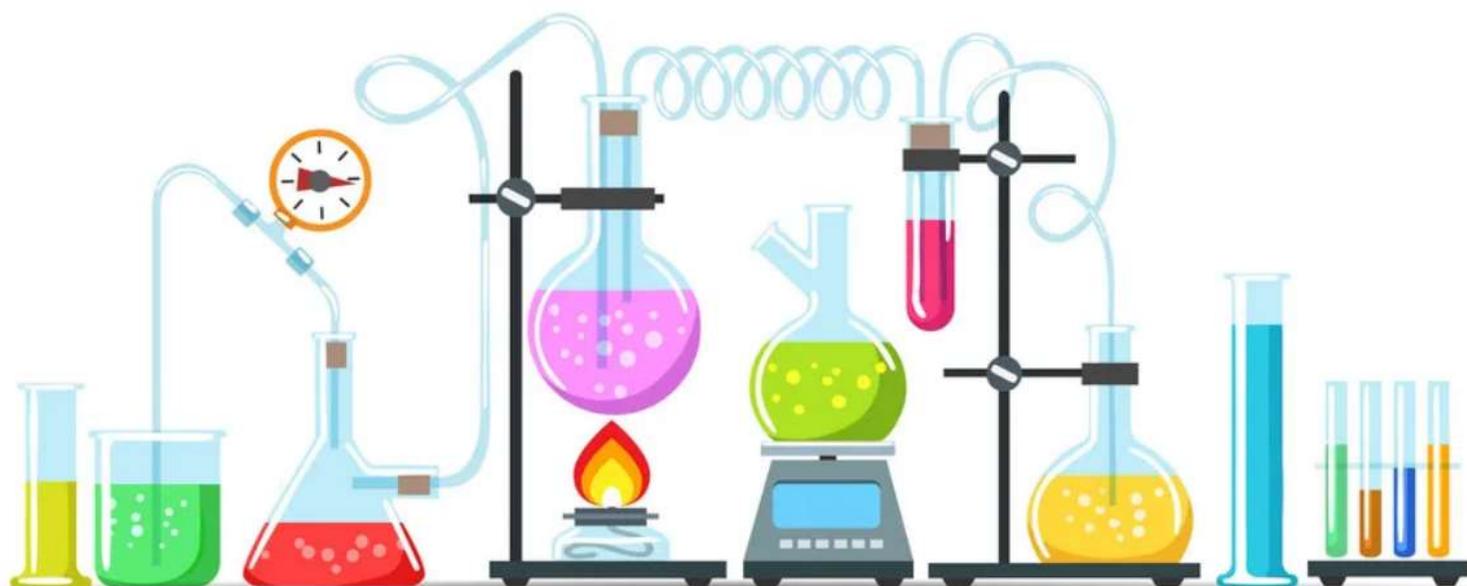


# CHEMISTRY



## THE d- AND f-BLOCK ELEMENTS

### Introduction to d-block elements

Group→1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1																	
2																	
3																	
4			<b>d-block Elements</b>														
5			<b>d-block Elements</b>														
6			<b>d-block Elements</b>														
7			<b>d-block Elements</b>														
			<b>f-block Elements</b>														
			<b>Lanthanides</b>														
			<b>Actinides</b>														

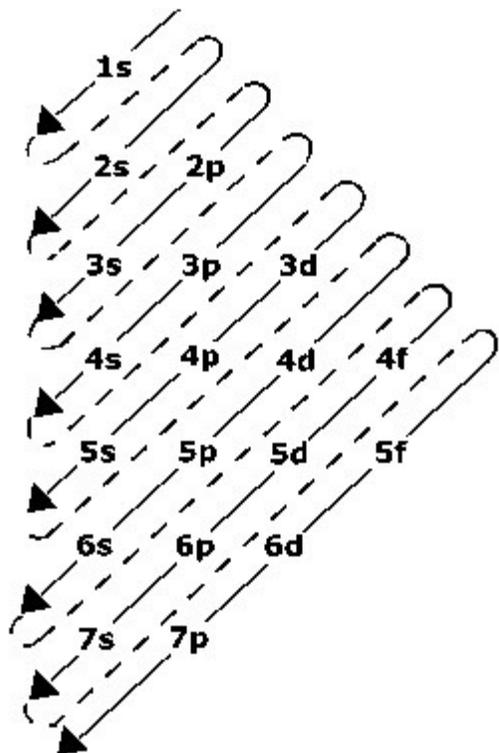
- In the periodic table the d block consist of the elements of group 3 to 12.
- The d orbital of the d-block elements in four periods are filled.
- The three series of the transitionmetals are 3d series from Sc to Zn, 4d series from Y to Cd and 5dseries from La to Hg.
- The fourth 6dseries begins from Ac and is incomplete till now.

### Position of d-block in periodic table

1	2	<b>d-block elements</b>										18	19	20			
H	He																
Li	Be																
Na	Mg																
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

- The d-block elements are found in the middle section of s- and p- block elements in the periodic elements.
- This lead to its name 'transition' due to its position between s- and p- block elements.

### Electronic Configurations of the d-Block Elements



- The electronic configuration of d-block elements is  $(n-1) d^{1-10} ns^{1-2}$ . They have two incomplete outershells.
- Where  $(n-1)$  = Inner d orbitals having electrons from 1-10.
- $ns$  = Outermost orbital may have one or two
- $(n-1) d^{10} n s^2$  represents the electronic configurations of Zn, Cd and Hg.
- They exhibit variable valency that differ by units of one.

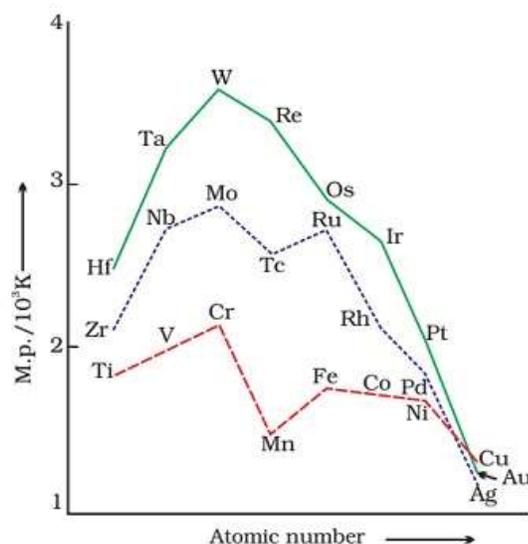
Element	Symbol	Electronic Configuration
Scandium	Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
Titanium	Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
Vanadium	V	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
Chromium	Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
Manganese	Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
Iron	Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
Cobalt	Co	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
Nickel	Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
Copper	Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
Zinc	Zn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

## Physical Properties

- The transition metals are hard and tough. They have low volatility but Zn, Cd and Hg are an exception.

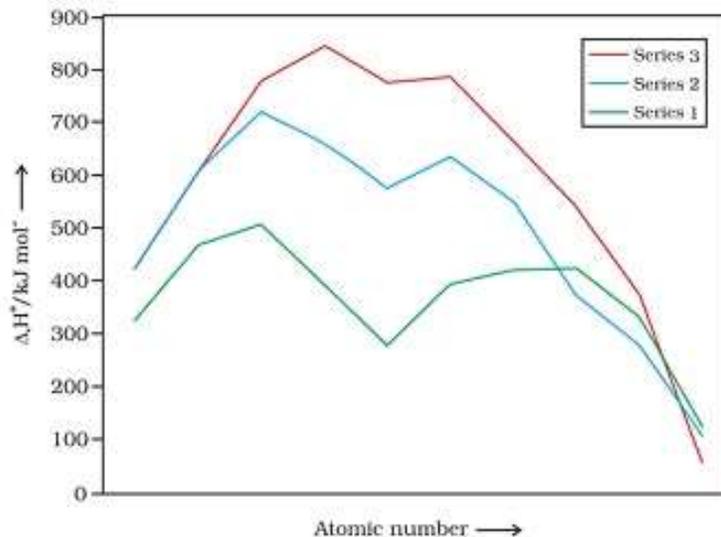


- They have high melting and boiling points due to the greater quantity of electrons from (n-1) d along with the ns electrons metallic



**Fig.** The trends in melting point of d-block elements.

- Metals possessing high boiling point are noble in their
- The metals belonging to second and third series have greater enthalpies of atomisation than the elements belonging to first series.



**Fig.** Enthalpies of atomisation

### Metallic characteristics:

- All transition metals exhibit metallic character.



- They are good conductors of heat and electricity.



**Fig.** Metal is used at the tip of the plug that is inserted into the socket

- They are hard and tough.
- Being metal they exhibit the property of malleability, ductility and sonorosity.



**Fig.** Aluminium is beaten into thin sheets to make aluminium foil used to pack food (Malleability)



**Fig.** bells in temples are made of metal that when struck against hard surface produces sound (Sonorosity)

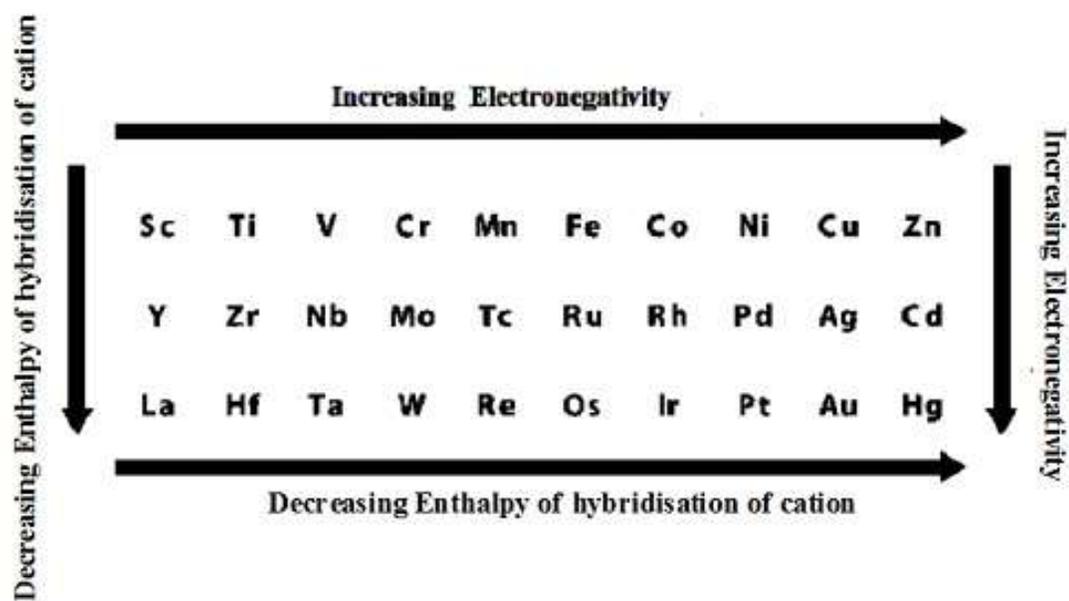


**Fig.** Metals are drawn into wires (Ductility)

- They form alloys by combining with some other metals.
- They are found to exist in face- centered cubic (fcc) structure, hexagonal close-packed (hcp) structure and body-centered cubic (bcc) structure.
- The transition elements exhibit covalent as well as metallic bonding within the atoms.

## Atomic radii

- The atomic radii of the elements of 3d-series decreases as the atomic number increases.
- The atomic radii increase from 3d to 4d, the atomic radii of the 4d and 5d transition series are very close due to lanthanoid contraction. For example, Zirconium and Hafnium.
- This decrease in the metallic radius due to increase in the atomic mass leads to an increase in the density of elements. Consequently the density increases from titanium to copper.



## Ionisation Enthalpies

- Transition elements have small size which results in high ionization energy.
- They exhibit less electro positivity than the s-block elements due to their ionization potentials lying between S and P block elements.
- They form covalent compounds.
- The d-block elements exhibit an increase in the ionization potentials from left to right due to the screening effect of the new electrons added into the (n-1) d subshell.
- The first transition series exhibit an increase in the second ionisation energies with the increase in atomic number due to stable electronic configuration.
- Ionization energy decreases down the group.
- Ionization energy increases across the period.

Increases across the period 

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
<b>La</b>	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
<b>Ac</b>	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn

Decreases down the group 

## Oxidation States

- The number allotted to an element in a compound representing the number of electrons lost or gained by an atom of the element of the compound is called oxidation state.

For example, the electron configuration of copper is  $[\text{Ar}] 3d^{10} 4s^1$ . It attains noble gas configuration by losing one electron. The energy required to lose one more electron is very less and hence copper loses 2 electrons and forms  $\text{Cu}^{2+}$  ion. Therefore copper exhibits +1 and +2 oxidation state. But +2 oxidation states are more common.

It forms compounds like  $\text{CuCl}_2$  and also with oxygen like  $\text{CuO}$ . In both the cases the oxidation state of Cu is +2.

- Transition elements exhibit varying oxidation states due to the minor energy difference between ns and (n -1) d orbitals.
- Along with ns electrons, (n -1) d electrons takes part in bonding. But due to the availability of few electrons for bonding Scandium does not show variable oxidation states.
- Due to presence of more d electrons, zinc has less orbital available for bonding and hence does not exhibit varying oxidation state.
- Among d-block elements the elements belonging to 8th group exhibit maximum oxidation state.
- Among the elements of 3d –series Manganese belonging to 7th group exhibits maximum oxidation state.
- Among the elements of 4d-Series Ruthenium belonging to 8th group exhibits maximum oxidation state.
- Among the elements of 5d-Series Osmium belonging to 8th group exhibits maximum oxidation state.
- The oxidation number of a free element is always 0.

- Oxidation number of (group I) elements like Li, Na, K, Rb, Cs is +1.
- Oxidation number of (group II) elements like Be, Mg, Ca, Sr, Ba is +2.
- Oxidation number of oxygen is -2.
- For example, oxidation state of Phosphorous in the compound  $\text{HPO}_3^{2-}$  can be calculated by the following method:

Oxidation state of H = +1

Oxidation state of O = -2

Oxidation state of  $\text{O}_3 = 3(-2)$  [Since it has 3 atoms of oxygen.]

Overall oxidation state of the compound = -2

Let P represent the oxidation state of Phosphorous.

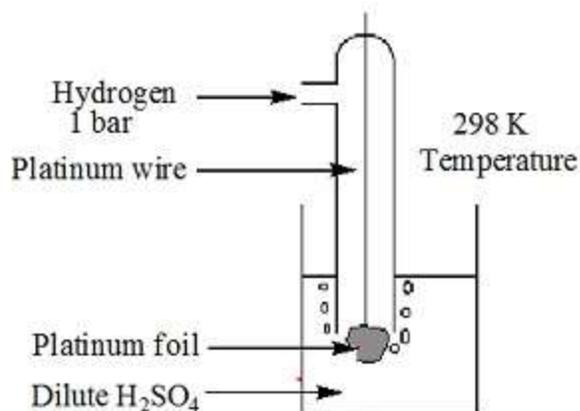
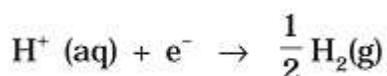
Therefore,

$$\text{HPO}_3^{2-} = +1 + P + 3(-2) = -2$$

- $P = +3$

### Standard hydrogen electrode

- The electrode is connected to a standard hydrogen electrode (SHE) to constitute a cell
- It consists of a platinum electrode coated with a layer of platinum black.



- The electrode is immersed in an acidic solution and the pure hydrogen gas is bubbled through it.
- The concentration of the reduced form and the oxidized form of hydrogen is sustained at unity with following conditions:
- Pressure of hydrogen gas = 1 bar

- Concentration of hydrogen ion in the solution = 1 molar

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E_{\text{cathode}} - 0 = E_{\text{cathode}}$$

- The measured Emf of the cell:

Pt | H<sub>2</sub> (1 bar) | H<sup>+</sup> (1M) || Cu<sup>2+</sup> (1M) | Cu is 0.34 V.

The positive value of the standard electrode potential signifies the easy reduction of Cu<sup>2+</sup> ions than H<sup>+</sup> ions.

- The measured Emf of the cell

Pt | H<sub>2</sub> (1 bar) | H<sup>+</sup> (1M) || Zn<sup>2+</sup> (1M) | Zn is -0.76 V.

The negative value of the standard electrode potential signifies that the hydrogen ions oxidizes the zinc (or it can be said that zinc can reduce hydrogen ions).

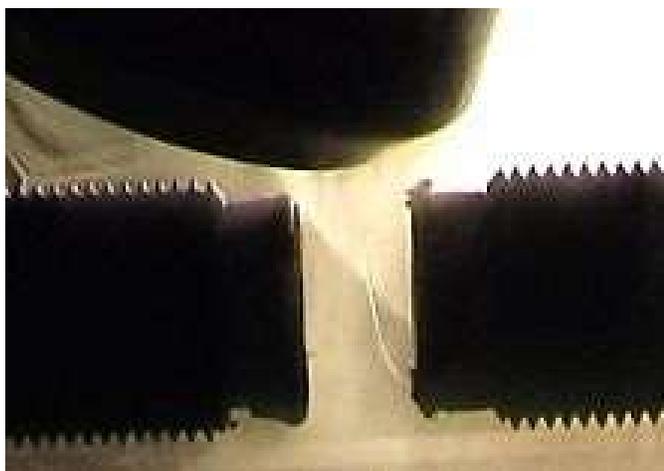
- An electrode with standard electrode potential greater than zero is stable in its reduced form compared to hydrogen gas.
- Whereas an electrode with negative standard electrode potential is less stable in its reduced form compared to hydrogen gas.
- This decreases the standard electrode potential which in turn decreases the oxidizing power of the specific electrode on the left and increases the reducing power of the electrode to the right of the reaction.

## Magnetic Properties

Substances, depending on their behaviour in an external magnetic field, are classified into 2 types:

### Paramagnetic

- They are weakly attracted on application of magnetic field due to presence of one or more unpaired electrons that gets attracted by the magnetic field.
- Application of a magnetic field magnetizes the paramagnetic substances in the same direction but lose their magnetism in the absence of magnetic field.
- O<sub>2</sub>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup> are some examples of such substances.



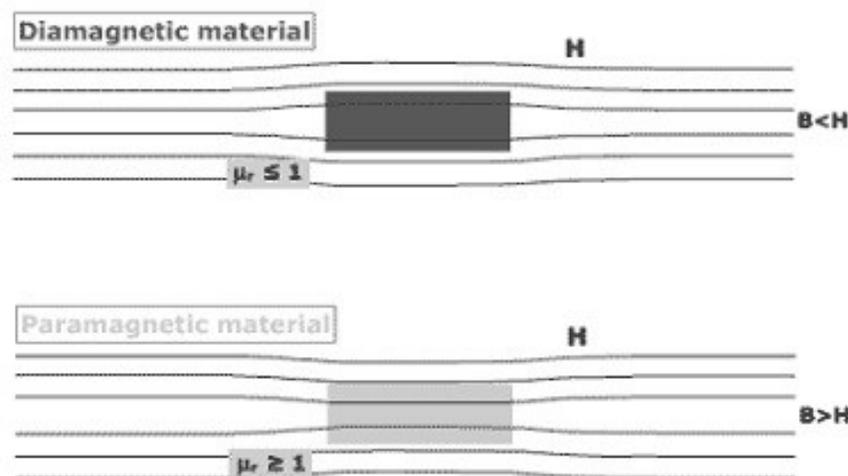
**Fig.** A trickle of liquid oxygen is deflected by a magnetic field, illustrating its paramagnetism.

### Diamagnetic

- They are weakly repelled by a magnetic field due to the absence of unpaired electrons.
- They are weakly magnetized on application of magnetic field in opposite direction.
- Pairing of electrons cancels out their magnetic moments and they lose their magnetic character.
- For example,  $\text{H}_2\text{O}$ ,  $\text{NaCl}$  and  $\text{C}_6\text{H}_6$  are some examples of such substances.



In 3d series the orbital angular momentum of the electrons of the elements is less due to which they exhibit less contribution.



The magnetic moment for these elements is calculated using the spin only formula

$$\mu = \sqrt{n(n+2)}$$

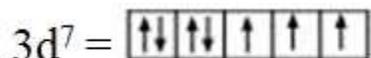
Where  $n$  = number of unpaired electrons

$\mu$  = magnetic moment in units of Bohr Magnetron (BM).

**PROBLEM:** Calculate the 'spin only' magnetic moment of  $M^{2+}(\text{aq})$  ion ( $Z = 27$ ).

**SOLUTION:**  $Z = 27 = [\text{Ar}] 3d^7 4s^2$

$M^{2+} = [\text{Ar}] 3d^7$



This means that it has 3 unpaired electrons.

$$n = 3$$

$$\Rightarrow \sqrt{n(n+2)} = \mu$$

$$\Rightarrow \sqrt{3(3+2)} = \mu$$

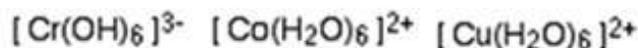
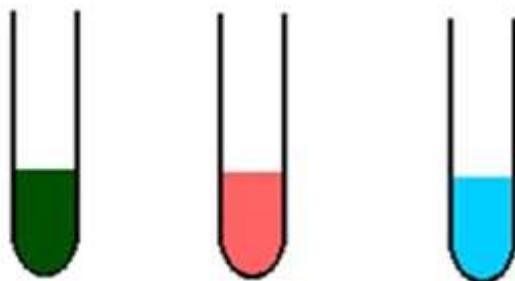
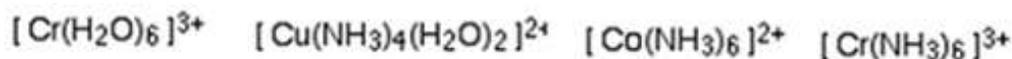
$$\Rightarrow \sqrt{15} = \mu$$

$$\mu \approx 4 \text{ BM}$$

### Formation of Coloured Ions

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

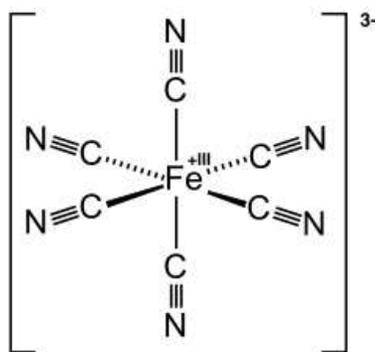
- This frequency generally lies in the visible
- The colour of the transition metal ions is due to the presence of unpaired or incomplete d-orbitals.
- The absorption of visible light and hence coloured nature of the transition metal cations is due to the promotion of one or more unpaired d-electron from a lower to a higher level within the same d-subshell. This promotion requires small amount of energy available in the visible light.
- $\text{Sc}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Cu}^+$  and  $\text{Zn}^{2+}$  have either entirely empty or entirely filled 3d-orbital, i.e. they do not have any unpaired d-electron, and hence appear colourless.



Configuration	Example	Colour
$3d^0$	$\text{Sc}^{3+}$	colourless
$3d^0$	$\text{Ti}^{4+}$	colourless
$3d^1$	$\text{Ti}^{3+}$	purple
$3d^1$	$\text{V}^{4+}$	blue
$3d^2$	$\text{V}^{3+}$	green
$3d^2$	$\text{V}^{2+}$	violet
$3d^3$	$\text{Cr}^{3+}$	violet
$3d^4$	$\text{Mn}^{3+}$	violet
$3d^4$	$\text{Cr}^{2+}$	blue
$3d^5$	$\text{Mn}^{2+}$	pink
$3d^5$	$\text{Fe}^{3+}$	yellow
$3d^6$	$\text{Fe}^{2+}$	green
$3d^6 3d^7$	$\text{Co}^{3+} \text{Co}^{2+}$	bluepink
$3d^8$	$\text{Ni}^{2+}$	green
$3d^9$	$\text{Cu}^{2+}$	blue
$3d^{10}$	$\text{Zn}^{2+}$	colourless

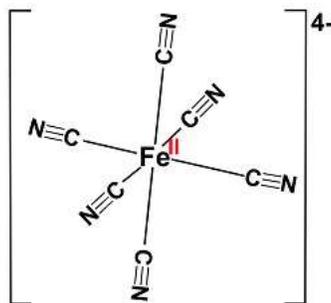
## Formation of Complex Compounds

- The cations of transition metals have great tendency to form complexes with several molecules or ions called ligands.
- The bonds involved in the formation of complexes are coordinate and hence the complexes are called coordinate complexes.
- The structure of these complex ions is linear, square, planar, tetrahedral, octahedral depending upon nature of hybridization of metal ions.
- The weak ligand like CO, NO forms complexes only when transition metals are in zero due to the availability of vacant orbitals in the donor atom of the ligand in addition to lone pair.
- The highly electronegative and basic ligand like F<sup>-</sup>, Cl<sup>-</sup> can form complexes with transition metals even though there are in high oxidation states due to the presence of small, highly charged or neutral ligands with lone pair of electrons that can form strong sigma bond by donating a lone pair of electrons.
- In a transition series the stability of complexes increases with the rise in atomic number.
- The transition metal atom reveals multiple oxidation state; the higher valent ion forms more stable complexes.
- A few examples are:  $[\text{Fe}(\text{CN})_6]^{3-}$



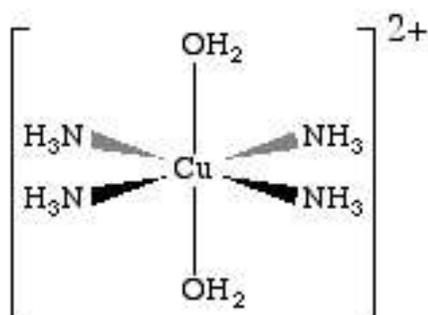
Octahedral Geometry

- $[\text{Fe}(\text{CN})_6]^{4-}$



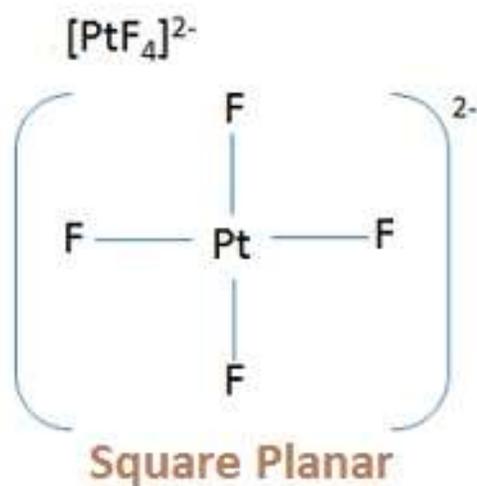
Octahedral Geometry

- $[\text{Cu}(\text{NH}_3)_4]^{2+}$



### Square Planar

- [PtCl<sub>4</sub>]<sup>2-</sup>



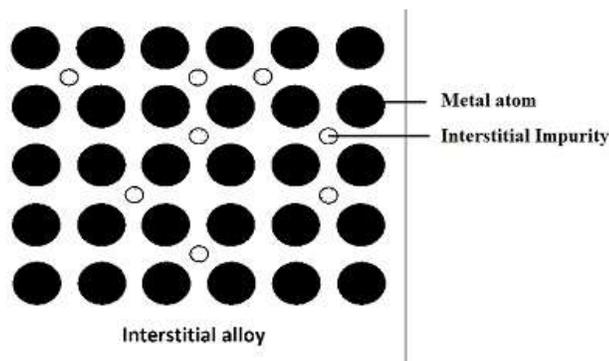
### Square Planar

### Formation of Interstitial Compounds

- Transition elements in combination with small atoms like H, B, C, N etc. leads to the formation of interstitial compounds that are non-stoichiometric in composition.

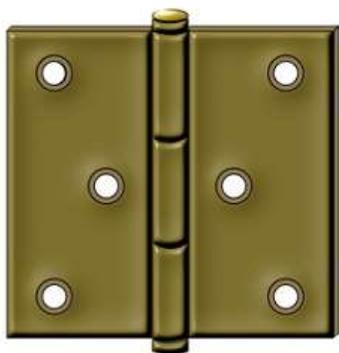
E.g.: TiH<sub>1.3</sub>, VH<sub>0.54</sub>

- The interstitial compounds so formed are chemically inert having higher melting points as compared to pure metals. These compounds are hard and tough and keeps metallic conductivity.



### Alloy Formation

- Alloys are homogeneous mixtures of more than one metal that can displace another metal from the crystal lattice due to their comparable sizes. This leads to the formation of alloys.
- The alloys so formed are hard with high melting points. For example, chromium, vanadium, tungsten, manganese, molybdenum are the ferrous alloys.
- Some other examples are brass (alloy of copper + zinc), stainless steel, bronze (alloy of copper + tin), etc.



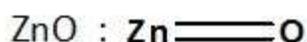
Hinges made of bronze



Medal made of Brass

### Non-stoichiometric Compounds

- The compounds in which there is no conformity in chemical composition with the ideal chemical formula are called non-stoichiometric compounds.
- These compounds are formed due to variable valency in transition metals and also due to the defects arising in solid state.
- The compounds formed with O, S, Se, Te, Fe, Zn etc. are the examples of such compounds.

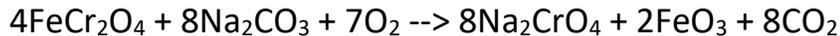


### Preparation of $\text{K}_2\text{Cr}_2\text{O}_7$

Potassium dichromate, ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) is an orange-ish inorganic chemical reagent. In different laboratory or industry it is basically used as an oxidizing agent usually for alcohols.

It can be prepared through the following process:

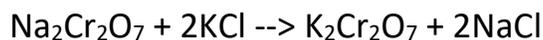
- At first the fusion of chromite ore  $\text{FeCr}_2\text{O}_4$  with sodium or potassium carbonate in the presence of access of air.



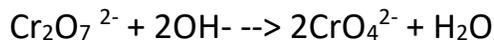
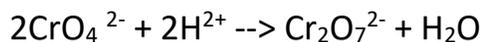
- Solution of sodium chromate is first filtered and then acidified with a solution of sulfuric acid which results in an orange sodium dichromate solution  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  can be crystallized.



- Sodium dichromate is more soluble than potassium dichromate and therefore it is fused with KCl that leads to the formation of orange crystals of potassium dichromate.



- At pH equal to 4 the dichromates and chromates exists in equilibrium and can be inter convertible.



- The yellow colour of chromate changes to orange coloured dichromate in the presence of acidic medium whereas the dichromate changes into chromate in the presence of basic medium.



- The chromate ion is tetrahedral and the dichromate ion consists of two tetrahedral sharing at one corner, with Cr-O-Cr bond angle 126 degree.

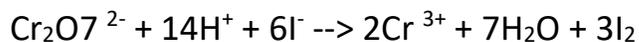
### Properties of Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ )

#### Oxidizing properties

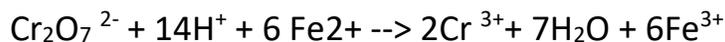
Potassium dichromate is a powerful oxidizing-agent in an acidic medium.



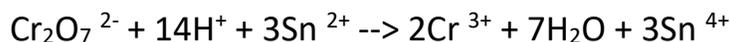
It oxidizes iodides to iodine.



It oxidizes ferrous salts to ferric salts.



It oxidizes stannous salts to stannic salts.

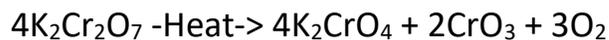


It oxidizes  $\text{H}_2\text{S}$  to sulphur.



#### Action of heat

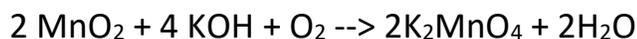
Application of heat leads to the decomposition of Potassium dichromate leading to the formation of potassium chromate, chromic oxide and oxygen.



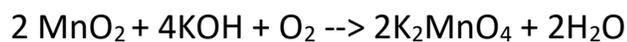
### Preparation of Pottassium Permanganate (KMnO<sub>4</sub>)

Pottassium Permanganate (KMnO<sub>4</sub>) is a dark purple solid consisting of two ions: a potassium ion (K<sup>+</sup>) and a permanganate ion (MnO<sub>4</sub><sup>-4</sup>). It is a strong oxidizing agent and also possess medication properties due to which it is extensively used to clean wounds and in dermatitis.

- Fusion of powdered **Pyrolusite ore (MnO<sub>2</sub>)** with an alkali metal hydroxide like KOH in the presence of air or an oxidizing agent like KNO<sub>3</sub> leads to the formation of dark green **potassium Manganate (K<sub>2</sub>MnO<sub>4</sub>)** which disproportionate either in a neutral or acidic medium and results in the formation of **potassium permanganate**.



- Potassium permanganate is commercially prepared by an alkaline oxidative fusion of Pyrolusite ore (MnO<sub>2</sub>) and again by the electrolytic oxidation of manganate (4) ion.



### Introduction to f-Block Elements

- These elements are also called inner transition elements because the last electron enters (n-2) f-orbital, i.e. inner to the penultimate energy level and forms a transition series.
- The general electronic configuration of these elements can be given as Hence, they have three incomplete shells, viz. (n-2), (n-1) and nth.

### Classification of f-block elements

✓ Lanthanoids:

- They are called Lanthanoids because they come immediately after Lanthanum.
- They are also called 4f-block elements or first inner transition series elements or lanthanides or lanthanons.

✓ Actinoids:

- They are called Actinoids because they come immediately after Actinium.
- They are also called 5f-block elements or second inner transition series elements

oractinides or actinons.

Though Lanthanum is a d-block element, it is included in the lanthanoid series because it closely resembles lanthanoids.

Like Lanthanum, Actinium is also included in the actinoid series.

**Important Points**

Study of lanthanoids is comparatively easier because they show only one stable oxidation state.

Chemistry of actinoids is more complicated because they show a wide range of oxidation states and most of them are radioactive.

The Lanthanoids:

❖ Electronic Configuration:

Name of the element	Symbol (Ln)	Atomic No. (Z)	Electronic configuration	Oxidation state	E.C. outside [Xe] core	
					Ln <sup>2+</sup> Ln <sup>4+</sup>	Ln <sup>3+</sup>
Lanthanum	La	57	[Xe] 5d <sup>1</sup> 6s <sup>2</sup>	+3	5d <sup>1</sup>	4f <sup>0</sup>
Cerium	Ce	58	[Xe] 4f <sup>2</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+3, +4	4f <sup>2</sup>	4f <sup>1</sup> 4f <sup>0</sup>
Praseodymium	Pr	59	[Xe] 4f <sup>3</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+3, +4	4f <sup>3</sup>	4f <sup>2</sup> 4f <sup>1</sup>
Neodymium	Nd	60	[Xe] 4f <sup>4</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+2, +3, +4	4f <sup>4</sup>	4f <sup>3</sup> 4f <sup>2</sup>
Promethium	Pm	61	[Xe] 4f <sup>5</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+3	4f <sup>5</sup>	4f <sup>4</sup>
Samarium	Sm	62	[Xe] 4f <sup>6</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+2, +3	4f <sup>6</sup>	4f <sup>5</sup>
Europium	Eu	63	[Xe] 4f <sup>7</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+2, +3	4f <sup>7</sup>	4f <sup>6</sup>
Gadolinium	Gd	64	[Xe] 4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>	+3	4f <sup>7</sup> 5d <sup>1</sup>	4f <sup>7</sup>
Terbium	Tb	65	[Xe] 4f <sup>9</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+3, +4	4f <sup>9</sup> 4f <sup>7</sup>	4f <sup>8</sup>
Dysprosium	Dy	66	[Xe] 4f <sup>10</sup> 5d <sup>1</sup> 6s <sup>2</sup>	+3, +4	4f <sup>10</sup> 4f <sup>8</sup>	4f <sup>9</sup>
Holmium	Ho	67	[Xe] 4f <sup>11</sup> 5d <sup>1</sup> 6s <sup>2</sup>	+3	4f <sup>11</sup>	4f <sup>10</sup>
Erbium	Er	68	[Xe] 4f <sup>12</sup> 5d <sup>1</sup> 6s <sup>2</sup>	+3	4f <sup>12</sup>	4f <sup>11</sup>
Thulium	Tm	69	[Xe] 4f <sup>13</sup> 5d <sup>1</sup> 6s <sup>2</sup>	+2, +3	4f <sup>13</sup>	4f <sup>12</sup>
Ytterbium	Yb	70	[Xe] 4f <sup>14</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+2, +3	4f <sup>14</sup>	4f <sup>13</sup>
Lutetium	Lu	71	[Xe] 4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup>	+3	4f <sup>13</sup> 5d <sup>1</sup>	4f <sup>14</sup>

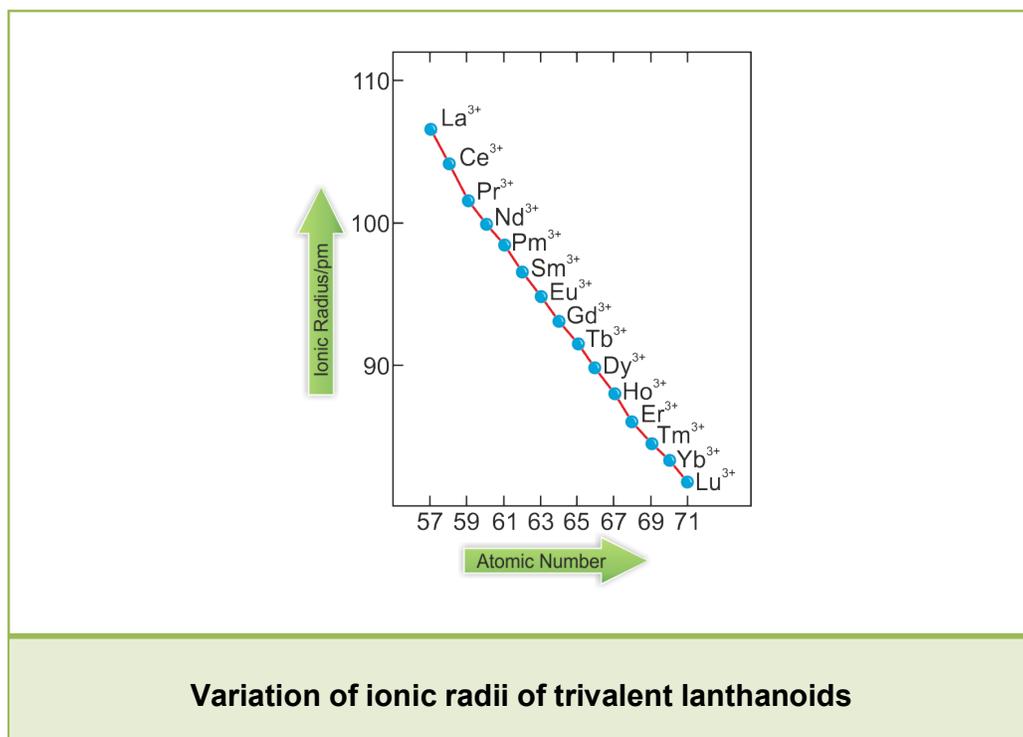
- Lanthanoids have the common electronic configuration of  $6s^2$  and electrons occupying 4f level variably. The electronic configuration of all the tripositive ions are of the form  $4f^n$  ( $n = 1 - 14$ ) with increasing atomic number.
- The electronic configuration of Europium ( $Z = 63$ ) is  $4f^7 6s^2$  and that of Gadolinium ( $Z = 64$ ) is  $4f^7 5d^1 6s^2$ . This can be explained on the basis of extra stability of the half-filled orbitals in their cores.
- The electronic configuration of Ytterbium ( $Z = 70$ ) is  $4f^{14} 6s^2$  and that of Lutetium ( $Z = 71$ ) is  $4f^{14} 5d^1 6s^2$ . This is also explained on the basis of extra stability of the filled orbitals in their cores.

❖ Oxidation states:

- The common oxidation state of the lanthanoids is +3.
- The +2 and +4 oxidation states are very less common. These are exhibited by those elements which attain a stable electronic configuration of  $f^0$ ,  $f^7$  or  $f^{14}$  by losing 2 or 4 electrons.
- Here, each element tries to attain the stable oxidation state by losing or gaining electrons, i.e.  
+3. Hence,  $Sm^{2+}$ ,  $Eu^{2+}$  and  $Yb^{2+}$  ions in solutions are good reducing agents and aqueous solutions of  $Ce^{4+}$  and  $Tb^{4+}$  are good oxidising agents.

❖ Atomic and ionic radii of Lanthanoids:

- In lanthanoids, if the atomic number increases, atomic and ionic radii decrease from  $La^{3+}$  to  $Lu^{3+}$ .



- *Causes of lanthanoid contraction:*

1. When we move from left to right along the lanthanoid series, the nuclear charge increases by one unit at each neighbouring element. The new electron is added to the same subshell. So, the attractive force between the electron and nucleus increases, and hence, the size decreases.
2. When a new electron is added to the f-subshell, the shielding effect of one electron by another is not perfect due to the shape of f-orbitals. Such a shielding cannot balance the effect of increased nuclear charge. Hence, contraction occurs.

- *Consequences of lanthanoid contraction:*

- (a) Difficulty in separation of lanthanoids:

1. Because of the slight difference in ionic radii of lanthanoids, their chemical properties are similar. This makes separation of lanthanoids more difficult.
2. Also, due to the difference in the size of lanthanoids, properties such as solubility, complex ion formation and hydration show differences. This helps separate the individual lanthanoids by the ion exchange method.

- (b) Similarity in the size of elements belonging to the same group of the second

and third transition series:

1. The size of elements belonging to the second transition series is always greater than that of the elements belonging to the same group of the first transition series. Also, the size of the atom of the third transition series, i.e. after lanthanum, is nearly the same as that of the atom of the element belonging to the same group of the second transition series.
2. Similarity in size of the atoms of the elements belonging to the same group of the 2<sup>nd</sup> and 3<sup>rd</sup> transition series is due to the effect of lanthanoid contraction.

(c) Effect on the basic strength of hydroxides:

Because the size of lanthanoid ions decreases from  $\text{La}^{3+}$  to  $\text{Lu}^{3+}$ , the covalent character of the hydroxides increases, and hence, the basic strength decreases. Therefore,  $\text{La}(\text{OH})_3$  is more basic, while  $\text{Lu}(\text{OH})_3$  is weakly basic.

### ❖ Characteristics of Lanthanoids:

(a) Silvery appearance and softness:

All lanthanoids are silvery white soft metals and tarnish easily in air. As the atomic number increases, their hardness also increases.

(b) Melting point:

They have a very high-melting point in the range 1000–1200 K except samarium, which has a high melting point of about 1623 K.

(c) Electrical and thermal conductivity:

They have metallic characteristics, and hence, they are good conductors of heat and electricity.

(d) Density:

They have high densities in the range of 6.77–9.74  $\text{g cm}^{-3}$ . Density and other properties differ smoothly with increasing atomic number except in Eu and Yb.

(e) Colour:

They are silvery white. Most of the trivalent ions are coloured in solid and in aqueous solution. This is due to f–f transition.

(f) Magnetic behaviour:

All the lanthanoids except  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$  show paramagnetism. This property is due to the presence of unpaired electrons in the incomplete 4f subshell.

(g) Ionisation enthalpies:

The first ionisation enthalpies of lanthanoids are about  $600 \text{ kJ mol}^{-1}$  and the second is about  $1200 \text{ kJ mol}^{-1}$ . The third ionisation enthalpy is low if it leads to a stable electronic configuration, i.e. empty, half-filled or completely filled.

(h) Electropositive character:

They are highly electropositive because they possess low ionisation enthalpy.

(i) Standard electrode potential:

The value of their standard electrode potential, i.e.  $E_0$  for half-reaction,  $\text{M}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{M}(\text{s})$ , lies in the range  $-2.2$  to  $-2.4 \text{ V}$ . Europium is an exception because its  $E_0$  value is  $-2.0 \text{ V}$ .

(j) Reducing agents:

They easily lose electrons; hence, they are good reducing agents.

(k) Complex formation:

Because of their large size and low charge density, they do not have much tendency to form complexes. This tendency of complex formation increases with increasing atomic number.

(l) Chemical behaviour:

The first few elements of the series are more reactive like calcium. As the atomic number increases, their behaviour becomes similar to that of aluminium. They show the following properties:

They combine with hydrogen on heating.

They form carbides when heated with carbon.

They form halides when burnt with halogens.

They react with dilute acids to liberate hydrogen gas.

They form oxides and hydroxides.

### ❖ Uses of lanthanoids:

1. It is mainly used in the production of alloy steels to improve the strength of steel. A well-known alloy is mischmetal which has the following composition:

- ✓ Lanthanoid metal = 95%  
(about 50% Ce, 40% La and the rest other lanthanoids)
- ✓ Iron = 5%
- ✓ S, C, Ca and Al = traces

The mischmetal is mostly used in making a magnesium-based alloy. It is pyrophoric alloy, i.e. an alloy which emits sparks when struck. It is used in making bullets, shells and lighter flints.

2. Their oxides are used in the glass industry—for polishing glass and to make optical glass.
3. Mixed oxides of lanthanoids are used as catalysts in petroleum cracking.
4. Ceric sulphate is a well-known oxidising agent used in volumetric analysis.

### Actinoids

#### ❖ Electronic Configuration:

Name of the element	Symbol (M)	Atomic No. (Z)	Electronic configuration	Oxidation state	E.C. outside [Rn] core M3+ M4+	
Actinium	Ac	89	[Rn] 6d1 7s2	+3	5f0	
Thorium	Th	90	[Rn] 6d2 7s2	+3, +4	5f1	5f0
Protactinium	Pa	91	[Rn] 5f2 6d1 7s2	+3,+4,+5	5f2	5f1
Uranium	U	92	[Rn] 5f3 6d1 7s2	+3, +4,+5,+6	5f3	5f2
Neptunium	Np	93	[Rn] 5f4 6d1 7s2	+3, +4,+5,+6,+7	5f4	5f3
Plutonium	Pu	94	[Rn] 5f6 6d0 7s2	+3, +4,+5,+6,+7	5f5	5f4
Americium	Am	95	[Rn] 5f7 6d0 7s2	+3, +4,+5,+6	5f6	5f5
Curium	Cm	96	[Rn] 5f7 6d1 7s2	+3, +4	5f7	5f6
Berkelium	Bk	97	[Rn] 5f9 6d0 7s2	+3, +4	5f7	5f7
Californium	Cf	98	[Rn] 5f10 6d0 7s2	+3	5f9	5f8
Einsteinium	Es	99	[Rn] 5f11 6d0 7s2	+3	5f10	5f9
Fermium	Fm	100	[Rn] 5f12 6d0 7s2	+3	5f11	5f10
Mendelevium	Md	101	[Rn] 5f13 6d0 7s2	+3	5f12	5f11
Nobelium	No	102	[Rn] 5f14 6d0 7s2	+3	5f13	5f12
Lawrencium	Lr	103	[Rn] 5f14 6d1 7s2	+3	5f14	5f13

- All the actinoids have common 7s2 configuration, and filling of the 5f and 6d subshells is variable.
  - The 14 electrons are being added to 5f, except in thorium (Z = 90), but this filling of the 5f subshell continues further after thorium till 5f orbitals are complete at Z = 103.
  - Irregularities in the electronic configurations of actinoids are concerned with the stabilities of f0, f7 and f14 configurations.
  - Although the 4f and 5f orbitals have similar shapes, 5f is less deeply buried than 4f. Hence, 5f electrons can participate in bonding.
- ❖ Oxidation state:
- The common oxidation state of all actinoids is +3.
  - Actinoids also possess the oxidation state of +4. Some of them show higher oxidation state. The oxidation state gradually increases from the extreme left to the middle of the series and then decreases.
  - The compounds of actinoids with +3 and +4 oxidation states undergo hydrolysis.
- ❖ Ionic radii and actinoid contraction:
- Like lanthanoids, actinoids also show contraction due to the poor shielding effect of the 5f-electrons.

- So, the radii of the atoms or ions of actinoids decrease gradually along the series.
- This contraction is greater from element to element in a series because 5f orbitals extend in the space beyond 6s and 6p orbitals.

❖ Characteristics of Actinoids:

(a) Silvery appearance:

Actinoids are metals with silvery appearance.

(b) Structural variability:

They have much more regularities in their metallic radii; hence, they show great structural variability.

(c) Colour:

They are silvery white metals. Their cations are generally coloured. The colour of these cations depends on the number of 5f-electrons.

The cations containing zero 5f electrons or seven 5f electrons are colourless.

The cations containing 2–6 5f electrons are coloured.

This colour mainly arises because of f–f transition.

(d) Melting and boiling points:

Actinoids have high melting and boiling points. They do not show any gradual change even with increasing atomic number.

(e) Density:

With the exception of thorium and americium, all actinoids have high densities.

(f) Ionisation enthalpies:

They have low ionisation enthalpies than lanthanoids. This is because 5f is less penetrating than 4f and hence is more effective in shielding from nuclear charge.

(g) Electropositive character:

They are highly electropositive.

(h) Magnetic behaviour:

They are strongly paramagnetic. The change in magnetic susceptibility of actinoids with increasing number of unpaired electrons is the same as lanthanoids, but the values are higher for actinoids.

(i) Reducing agents:

All the actinoids are strong reducing agents.

(j) Radioactivity:

All the actinoids are radioactive. The first few members of the series have long half-lives. The remaining have half lives ranging from very few days to few minutes.

(k) Chemical behaviour:

They are highly reactive in the crushed form. They show the following properties:

They react with boiling water to give a mixture of oxide and hydride.

They combine with most of the non-metals at moderate temperature.

They react readily with HCl but the reaction with  $\text{HNO}_3$  is less effective because it forms a protective oxide layer on the surface.

Alkalies have no action on them.

❖ Uses of actinoids:

#### Uses of thorium

- It is used in atomic reactors and in treatment of cancer.
- Its salts are used in making incandescent gas mantles.

#### Uses of uranium

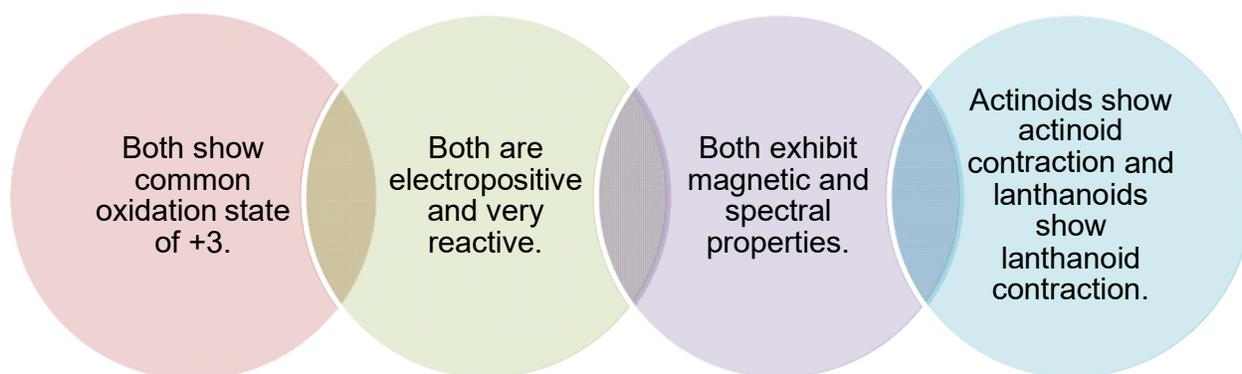
- It is used as nuclear fuel.
- Its salts are used in glass, textile, ceramic industries and in medicines.

#### Uses of plutonium

- It is used as a fuel for atomic reactors.
- It is also used for making bombs.

## Comparison of Lanthanoids and Actinoids

➤ Similarities:



➤ Differences:

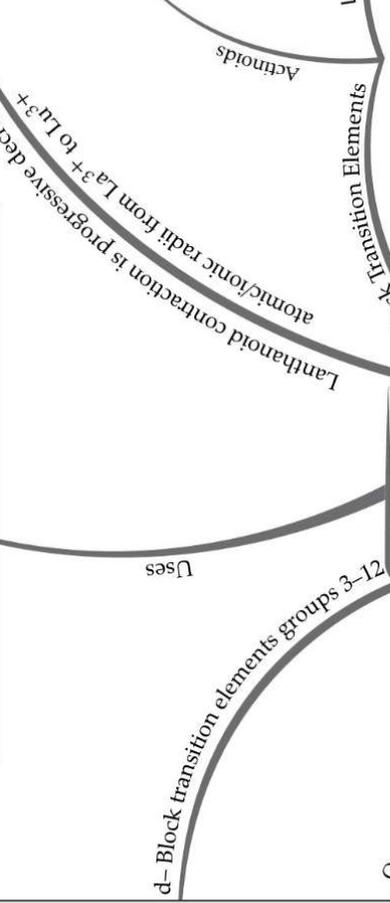
LANTHANOIDS	ACTINOIDS
They also show +2 and +4 oxidation states in few cases.	They also show higher oxidation states such as +4, +5, +6 and +7.
Most of their ions are colourless.	Their ions are coloured.
They have low tendency towards complex formation.	They have high tendency towards complex formation.
Their compounds are weakly basic.	Their compounds are strongly basic.
They do not form oxocations.	They form oxocations $\text{UO}_2^{2+}$ , $\text{PuO}_2^{2+}$ and $\text{UO}_2^+$ .
They are non-radioactive (except Promethium).	They are radioactive.
Their magnetic properties can be explained easily.	Their magnetic properties cannot be explained easily.

# MIND MAP : LEARNING MADE SIMPLE

## CHAPTER - 8

- Uses**
- Helps in production of iron and steels.
  - TiO in pigment industry
  - MnO<sub>2</sub> in dry battery cells.
  - As catalysts in industry.
  - Ni complexes useful in the polymerization of alkynes and other organic compounds such as benzene.
  - Ag Br in photographic industry.

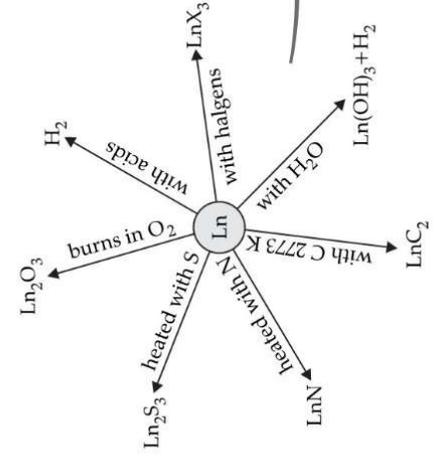
- Position : Between s- and p-blocks
- Electronic configuration :  $(n-1)d^{1-10}ns^{1-2}$
- Physical properties : Show typical metallic properties, melting and boiling point are high; High enthalpies of atomization
- Decrease in radius with increasing atomic number. Lanthanoid contraction is due to imperfect shielding of one e<sup>-</sup> by another in same set of orbitals.
- Ionisation enthalpies : Increases from left to right
- Oxidation states : Variable ; higher ON stable
- Trends in M<sup>2+</sup>/M E° : E° for Mn, Ni and Zn are more negative than expected.
- Trends in M<sup>3+</sup>/M<sup>2+</sup> E° : variable
- Chemical reactivity and E° values : Variable; Ti<sup>2+</sup>, V<sup>2+</sup> and Cr<sup>2+</sup> are strong reducing agents.
- Magnetic properties : Diamagnetism and paramagnetism. Magnetic moment increases with increasing atomic number.
- Formation of coloured ions : Form coloured compounds due to d - d transitions
- Formation of complex compounds : Form a large number of complex compounds
- Catalytic properties : Due to variable oxidation states and ability to form complexes.
- Forms interstitial compounds : Non - stoichiometric and are neither ionic nor covalent.
- Alloy formation : Due to similar atomic sizes.



- Electronic : configuration  $[Rn]5f^{1-14}6d^{0-2}7s^2$ .
- Ionic sizes : Gradual decrease along the series
- Oxidation states : Most common is +3. The show ON of +4, +5, +6 and +7.
- General characteristics :**
  - Silvery in appearance
  - Display variety of structures
  - Highly reactive metals
  - Irregularities in metallic radii, greater than in Lanthanoids.
  - Magnetic properties more complex than lanthanoids.

- Electronic configuration  $4f^{1-14}5d^{0-1}6s^2$
- Atomic and ionic sizes
  - Decreases from La to Lu
- Oxidation states
  - Most common is +3. Some elements exhibit +2 and +4.
- General characteristics
  - Silvery white soft metals and tarnish rapidly in air.
  - Hardness increases with increasing atomic number.
  - Metallic structure and good conductors of heat and electricity.
  - Variable density
  - Trivalent Lanthanoid ions are coloured.
- Ionisation Enthalpies : Low third ionisation enthalpies
- Good reducing agents

Chemical Properties



Oxides and oxoanions of metals

**Potassium dichromate K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>**

Preparation :  $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$

$2\text{Na}_2\text{CrO}_4 + 2\text{H}^+ \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{Na}^+ + \text{H}_2\text{O}$

$\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$

Properties :  $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

Oxidises iodides to iodine, H<sub>2</sub>S to S, SO<sub>3</sub><sup>2-</sup> to SO<sub>4</sub><sup>2-</sup>, NO<sub>2</sub> to NO<sub>3</sub>

**Potassium permanganate KMnO<sub>4</sub>**

Preparation :  $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \rightarrow 2\text{KMnO}_4 + 2\text{H}_2\text{O}$

$3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O} + \text{H}_2\text{O}^+$

$2\text{Mn}^{2+} + 5\text{S}_2\text{O}_3^{2-} + 8\text{H}_2\text{O} \rightarrow 2\text{MnO}_4^- + 10\text{SO}_4^{2-} + 16\text{H}^+$

Properties : Intense colour, weak temperature dependent paramagnetism

$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$

Oxidizes I<sup>-</sup> to I<sub>2</sub>, Fe<sup>2+</sup> to Fe<sup>3+</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup> to CO<sub>2</sub>, S<sup>2-</sup> to S, SO<sub>3</sub><sup>2-</sup> to SO<sub>4</sub><sup>2-</sup>, NO<sub>2</sub> to NO<sub>3</sub>

## Important Questions

### Multiple Choice questions-

Question 1. Which transition metal can show highest oxidation state?

- (a) Sc
- (b) Ti
- (c) Os
- (d) In

Question 2. Which of the following is not an actinoid?

- (a) Thorium
- (b) Californium
- (c) Uranium
- (d) Terbium

Question 3. Which of the following would be diamagnetic?

- (a)  $\text{Cu}^{2+}$
- (b)  $\text{Ni}^{2+}$
- (c)  $\text{Cd}^{2+}$
- (d)  $\text{Ti}^{3+}$

Question 4. Misch metal is an alloy of

- (a) La
- (b) Th
- (c) Ac
- (d) none of these

Question 5. Maximum magnetic moment is shown by

- (a)  $3d^8$

(b)  $3d^7$

(c)  $3d^9$

(d)  $3d^5$

Question 6. Maximum oxidation number of manganese is in

(a)  $K_2MnO_4$

(b)  $MnO_2$

(c)  $KMnO_4$

(d)  $Mn_2O_4$

Question 7. Electronic configuration of  $Fe^{2+}$  ion is

(a)  $[Ar] 4s^2 3d^4$

(b)  $[Ar] 4s^1 3d^5$

(c)  $[Ar] 3d^6$

(d)  $[Ar] 3d^8$

Question 8. Electronic configuration of Cr ( $Z = 24$ ) is

(a)  $3d^4 4s^2$

(b)  $3d^6 4s^0$

(c)  $3d^5 4s^1$

(d) none of these

Question 9. Increasing order of paramagnetism is

(a)  $Cu^{2+}$ ,  $CO^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$

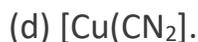
(b)  $CO^{2+}$ ,  $Cu^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$

(c)  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $CO^{2+}$ ,  $Mn^{2+}$

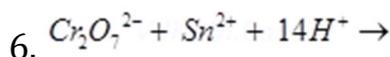
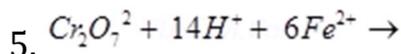
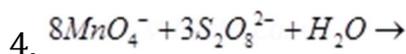
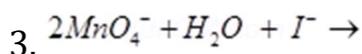
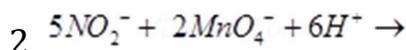
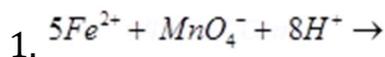
(d)  $Mn^{2+}$ ,  $CO^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$

Question 10. Copper sulphate dissolves in excess of KCN to give:

(a)  $[Cu(CN)_4]^{3-}$

**Very Short Questions-**

1. Zinc, cadmium and mercury are not considered as transition metals. Why?
2. Write the general configuration of d- block elements.
3. What are the factors that decide the ionization potential?
4. What are interstitial compounds. Give two examples
5. What is the ore of  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{KMnO}_4$  ?
6. What is the effect of adding a base to potassium dichromate?
7. Draw the structure of chromate and dichromate ions?
8. Draw the structure of manganate and permanganate ions?
9. Complete and balance: -



10. Name the two series of f-block.
11. The chemistry of actinoids is more complicated than lanthanoids. Why?
12. What is the general valence configuration of f-block elements?
13. What is the most common oxidation state of lanthanoids and actinoids?
14. Actinoid contraction is more than lanthanoid contraction. Give reason.
15. What is the composition of mischmetal? Give its one use.
16. Actinoids show larger number of oxidation states than lanthanoids. Why?

**Short Questions-**

1. Give an explanation for the catalytic properties shown by transition metals.
2. Write some characteristics of interstitial compounds.
3. Describe the steps of preparation of  $\text{K}_2\text{Cr}_2\text{O}_7$  ?
4. Give some of the uses of  $\text{K}_2\text{Cr}_2\text{O}_7$  ?
5. What happens when
  - (a) A lanthanoid reacts with dil- acid
  - (b) A lanthanoid reacts with water.
6. Transition metals generally form coloured ions. Why? Which of the following will be coloured?
7. Explain the steps of preparation of potassium dichromate?
8. What is the lanthanoid contraction? What are its causes and consequences?

### Long Questions-

1. Give reasons-

- (i) Transition metals have high melting points.
- (ii) Second and third transition series have similar radii.
- (iii) Second ionization is difficult from Cu and Cr whereas it is easy for Zn.
- (iv) Most of the transition elements are paramagnetic.
- (v) Transition elements form alloys.

2. Silver atom has completely filled  $d$  orbitals ( $4d^{10}$ ) in its ground state. How can you say that it is a transition element?

3. In the series Sc ( $Z = 21$ ) to Zn ( $Z = 30$ ), the enthalpy of atomization of zinc is the lowest, i.e.,  $126\text{kJmol}^{-1}$ . Why?

4. Which of the  $3d$  series of the transition metals exhibits the largest number of oxidation states and why?

5. The  $E^\ominus(M^{2+}/M)$  value for copper is positive ( $+0.34\text{V}$ ). What is possibly the reason for this? (Hint: consider its high  $\Delta_{\text{ion}}H^\ominus$  and low  $\Delta_{\text{hyd}}H^\ominus$ )

6. How would you account for the irregular variation of ionization enthalpies (first and second) in the first series of the transition elements?

7. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?

8. Which is a stronger reducing agent  $\text{Cr}^{2+}$  or  $\text{Fe}^{2+}$  and why?

### Assertion and Reason Questions-

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

- b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- c) Assertion is correct statement but reason is wrong statement.
- d) Assertion is wrong statement but reason is correct statement.

**Assertion:** Co (IV) is known but Ni (IV) is not.

**Reason:** Ni (IV) has  $d^6$  electronic configuration.

**2.** In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- c) Assertion is correct statement but reason is wrong statement.
- d) Assertion is wrong statement but reason is correct statement.

**Assertion:** Transition metals form substitutional alloys.

**Reason:** Alloys are made to develop some useful properties which are absent in the constituent elements.

## Case Study Questions-

**1.** Read the passage given below and answer the following questions:

The f-block elements are those in which the differentiating electron enters the  $(n-2)f$  orbital. There are two series of f-block elements corresponding to filling of 4f and 5f-orbitals. The series of 4f-orbitals is called lanthanides. Lanthanides show different oxidation states depending upon stability of  $f^0$ ,  $f^7$  and  $f^{14}$  configurations, though the most common oxidation state is +3. There is a regular decrease in size of lanthanide ions with increase in atomic number which is known as lanthanide contraction.

The following questions are multiple choice questions. Choose the most appropriate answer:

- (i) The atomic numbers of three lanthanide elements X, Y and Z are 65, 68 and 70 respectively, their  $Ln^{3+}$  electronic configuration is:
  - a)  $4f^8, 4f^{11}, 4f^{13}$
  - b)  $4f^{11}, 4f^8, 4f^{13}$
  - c)  $4f^0, 4f^2, 4f^{11}$

d)  $4f^3, 4f^7, 4f^9$

(ii) Lanthanide contraction is observed in:

- a) Gd
- b) At
- c) Xe
- d) Te

(iii) Which of the following is not the configuration of lanthanoid?

- a)  $[\text{Xe}]4f^{10}6s^2$
- b)  $[\text{Xe}]4f^{15}d^16s^2$
- c)  $[\text{Xe}]4d^{14}5d^{10}6s^2$
- d)  $[\text{Xe}]4f^75d^16s^2$

(iv) Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

- a) Cerium ( $Z = 58$ )
- b) Europium ( $Z = 63$ )
- c) Lanthanum ( $Z = 57$ )
- d) Gadolinium ( $Z = 64$ )

(v) Identify the incorrect statement among the following.

- a) Lanthanoid contraction is the accumulation of successive shrinkages.
- b) The different radii of Zr and Hf due to consequence of the lanthanoid contraction.
- c) Shielding power of 4f electrons is quite weak.
- d) There is a decrease in the radii of the atoms or ions as one proceeds from La to Lu.

**2.** Read the passage given below and answer the following questions:

The transition elements have incompletely filled d-subshells in their ground state or in any of their oxidation states. The transition elements occupy position in between s- and p-blocks in groups 3-12 of the Periodic table. Starting from fourth period, transition elements consists of four complete series : Sc to Zn, Y to Cd and La, Hf to Hg and Ac, Rf to Cn. In general, the electronic configuration of outer orbitals of these elements is  $(n - 1)d^{1-10} n^{1-2}$ . The electronic configurations of outer orbitals of Zn, Cd, Hg and Cn are represented by the general formula  $(n - 1)d^{10}ns^2$ . All the transition elements have typical metallic properties such as high tensile strength, ductility, malleability. Except mercury, which is liquid at room temperature, other transition elements have typical metallic structures. The transition metals and their compounds also exhibit catalytic property and paramagnetic behaviour. Transition metal also forms alloys.

An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Which of the following characteristics of transition metals is associated with higher catalytic activity?

- a) High enthalpy of atomisation.
- b) Variable oxidation states.
- c) Paramagnetic behaviour.
- d) Colour of hydrated ions.

(ii) Transition elements form alloys easily because they have.

- a) Same atomic number.
- b) Same electronic configuration.
- c) Nearly same atomic size.
- d) Same oxidation states.

(iii) The electronic configuration of tantalum (Ta) is:

- a)  $[\text{Xe}]4f^05d^16s^2$
- b)  $[\text{Xe}]4f^{14}5d^26s^2$
- c)  $[\text{Xe}]4f^{14}5d^36s^2$
- d)  $[\text{Xe}]4f^{14}5d^46s^2$

(iv) Which one of the following outer orbital configurations may exhibit the largest number of oxidation states?

- a)  $3d^54s^1$
- b)  $3d^54s^2$
- c)  $3d^24s^2$
- d)  $3d^34s^2$

(v) The correct statement(s) among the following is/ are:

- I. All d and f-block elements are metals.
- II. All d and f-block elements form coloured ions.
- III. All d and f-block elements are paramagnetic.

- a) (I) only
- b) (I) and (II) only

- c) (II) and (III) only  
 d) (I), (II) and (III)

### MCQ Answers-

1. Answer: (c) Os
2. Answer: (d) Terbium
3. Answer: (c)  $\text{Cd}^{2+}$
4. Answer: (a) La
5. Answer: (d)  $3d^5$
6. Answer: (c)  $\text{KMnO}_4$
7. Answer: (c)  $[\text{Ar}] 3d^6$
8. Answer: (c)  $3d^5 4s^1$
9. Answer: (c)  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{CO}^{2+}$ ,  $\text{Mn}^{2+}$
10. Answer: (a)  $[\text{Cu}(\text{CN})_4]^{3-}$

### Very Short Answers-

**Ans 1.** Zinc, cadmium and mercury have fully filled  $d^{10}$  configuration. Therefore, they are not considered as transition metal.

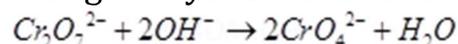
**Ans 2.** General electronic configuration of d- block elements is  $(n-1)d^{1-10}ns^{1-2}$ .

**Ans 3.** The ionization potential values are governed by various ionization enthalpy values, bond enthalpy values and hydration enthalpy values.

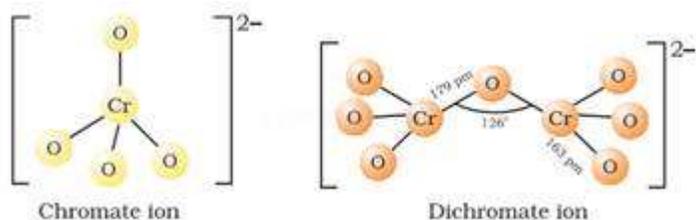
**Ans 4.** Compounds formed by trapping small atoms like H, C, or N inside the crystal lattices of metals eg.  $\text{TiC}$ ,  $\text{Mn}_4\text{N}$  etc.

**Ans 5.** Potassium dichromate  $\rightarrow$  chromite ore ( $\text{FeCr}_2\text{O}_4$ ) Potassium Permanganate  $\rightarrow$   $\text{MnO}_2$  pyrolusite.

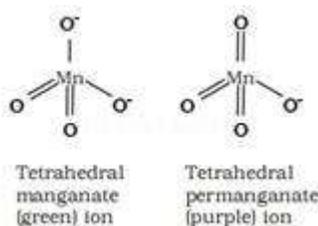
**Ans 6.** When a base is added to orange coloured potassium dichromate its colour changes to yellow due to formation of potassium chromate.



**Ans 7.**



**Ans 8.**



**Ans 9.**

- $5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$
- $5\text{NO}_2^- + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{NO}_3^- + 3\text{H}_2\text{O}$
- $2\text{MnO}_4^- + \text{H}_2\text{O} + \text{I}^- \rightarrow 2\text{MnO}_2 + 2\text{OH}^- + \text{IO}_3^-$
- $8\text{MnO}_4^- + 3\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow 8\text{MnO}_2 + 6\text{SO}_4^{2-} + 2\text{OH}^-$
- $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$
- $\text{Cr}_2\text{O}_7^{2-} + \text{Sn}^{2+} + 14\text{H}^+ \rightarrow \text{Sn}^{4+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

**Ans 10.** The two series are-

- 4f series or Lanthanoids
- 5f series or actinoids.

**Ans 11.** The complications in the actinoid series is due to

- Existence of a wide range of oxidation states.
- Their radioactivity.

**Ans 12.** The general electronic configuration of f-block elements is  $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

**Ans 13.** The common oxidation states of

- (1) 4f series is +3  
 (2) 5f series is +3, +4, +5, +6 & +7

**Ans 14.** The actinoid contraction is more than Lanthanoid contraction as the shielding Power of 5f orbitals is poorer than 4f orbitals.

**Ans 15.** Mischmetal is an alloy of a Lanthanoid metal and iron and traces of S, C, Ca & Al. It is used in Magnesium based alloy to produce bullets, shell and lighter Flint.

**Ans 16.** Actinoids can show many oxidation states as in actinoids 5f orbitals are filled which are not as buried as Lanthanoids and can also participate in bonding to a greater extent besides 6d and 7s electrons.

### Short Answers-

Ans 1. Catalytic properties shown by transition metals can be explained due to

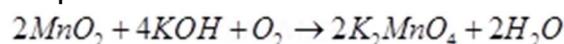
- (i) Presence of variable valency and ability of elements to form complexes.  
 (ii) Surface of metals where the reaction can occur.

Ans 2. Some characteristics of interstitial compounds are

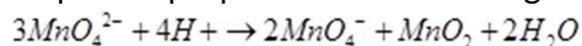
- (i) They have high melting points.  
 (ii) They are very hard.  
 (iii) They retain metallic lustre.  
 (iv) They are chemically inert.

Ans 3. Potassium Permanganate is prepared in two steps:

Step 1: Fusion of  $MnO_2$  with KOH and oxidizing agent to give dark green  $K_2MnO_4$ .



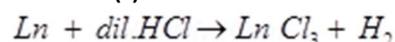
Step 2: Disproportionation of manganate ions to give permanganate ions.



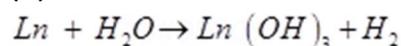
**Ans 4.** Uses of potassium permanganate –

- (a) As an oxidizing agent.  
 (b) For bleaching of wool, cotton & silk.  
 (c) For decolourisation of oils.

**Ans 5.** (i) When a Lanthanoid reacts with dilute- acid, it liberates hydrogen gas.



(ii) When a Lanthanoid reacts with water, it forms hydroxide.

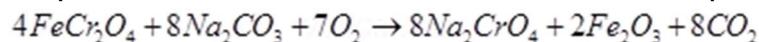


Ans 6. Transition metals form coloured ions due to d-d transition. Coloured ions will be those which have unpaired electrons.

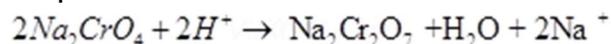
$Sc^{3+}$	$3d^0$	Colourless
$V^{2+}$	$3d^3$	Coloured
$Mn^{2+}$	$3d^5$	Coloured
$Cu^+$	$3d^{10}$	Colourless
$Ni^{2+}$	$3d^8$	Coloured.

**Ans 7.** Preparation of potassium dichromate takes place in three steps.

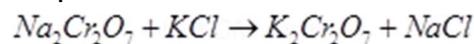
Step 1: Fusion of chromite ore with sodium or potassium carbonate in free excess of air.



Step 2: Conversion of Sodium Chromate to Sodium Dichromate by acidifying it.



Step 3: Conversion of sodium dichromate to potassium dichromate by reacting it with KCl.



Ans 8. Lanthanoid contractions – The cumulative effect of the regular decrease in size or radii of Lanthanoid with increase in atomic number is called Lanthanoid contraction.

Causes – The shape of f orbitals is diffused. They have poor shielding effect due to which the effective nuclear charge increase with increase in atomic number. This causes a decrease in atomic radii

Consequences – Due to Lanthanoid contraction-

1. Radii of the members of the third transition series is similar to those of second transition series.
2. It becomes difficult to separate Lanthanoids.

## Long Answers-

Ans.(i) In transition metals besides ns electrons, (n-1)d electrons can also participate in bonding making stronger metallic bonds. This increases their melting points.

(ii) Due to lanthanoid contraction, there is a decrease in size of 5d series. This makes their sizes same as sizes of elements of 4d series.

(iii) In Cr the electronic configuration is  $3d^5 4s^1$  and for Cu, it is  $3d^{10} 4s^1$ . In these after first ionization, which removes the electron from 4s, second ionization requires disturbance in half filled or fully filled configuration which requires high enthalpy whereas the configuration of Zn is  $3d^{10} 4s^2$ . Here after second ionization, the configuration of Zn is completely filled. Therefore, second ionization is easier for Zn but difficult for Cr and Cu.

(iv) Para magnetism in transition elements arises due to presence of one or more unpaired electrons in atomic orbitals.

(v) Due to similarity in their sizes, transition metals can take each others position in

their crystal lattice. Therefore they are able to form alloys.

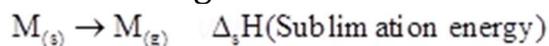
**Ans.** Ag has a completely filled  $4d$  orbital ( $4d^{10}5s^1$ ) in its ground state. Now, silver displays two oxidation states (+1 and +2). In the +1-oxidation state, an electron is removed from the  $s$ -orbital. However, in the +2-oxidation state, an electron is removed from the  $d$ -orbital. Thus, the  $d$ -orbital now becomes incomplete ( $4d^9$ ). Hence, it is a transition element.

**Ans.** The extent of metallic bonding an element undergoes decides the enthalpy of atomization. The more extensive the metallic bonding of an element, the more will be its enthalpy of atomization. In all transition metals (except Zn, electronic configuration:  $3d^{10}4s^2$ ), there are some unpaired electrons that account for their stronger metallic bonding. Due to the absence of these unpaired electrons, the inter-atomic electronic bonding is the weakest in Zn and as a result, it has the least enthalpy of atomization.

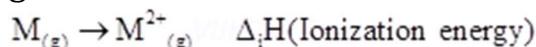
**Ans.** Mn ( $Z = 25$ ) =  $3d^5 4s^2$  Mn has the maximum number of unpaired electrons present in the  $d$ -subshell (5 electrons). Hence, Mn exhibits the largest number of oxidation states, ranging from +2 to +7.

**Ans.** The  $E^\ominus(M^{2+}/M)$  value of a metal depends on the energy changes involved in the following:

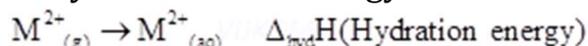
1. Sublimation: The energy required for converting one mole of an atom from the solid state to the gaseous state.



2. Ionization: The energy required to take out electrons from one mole of atoms in the gaseous state.



3. Hydration: The energy released when one mole of ions are hydrated.



Now, copper has a high energy of atomization and low hydration energy. Hence, the  $E^\ominus(M^{2+}/M)$  value for copper is positive.

**Ans.** Ionization enthalpies are found to increase in the given series due to a continuous filling of the inner  $d$ -orbitals. The irregular variations of ionization enthalpies can be attributed to the extra stability of configurations such as  $d^0, d^5, d^{10}$ . Since these states are exceptionally stable, their ionization enthalpies are very high.

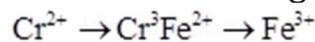
In case of first ionization energy, Cr has low ionization energy. This is because after losing one electron, it attains the stable configuration ( $3d^5$ ). On the other hand, Zn has exceptionally high first ionization energy as an electron has to be removed from stable and fully-filled orbitals ( $3d^{10}4s^2$ ).

Second ionization energies are higher than the first since it becomes difficult to remove an electron when an electron has already been taken out. Also, elements like Cr and Cu have exceptionally high second ionization energies as after losing the first electron, they

have attained the stable configuration ( $\text{Cr}^+ : 3d^5$  and  $\text{Cu}^+ : 3d^{10}$ ). Hence, taking out one electron more from this stable configuration will require a lot of energy.

**Ans.** Both oxide and fluoride ions are highly electronegative and have a very small size. Due to these properties, they are able to oxidize the metal to its highest oxidation state.

**Ans.** The following reactions are involved when  $\text{Cr}^{2+}$  and  $\text{Fe}^{2+}$  act as reducing agents.



The  $E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}}$  value is  $-0.41$  V and  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}$  is  $+0.77$  V. This means that  $\text{Cr}^{2+}$  can be easily oxidized to  $\text{Cr}^{3+}$ , but  $\text{Fe}^{2+}$  does not get oxidized to  $\text{Fe}^{3+}$  easily. Therefore,  $\text{Cr}^{2+}$  is a better reducing agent than  $\text{Fe}^{2+}$ .

## Assertion and Reason Answers-

1. (d) Assertion is wrong statement but reason is correct statement.

### Explanation:

Both Co and Ni have (IV) oxidation state. Ni (IV) has  $3d^6$  electronic configuration.

Metals	Outer electronic configuration	Oxi. states
Co	$3d^7 4s^2$	+2, +3, +4
Ni	$3d^8 4s^2$	+2, +3, +4

2. (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

### Explanation:

Transition metals form substitutional alloys since they have nearly the same size, they can substitute one another in the crystal lattice.

## Case Study Answers-

1. Answer :

(i) (a)  $4f^8$ ,  $4f^{11}$ ,  $4f^{13}$

### Explanation:

Terbium (65),  $4f^8$ ; Dysprosium (Dy),  $4f^9$ ; Ytterbium (Yb),  $4f^{13}$ .

(ii) (a) Gd

(iii) (c)  $[\text{Xe}]4d^{14}5d^{10}6s^2$

(iv) (a) Cerium ( $Z = 58$ )

(v) (b) The different radii of Zr and Hf due to consequence of the lanthanoid contraction.

**Explanation:**

The almost identical radii of Zr (160pm) and Hf (159pm), a consequence of lanthanoid contraction.

**2. Answer :**

(i) (b) Variable oxidation states.

**Explanation:**

The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states to form complexes.

(ii) (c) Nearly same atomic size.

**Explanation:**

Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals.

(iii) (c)  $[\text{Xe}]4f^{14}5d^36s^2$

(iv) (b)  $3d^54s^2$

**Explanation:**

Greater the number of valence electrons, more will be the number of oxidation states exhibited by the element.

(v) (a) (i) only

**Explanation:**

All the d-block elements are metals, they exhibit most properties of metals like lustre, malleability, ductility, high density, high melting and boiling point, hardness, conduction of heat and electricity, etc. All the f-block elements are also metals but they are not good conductors of heat and electricity.