\text{Zn}} 5\text{MnO}_2 + 4\text{H}^+$

#### Concept Ladder



Potassium permanganate act as an oxidising agent in alkaline, neutral and acidic solution.

#### Previous Year's Question



Which one of the following ions exhibits d-d transition and paramagnetism as well ?

[NEET-2018]

- $\text{CrO}_4^{2-}$
- $\text{Cr}_2\text{O}_7^{2-}$
- $\text{MnO}_4^-$
- $\text{MnO}_4^{2-}$

**Important Oxides of 3d-Series**

<b>Sc</b>		Sc <sub>2</sub> O <sub>3</sub> (b)				
<b>Ti</b>	TiO(b)	Ti <sub>2</sub> O <sub>3</sub> (b)	TiO <sub>2</sub> (c)			
<b>V</b>	VO(b)	V <sub>2</sub> O <sub>3</sub> (b)	VO <sub>2</sub> (c)	V <sub>2</sub> O <sub>5</sub> (a)		
<b>Cr</b>	CrO(b)	Cr <sub>2</sub> O <sub>3</sub> (c)	CrO <sub>2</sub> (c)		CrO <sub>3</sub> (a)	
<b>Mn</b>	MnO(b)	Mn <sub>2</sub> O <sub>3</sub> (b)	MnO <sub>2</sub> (c)	Mn <sub>3</sub> O <sub>4</sub> (c)	[MnO <sub>3</sub> (a)]	Mn <sub>2</sub> O <sub>7</sub> (a)
<b>Fe</b>	FeO(b)	Fe <sub>2</sub> O <sub>3</sub> (b)		Fe <sub>3</sub> O <sub>4</sub> (b)		
<b>Co</b>	CoO(b)	[Co <sub>2</sub> O <sub>3</sub> <sup>h</sup> (b)]	[CoO <sub>2</sub> <sup>h</sup> ]			
<b>Ni</b>	NiO(b)	[Ni <sub>2</sub> O <sup>h</sup> (b)]	[NiO <sub>2</sub> <sup>h</sup> ]	Mixed		
<b>Cu</b>	CuO(b)					
<b>Zn</b>	ZnO(b)					

where a = acidic; b = basic; c = amphoteric; h = hydrated

**f-Block Elements**

- f-block elements are also known as inner-transition elements.
- f-block consists of the two series, lanthanoids and actinoids.
- Lanthanide series (Z = 58 – 71) (Ce–Lu).  
Actinide series (Z = 90 – 103) (Th–Lw).
- General electronic configuration is  $(n-2)f^{1-14}(n-1)d^{0-1}, ns^2$

**4f-series (Lanthanides) :**

- These elements are called rare earth.

- As many of elements are not particularly rare so this name is not appropriate for the whole series. Promethium is a radioactive element.

#### 5f-series (Actinides) :

- The members of actinides are radioactive and majority of them are not found in nature. Elements from  $Z = 93$  onwards are called transuranic elements and discovered by synthetic methods.

#### Lanthanoids : (4f-block elements)

##### General characteristics :

##### (1) Electronic configuration :

- General electronic configuration  $[\text{Xe}] 4f^{1-14}, 5d^{0-1}, 6s^2$ .
- Lanthanide have outer three shells incomplete.
- They have electronic configuration with  $6s^2$  common but with variable occupancy of 4f level. The energies of 5d and 4f orbit are also nearly similar and thus their filling show certain irregularities.
- It is energetically favourable to move the single electron on 5d into the 4f level in most of the elements but not in case of Ce, Gd and Lu.
- In Gd and Lu besides 5d, the 4f orbitals are half-filled or fully filled. Give extra stability.  
Gd ( $Z = 64$ )  $[\text{Xe}] (4f^7 5d^1 6s^2)$   
Lu ( $Z = 74$ ),  $[\text{Xe}] (4f^{14}, 5d^1 6s^2)$
- Eu ( $Z = 63$ ) and Yb ( $Z = 70$ ) also shows extra stability of half filled and fully filled f-orbitals.

#### Definitions

The elements constituting the f-block are those in which the 4f and 5f orbitals are progressively filled in the latter two long periods.



#### Previous Year's Question

Lanthanoids are

[AIPMT]

- 14 elements in the sixth period (atomic no. 90 to 103) that are filling 4f sublevel
- 14 elements in the seventh period (atomic number = 90 to 103) that are filling 5f sublevel
- 14 elements in the sixth period (atomic number = 58 to 71) that are filling the 4f sublevel
- 14 elements in the seventh period (atomic number = 58 to 71) that are filling 4f sublevel.

#### Concept Ladder



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 6d electrons are at about the same potential energy and that the atoms have a tendency to retain stable half filled configuration.



Atomic Number	Name	Symbol	Electronic Configurations*			Radii/pm		
			Ln	Ln <sup>2+</sup>	Ln <sup>3+</sup>	Ln <sup>4+</sup>	Ln	Ln <sup>3+</sup>
57	Lanthanum	La	5d <sup>1</sup> 6s <sup>2</sup>	5d <sup>1</sup>	4f <sup>0</sup>		187	106
58	Cerium	Ce	4f <sup>1</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>2</sup>	4f <sup>1</sup>	4f <sup>0</sup>	183	103
59	Praseodymium	Pr	4f <sup>3</sup> 6s <sup>2</sup>	4f <sup>3</sup>	4f <sup>2</sup>	4f <sup>1</sup>	182	101
60	Neodymium	Nd	4f <sup>4</sup> 6s <sup>2</sup>	4f <sup>4</sup>	4f <sup>3</sup>	4f <sup>2</sup>	181	99
61	Promethium	Pm	4f <sup>5</sup> 6s <sup>2</sup>	4f <sup>5</sup>	4f <sup>4</sup>		181	98
62	Samarium	Sm	4f <sup>6</sup> 6s <sup>2</sup>	4f <sup>6</sup>	4f <sup>5</sup>		180	96
63	Europium	Eu	4f <sup>7</sup> 6s <sup>2</sup>	4f <sup>7</sup>	4f <sup>6</sup>		199	95
64	Gadolinium	Gd	4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>7</sup> 5d <sup>1</sup>	4f <sup>7</sup>		180	94
65	Terbium	Tb	5f <sup>9</sup> 6s <sup>2</sup>	4f <sup>9</sup>	4f <sup>8</sup>	4f <sup>7</sup>	178	92
66	Dysprosium	Dy	4f <sup>10</sup> 6s <sup>2</sup>	4f <sup>10</sup>	4f <sup>9</sup>	4f <sup>8</sup>	177	91
67	Holmium	Ho	4f <sup>11</sup> 6s <sup>2</sup>	4f <sup>11</sup>	4f <sup>10</sup>		176	89
68	Erbium	Er	4f <sup>12</sup> 6s <sup>2</sup>	4f <sup>12</sup>	4f <sup>11</sup>		175	88





Atomic Number	Name	Symbol	Electronic Configurations*			Radii/pm		
			Ln	Ln <sup>2+</sup>	Ln <sup>3+</sup>	Ln <sup>4+</sup>	Ln	Ln <sup>3+</sup>
69	Thulium	Tm	4f <sup>13</sup> 6s <sup>2</sup>	4f <sup>13</sup>	4f <sup>12</sup>		174	87
70	Ytterbium	Yb	4f <sup>14</sup> 6s <sup>2</sup>	4f <sup>14</sup>	4f <sup>13</sup>		173	86
71	Lutetium	Lu	4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>14</sup> 5d <sup>1</sup>	4f <sup>14</sup>	–	–	–

## (2) Atomic and ionic radii :

- In lanthanide series, with increasing atomic number, there is a progressive decrease in the atomic radii as well as ionic radii of trivalent ions from La<sup>3+</sup> to Lu<sup>3+</sup>. This is due to lanthanide contraction.
- Lanthanoid contraction :** The atomic and ionic radii of trivalent ions (M<sup>3+</sup>) decreases regularly due to increase in atomic no. from Ce to Lu. This continuous decrease in size of atoms and ions is known as lanthanoid contraction.
- Due to decreases in the size of the lanthanide ions from Ce<sup>3+</sup> to Lu<sup>3+</sup>, the covalent character of M—OH bond increases and hence the basic strength decreases. Thus, Ce(OH)<sub>3</sub> is most basic while Lu(OH)<sub>3</sub> is least basic.

### Previous Year's Question

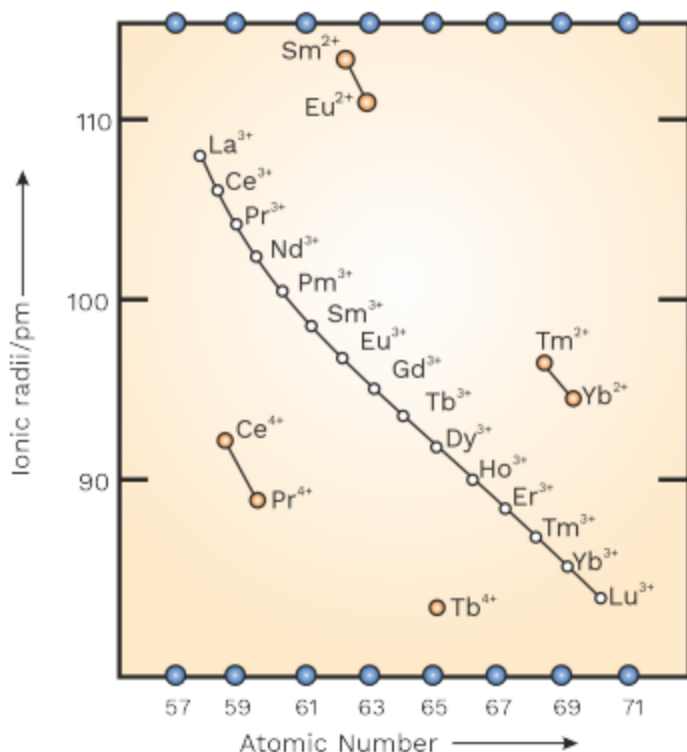


The electronic configurations of Eu (Atomic No. 63), Gd (Atomic No. 64) and Tb (Atomic No. 65) are : **[NEET-2016 Phase-I]**

- (1) [Xe]4f<sup>7</sup>6s<sup>2</sup>, [Xe]4f<sup>8</sup>6s<sup>2</sup> and [Xe]4f<sup>9</sup>5d<sup>1</sup>6s<sup>2</sup>
- (2) [Xe] 4f<sup>7</sup>5d<sup>16</sup>s<sup>2</sup>, [Xe]4f<sup>7</sup> 5d<sup>1</sup> 6s<sup>2</sup> and [Xe]4f<sup>9</sup>6s<sup>2</sup>
- (3) [Xe]4f<sup>6</sup>5d<sup>1</sup>6s<sup>2</sup>, [Xe]4f<sup>7</sup>5d<sup>1</sup>6s<sup>2</sup> and [Xe] 4f<sup>8</sup>5d<sup>1</sup>6s<sup>2</sup>
- (4) [Xe]4f<sup>7</sup>6s<sup>2</sup>, [Xe]4f<sup>7</sup>5d<sup>1</sup>6s<sup>2</sup> and [Xe]4f<sup>9</sup>6s<sup>2</sup>

### Effect of Lanthanoid Contraction

Size  $\rightarrow 4d \approx 5d$   
 Ionization energy  $\rightarrow 5d > 3d > 4d$   
 Electron negativity  $\rightarrow 5d > 4d$   
 density  $\rightarrow 5d \gg 4d$



### Previous Year's Question

The correct order of ionic radii of  $Y^{3+}$ ,  $La^{3+}$ ,  $Eu^{3+}$  and  $Lu^{3+}$  is

[AIPMT-2003]

- (1)  $La^{3+} < Eu^{3+} < Lu^{3+} < Y^{3+}$
- (2)  $Y^{3+} < La^{3+} < Eu^{3+} < Lu^{3+}$
- (3)  $Lu^{3+} < Y^{3+} < Eu^{3+} < La^{3+}$
- (4)  $Lu^{3+} < Eu^{3+} < La^{3+} < Y^{3+}$

### (3) Oxidation state :

- 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.
- All the lanthanides have +3 oxidation state and only Cerium (Ce), Praseodymium (Pr), and Terbium (Tb) exhibit higher oxidation state (+4).

### Concept Ladder



Among lanthanoid  $Ln(III)$  compounds are predominant. However occasionally in solutions or in solid compounds +2 and +4 ions are also obtained.



- Oxidation state +2 and +4 occur specifically when they lead to :
  - (i) A inert gas configuration e.g.  $\text{Ce}^{4+}$  ( $f^0$ )
  - (ii) A half filled 'f' orbital e.g.  $\text{Eu}^{2+}$ ,  $\text{Tb}^{4+}$ , ( $f^7$ )
  - (iii) A compound filled 'f' orbital e.g..  $\text{Yb}^{2+}$  ( $f^{14}$ )
- Lower oxidation state act as reducing agent ( $\text{Eu}^{2+}$ ,  $\text{Yb}^{2+}$ ) and higher oxidation state act as oxidising agent ( $\text{Ce}^{4+}$ ,  $\text{Tb}^{4+}$ ).
- Lanthanoids show limited no. of oxidation state as the energy gap between 5d and 4f subshell is significant.

#### (4) Magnetic properties :

- In lanthanide series, the number of unpaired electrons in tri-positive lanthanide ion regularly increase from La to Gd (0 to 7) and then continuously decrease upto Lu (7 to 0). So La and Lu ions are diamagnetic and all other tri-positive lanthanides are paramagnetic.

#### (5) Other properties :

- The lanthanide ions have unpaired electrons in their 4f orbitals. Thus these ions absorb visible region of light and undergo f-transition and hence exhibit colour. The colour exhibited depends on the number of unpaired electrons in the 4f orbitals. The ions often with  $4f^0$  configuration have similar colour to those ions have  $4f^{14}$  configuration.
- All the lanthanoids are silvery white soft metals and tarnish rapidly.
- Hardness increases with increasing atomic number Samarium (Sm) being steel hard.
- It is difficult to separate lanthanoids in pure state.
- These are good conductor of electricity.

#### Concept Ladder



All Lanthanoid ion ( $\text{Ln}^{3+}$ ) are coloured and para magnetic and colour arises due to f-f transition (Except  $\text{Lu}^{3+}$ )

#### Rack your Brain



What are the oxidation state of first member of lanthanoid series?

#### Previous Year's Question



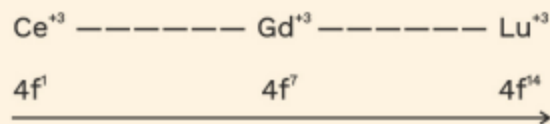
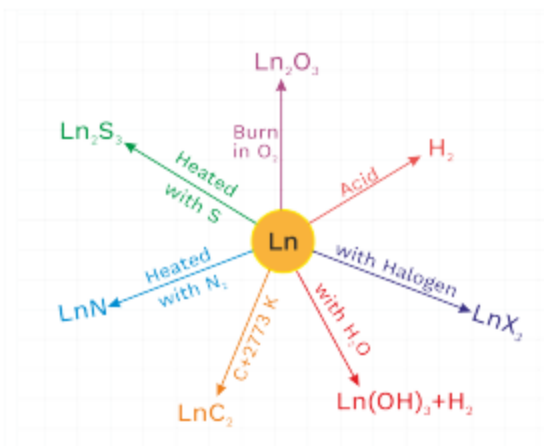
Which of the following oxidation state is the most common among the lanthanoids?

[AIPMT]

- |       |       |
|-------|-------|
| (1) 4 | (2) 2 |
| (3) 5 | (4) 3 |

- Alloys of lanthanides with Fe are called misch metals.
  - Ionisation Energies :** Lanthanides have fairly low ionisation energies comparable to alkaline earth metals.
  - Electropositive 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.
- $\text{Lu}^{+3}$  is smallest in size can only form complex.

#### Lanthanoids Reactions :



Ionic size decreases  
 Ionization energy increases  
 Basic character of oxide/Hydroxide decreases  
 Covalent character of Halide increases  
 Hydrolysis of Halide increases  
 Complex tendency increases

#### Concept Ladder



$\text{La}^{3+}$  ( $Z = 57$ ) and  $\text{Lu}^{3+}$  ( $Z = 71$ ) do not show any colour in solution.

#### Rack your Brain



Why all the lanthanoids are act as strong reducing agents?

#### Previous Year's Question



Which one of the following statements related to lanthanons is incorrect ?

[NEET-2016 Phase-II]

- All the lanthanons are much more reactive than aluminium
- $\text{Ce}(+4)$  solutions are widely used as oxidizing agent in volumetric analysis
- Europium shows +2 oxidation state
- The basicity decreases as the ionic radius decreases from Pr to Lu.



## Effect of Lanthanoid Contraction

### (1) Effect on Post Lanthanoid

- In 5d period the elements after Hf (including in also) are termed as post lanthanoids.

#### Atomic Size

- In general, on moving down the group the size of atoms increases but due to lanthanoid contraction atomic size of Hf  $\approx$  Zr. Also, ionic size of  $\text{Hf}^{+4} \approx \text{Zr}^{+4}$ .

Size of 4d  $\approx$  5d

Size of Pd  $\approx$  Pt

Size of Ag  $\approx$  Au

### (2) Properties of 4d & 5d series are similar

- Due to this reason they exist in nature in combined form and difficulty arises in their separation.

- (3) Within lanthanoid series properties of elements are similar so they are difficult to separate as they also formed in combined form.

$\text{Cr}^{+3}$ ----- $\text{Lu}^{+3}$

## Uses of Lanthanoids

### (1) Misch Metal

- 95% Ce + 5% Fe, it is alloy.

### (2) Crooke Glass

- $\text{CeO}_2$  in ordinary glass  $\text{SiO}_2$  is present. Crooke glass prevent UV light.

### (3) Lanthanoid Oxide ( $\text{Ln}_2\text{O}_3$ )

- It is used in T.V. screen and used as catalyst in petroleum cracking.

## Rack your Brain



Why  $\text{Eu}^{2+}$  is a good reducing agent ?

## Concept Ladder



Lanthanide contraction brings some differences in properties like solubility, complex ion formation, hydration etc.

## Previous Year's Question



The lanthanide contraction is responsible for the fact that

[AIPMT]

- Zr and Hf have about the same radius
- Zr and Zn have the same oxidation state
- Zr and Y have about the same radius
- Zr and Nb have similar oxidation state.

**Q.9** Which metal oxide used in T.V. screen?

- (1) W                                      (2) Cr                                      (3) Mo                                      (4) Yb

**A.9** (4)  
As W, Cr and Mo are d-block elements.

### Actinides : (5f-block elements)

- The elements in which the last electron enters 5f-orbitals of  $(n-2)^{\text{th}}$  main are known as actinides.
- The man-made 11 elements  $\text{Np}_{93} - \text{Lr}_{103}$  are placed after uranium in the periodic table and are collectively called **trans-uranic** elements.
- Th, Pa and U first three actinides are natural elements.

### General characteristics :

#### (1) Electronic configuration :

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

### Concept Ladder



All the actinides are unstable and synthetic elements (except Ac, Th, Pa and U).

Atomic Number	Name	Symbol	Electronic configurations *			Radii/pm	
			M	M <sup>3+</sup>	M <sup>4+</sup>	M <sup>3+</sup>	M <sup>4+</sup>
89	Actinium	Ac	$6d^1 7s^2$	$5f^0$		111	
90	Thorium	Th	$6d^1 7s^2$	$5f^1$	$5f^0$		99
91	Protactinium	Pa	$5f^2 6d^1 7s^2$	$5f^2$	$5f^1$		96
92	Uranium	U	$5f^3 6d^1 7s^2$	$5f^3$	$5f^2$	103	93
93	Neptunium	Np	$5f^4 6d^1 7s^2$	$5f^4$	$5f^3$	101	92
94	Plutonium	Pu	$5f^6 7s^2$	$5f^5$	$5f^4$	100	90
95	Americium	Am	$5f^7 7s^2$	$5f^6$	$5f^5$	99	89



Atomic Number	Name	Symbol	Electronic configurations *			Radii/pm	
			M	M <sup>3+</sup>	M <sup>4+</sup>	M <sup>3+</sup>	M <sup>4+</sup>
96	Curium	Cm	5f <sup>7</sup> 6d <sup>1</sup> 7s <sup>2</sup>	5f <sup>7</sup>	5f <sup>7</sup>	99	88
97	Berkelium	Bk	5f <sup>9</sup> 7s <sup>2</sup>	5f <sup>8</sup>	5f <sup>7</sup>	98	87
98	Californium	Cf	5f <sup>10</sup> 7s <sup>2</sup>	5f <sup>9</sup>	5f <sup>8</sup>	98	86
99	Einsteinium	Es	5f <sup>11</sup> 7s <sup>2</sup>	5f <sup>10</sup>	5f <sup>9</sup>	–	–
100	Fermium	Fm	5f <sup>12</sup> 7s <sup>2</sup>	5f <sup>11</sup>	5f <sup>10</sup>	–	–
101	Mendelevium	Md	5f <sup>13</sup> 7s <sup>2</sup>	5f <sup>12</sup>	5f <sup>11</sup>	–	–
102	Nobelium	No	5f <sup>14</sup> 7s <sup>2</sup>	5f <sup>13</sup>	5f <sup>12</sup>	–	–
103	Lawrencium	Lr	5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>2</sup>	5f <sup>14</sup>	5f <sup>13</sup>	–	–

## (2) Oxidation state :

- The actinoids show in general + 3 oxidation state.
- Actinoids show a variety of oxidation state. It is because of a small energy difference between 5f, 6d and 7s subshells.
- The element in the first half of the series frequently exhibit higher oxidation states. For example the maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements.

### Previous Year's Question



The reason for greater range of oxidation states in actinoids is attributed to : **[NEET-2017]**

- (1) Actinoid contraction
- (2) 5f, 6d and 7s levels having comparable energies
- (3) 4f and 5d levels being close in energies
- (4) The radioactive nature of actinoids



Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3		3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4						
		5	5	5	5	5								
			6	6	6	6								
				7	7									

### (3) Atomic size :

- In actinoid series size of atom or ions gradually decreases. It is considered as actinoids contraction (similar to lanthanoid contraction). Due to poor shielding by 5f-electrons the contraction becomes greater varies from element to element in the series.

#### General characteristics and comparison with lanthanoids :

- Instead of having same color (silver) all actinoid metals display the variety of structures, this variety is due to irregularities in metallic radii which are far greater than in lanthanoids.
- The actinoids are highly reactive metals.
- The magnetic properties of the actinoids are more complex than those of the lanthanoids.
- Actinoids compound or their ions are coloured most probably due to f-f transition.
- Actinide contraction is greater than lanthanoid contraction due to poor shielding by 5f-electrons in actinides than that of 4f-electrons in the lanthanoids.

### Concept Ladder



- Lanthanoids form primarily +3 ions, while the actinoids usually have higher oxidation states in their compounds, +4 or even +6 being typical.
- The actinoids exhibit a large number of oxidation states than the corresponding members in the lanthanoid series.

### Rack your Brain



Why actinoid contraction is more than lanthanoid contraction.





**Differences :**

S.N.	Lanthanides	S.N.	Actinides
1.	In addition to +3 oxidation state, they exhibit +2 and +4 oxidation states only.	1.	In addition to +3 oxidation state, they show +4, +5, +6 and +7 oxidation states.
2.	Most of their ions are colourless.	2.	Most of their ions are coloured.
3.	They do not form complexes easily.	3.	They have much greater tendency to form complexes.
4.	They do not form oxo cations.	4.	They form oxo cations such as $\text{UO}_2^{2+}$ , $\text{PuO}_2^{2+}$
5.	Their compounds are less basic.	5.	Their compounds are more basic.
6.	Except promethium, they are non-radioactive.	6.	They are radioactive.
7.	Their magnetic properties can be easily explained.	7.	Their magnetic properties cannot be explained.



**Q10** What are the characteristics of the transition elements and why are they called transition elements ?

**A10** They are called transition elements because their position in the periodic table is between s & p blocks their properties are transitional between highly reactive s-metals & constant bond forming p elements. Zn, Cd, Hg has  $ns^2 (n - 1)d^{10}$  configuration. So, they are not included in transition elements.

**Q11** On what ground can you say that scandium ( $Z = 21$ ) is a transition element but zinc ( $Z = 30$ ) is not ?

**A11** Due to incompletely filled 3d orbitals in case of Sc atom, in its ground state ( $3d^1$ ), it is considered as transition element. On the other hand, Zn atom has completely filled d orbitals ( $3d^{10}$ ) in its ground state as well as in its excited state, hence it is not considered as a transition elements.

**Q12** Why Cr and Cu show exceptional configuration?

**A12** By deviating from normal configuration, Cr and Cu acquires half-filled and fully filled configuration which gives them extra stability. Hence they show exceptional configuration.



**Q13** What are interstitial compounds ? Why are such compounds well known for transition metals ?

**A13** Interstitial compounds are those which can be formed when small atoms like H, B, N, C etc. are fixed inside the crystal lattices of metals. They are generally nonstoichiometric and neither typically covalent nor ionic.

Most of transition metals form these type of compounds with small non-metal atoms such as H, B, N and C. These small atoms enter into the void sites between the packed atoms of crystallisation transition metals. For example, steel and cast iron become hard by forming interstitial compound with carbon.





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- (i) Uranium exhibits oxidation states of +3, +4, +5, +6 in its compounds. However, the dominant oxidation state in actinoids is +3.
  - (ii) Nobelium, No is stable in +2 state because of completely filled  $f^{14}$  orbitals in this state.
  - (iii) Berkelium, BK in +4 oxidation state is more stable due to  $f^7$  (exactly half filled) configuration.
  - (iv) Higher oxidation states are exhibited in oxoions are  $UO_2^{2+}$ ,  $PuO_2^{2+}$ ,  $NpO^+$  etc .

**Q16** Give reason for each of the following :

- (1) Size of trivalent lanthanide cations decreases with increase in the atomic number.
- (2) Transition metal fluorides are ionic in nature, whereas bromides and chlorides are usually covalent in nature.
- (3) Chemistry of all the lanthanides is quite similar.

**A16** (1) d-orbitals have poor shielding effect. As atomic number increases, there is increase in nuclear charge also. So, the size decreases.  
(2) The electronegativity difference between transition metals & F is high but not so for Cl, Br.  
(3) Most of them have similar sizes, they show a common stable oxidation state (+3).

**Q17** (1) What is meant by disproportionation of an oxidation state ? Give one example.  
(2) What is the effect of lanthanoid ?

**A17** (1) When any atom or ion undergo oxidation and reduction simultaneously it is called disproportionation.  
(2) From 4<sup>th</sup> group onwards (e.g, Zr and Hf), the size of respective 4d and 5d series elements becomes comparable.

**Q18** What are alloys ? Name an important alloy which contains some of the lanthanide metals. Mention its uses.

**A18** Alloy is a mixture a solid solution compared of a metal and another element. Misch metal contains Lanthanoids. It is used in preparation of f-block elements. When mixed with iron, its used in lighters.



## Chapter Summary



- ♦ The transition elements are defined on the basis of their incompletely filled d-orbital. Since Zn, Cd, Hg elements have  $d^{10}$  configuration and are not considered as transition elements but they are d-block elements.
- ♦ The d-block consisting of group 3 to group 12 occupies the large middle section of the periodic table. In these elements the inner d-orbitals are successively filled. f-block elements are placed outside, at the bottom of the periodic table, 4f and 5f orbitals are progressively filled for the elements of this block.
- ♦ Metallic nature and physical state : All the transition metals have metallic properties. They have tensile strength, ductile, malleable, high thermal conductivity, high electrical conductivity, metallic lustre, high M.P. and B.P.
- ♦ All d-block elements are solid at room temperature exceptionally Hg is liquid.
- ♦ Chromium and copper have high ionization enthalpy than their neighbours elements.
- ♦ Transition element tend to be unreactive with increasing atomic number in the series.
- ♦ The atomic radii do not change very much in a transition series with an increase in atomic number.
- ♦ Generally middle members of transition series have higher oxidation states.
- ♦ Unlike  $Cr^{3+}$ ,  $Mn^{2+}$ ,  $Fe^{3+}$  and the subsequent other  $M^{2+}$  ions of the 3d-series of elements, the 4d and the 5d-series metals generally do not form stable cationic species.
- ♦ The transition elements will vary widely in their chemical behaviour. In first series all the metals are relatively reactive except copper. All of them can be dissolved in mineral acids as they are sufficiently electropositive in nature.
- ♦ The first transition series metal oxides are generally formed from the reaction of metals with oxygen at high temperatures. Potassium permanganate and potassium dichromate are common examples.
- ♦ The two series of inner transition elements, lanthanides and actinides constitute the f-block of the periodic table. After filling the inner orbitals, 4f, there is a gradual decrease in the atomic as well as ionic sizes of these metals along the series (lanthanide contraction).
- ♦  $La^{3+}$  ( $Z = 57$ ) and  $Lu^{3+}$  ( $Z = 71$ ) do not show any colour in solution.
- ♦ Lanthanides form primarily +3 ions, while the actinides usually have higher O.S. in their compounds, +4 or even +6 being typical.
- ♦ The actinoids exhibit a large no. of O.S. than the corresponding members in the lanthanoid series.



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- ♦ The chemistry of the actinoids is more complex in view of their ability to exist in different oxidation states.
  - ♦ Furthermore many of the actinoid elements are radioactive which make the study of these elements rather difficult.
  - ♦  $\text{La(OH)}_3$  is more basic than  $\text{Lu(OH)}_3$ .
  - ♦  $\text{Ce}^{4+}$  is a good oxidizing agent in aqueous solution.