

d & f-BLOCK ELEMENTS

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## NEET SYLLABUS

d and f Block Elements : General introduction, electronic configuration, characteristics of transition metals, general trends in properties of the first row transition metals- metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation. Preparation and properties of  $K_2Cr_2O_7$  and  $KMnO_4$ .

Lanthanoids - electronic configuration, oxidation states, chemical reactivity, and lanthanoid contraction and its consequences.

Actinoids: Electronic configuration, oxidation states and comparison with lanthanoids.

#### **OBJECTIVES**

#### After studying this unit, you will be able to :

- *learn the positions of the d– and f-block elements in the periodic table;*
- know the electronic configurations of the transition (d-block) and the inner transition (fblock) elements;
- appreciate the relative stability of various oxidation states in terms of electrode potential values;
- describe the preparation, properties, structures and uses of some important compounds such as K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and KMnO<sub>4</sub>;
- understand the general characteristics of the d- and f-block elements and the general horizontal and group trends in them;
- describe the properties of the f-block elements and give a comparative account of the lanthanoids and actinoids with respect to their electronic configurations, oxidation states and chemical behaviour.

"d  $\mathcal{K}$  f-block elements signify special people in society, on whom no social or economic rule is applicaton."

**Mitch Album** 

# d & f-BLOCK ELEMENTS

#### 2.0 INTRODUCTION :

- d-block elements are often called as 'transition elements because their position in periodic table is between the s-block and p-block elements.
- (ii) Their properties are transitional between the highly reactive metallic elements of s-block (which form ionic compounds) and the elements of p-block (which are largely covalent).
- (iii) Typically the transition elements have an incompletely filled d-orbital. A transition element may be defined as the element whose atom in ground state or ion in one of common oxidation states, has partly filled d-sub shell i.e. having electrons between 1 to 9.
- (iv) Group 12 (the zinc group) elements have completely filled d-orbitals in the ground state as well as in their common oxidation states. Therefore, they are not regarded as transition elements.
- (v) The general electronic configuration of d-block elements is  $(n-1) d^{1-10} ns^{1-2}$ , where n is the outer most shell. However, palladium does not follow this general electronic configuration. It has electron configuration [Kr]<sup>36</sup>  $4d^{10} 5s^{0}$  in order to have stability.
- (vi) Zn, Cd and Hg are involved in transition series but they are called non transition elements due to completely filled d-orbitals.

	1st Series									
Z 4s 3d	Sc 21 2 1	Ti 22 2 2	V 23 2 3	Cr 24 1 5	Mn 25 2 5	Fe 26 2 6	Co 27 2 7	Ni 28 2 8	Cu 29 1 10	Zn 30 2 10
				2r	nd Series					
Z 5s 4d	Y 39 2 1	Zr 40 2 2	Nb 41 1 4	Mo 42 1 5	Tc 43 1 6	Ru 44 1 7	Rh 45 1 8	Pd 46 0 10	Ag 47 1 10	Cd 48 2 10
				3r	d Series					
Z 6s 5d	La 57 2 1	Hf 72 2 2	Ta 73 2 3	W 74 2 4	Re 75 2 5	Os 76 2 6	Ir 77 2 7	Pt 78 1 9	Au 79 1 10	Hg 80 2 10

#### 2.1 GENERAL TRENDS IN THE CHEMISTRY OF TRANSITION ELEMENTS.

#### (A) Metallic character :

- (i) In d-block elements the last but one (i.e. the penultimate) shell of electrons is expanding. Thus they have many physical and chemical properties in common.
- (ii) Nearly all the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre.
- (iii) Most transition elements have ccp/hcp type structures.
- (iv) The transition elements are very much hard and have low volatility, they have high enthalpy of atomisation.
- (v) Cr, Mo and W have maximum number of unpaired electrons and therefore, these are very hard metals and have maximum enthalpies of atomisation in their respective period.
- (vi) The metals with very high enthalpy of atomisation (i.e., very high boiling point) tend to be noble in their reactions.
- (vii) The metals of the 4d and 5d series have greater enthalpies of atomisation than the corresponding elements of the 3d and this is an important factor indicating for the occurrence of much more frequent metal-metal bonding in compounds of the heavy transition metals.



Graph showing Trends in enthalpies of atomisation of transition elements

#### (B) MELTING AND BOILING POINTS

(i) Melting and boiling point of d-block > s-block

Reason : Stronger metallic bond formed present by unpaired d-electrons.

- (ii) In Zn, Cd, and Hg there is no unpaired electron present in d-orbital, hence due to absence of covalent bond melting and boiling point are very low in series. (Volatile metals Zn, Cd, Hg)
- (iii) In 3d series Sc to Cr melting and boiling point increases then Mn to Zn melting and boiling point decreases
- (iv) As the number of unpaired d-electron increases, the number of covalent bond and bond energy between the atoms is expected to increase up to Cr-Mo-W family where each of the d-orbital has only unpaired electron and the opportunity for covalent sharing is greatest.

#### ALLEN

- (v) Mn and Tc have comparatively low melting point, due to weak metallic bond because of stable Half filled (d<sup>5</sup>) configuration and high IP.
- (vi) Lowest melting point Hg (- 38°C) ; Highest melting point W ( $\simeq$  3400°°C)



# Illustrations

**Illustration1 :** Why do the transition elements have higher boiling & melting points ?

**Solution** Because of having larger number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence stronger bonding between atoms. Hence strong metallic bonds between the atoms of these elements attribute to their high melting and boiling points.

- (C) DENSITY :
  - (i) The atomic volumes of the transition elements are low compared with the elements of group 1 and 2. This is because the increased effective nueclear charge. In addition, the extra electrons added occupy inner orbitals. Consequently the densities of the transition metals are high.
  - (ii) Across a period from left to right atomic volumes decrease and atomic masses increase. Hence the densities also increase across a period.

 $Sc \leq Ti \leq V \leq Cr \leq Mn \leq Fe \leq Co \leq Ni \approx Cu > Zn$ 

(zinc is an exception, having large atomic volume and hence has lower density)

- (iii) 3d < 4d << 5d Series
- (iv) Maximum density :  $Ir \ge Os$

#### (D) Ionisation energies or Ionisation enthalpies :

- (i) The first ionisation energy of Zn, Cd, and Hg are very high because of their fully filled  $(n-1) d^{10} ns^2$  configuration.
- (ii) Order of second ionisation energy : Sc < Ti < V < Mn < Cr

#### (E) Oxidation states :

- (i) The transition metals exhibit a large number of oxidation states. With the exception of a few elements, most of these show variable oxidation states. These different oxidation states are related to the electronic configuration of their atoms.
- (ii) The existence of the transition elements in different oxidation states means that their atoms can lose different number of electrons. This is due to the participation of inner (n 1) d-electrons in addition to outer ns-electrons because, the energies of the ns and (n 1) d-sub-shells are nearly same.
- (iii) In general oxidation state of d-block element is given as minimum oxidation state = number of 's' electrons

maximum oxidation state = number of 's' electrons + unpaired 'd' electron

Element	Outer electronic configuration	Oxidation states
Sc	$3d^{1}4s^{2}$	+3
Ti	$3d^24s^2$	+2, +3, +4
V	$3d^34s^2$	+2, +3, +4, +5
Cr	$3d^54s^1$	+2, +3, (+4), (+5), +6
Mn	$3d^54s^2$	+2, +3, +4, (+5), +6, +7
Fe	$3d^64s^2$	+2, +3, (+4), (+5), (+6)
Co	$3d^74s^2$	+2, +3, (+4)
Ni	$3d^84s^2$	+2, +3, +4
Cu	$3d^{10}4s^1$	+1, +2
Zn	$3d^{10}4s^2$	+2

#### Different oxidation states of first transition series.

#### • Oxidation states given in parenthesis are unstable.

Higher oxidation state in d-block = +8 (Os, Ru)

Zero oxidation state for e.g.  $[Ni(CO)_4]$ ,  $[Fe(CO)_5]$ 

(iv) Relative stability of oxidation state :



(v) On moving in a period stability of higher oxidation state decreases

**e.g.**  $VO_3^- > CrO_4^{2-} > MnO_4^-$ 

(vi) On moving down the group stability of higher oxidation state increases

**e.g.** 
$$CrO_{3}^{+6} < MO_{3}^{+6} < WO_{3}^{+6}$$

$$MnO_{4}^{-} < TcO_{4}^{-} < ReO_{4}^{-}$$

#### (F) ELECTRODE POTENTIALS :

In addition to ionisation enthalpy, the other factors such as enthalpy of sublimation, hydration enthalpy, ionisation enthalpy etc. determine the stability of a particular oxidation state in solution. This can be explained in terms of their electrode potential values. The oxidation potential of a metal involves the following process:

This process actually takes place in the following three steps as given in following flowchart :



The oxidation potential which gives the tendency of the overall change to occur, depends upon the net effect of these three steps. The overall energy change is  $\Delta H = \Delta_{sub} H^{\Theta} + \Delta H + \Delta_{hud} H$ 

If SOP is +ve  $\rightarrow$  Means Oxidation easy

If SRP is +ve  $\rightarrow$  Means reduction easy

#### Some important examples :

1.  $E^{o}_{M^{*2}/M} \Rightarrow$  +ve only for Cu among 3d elements because HE of Cu<sup>+2</sup> is not enough to compensate for sublimation energy, IP<sub>1</sub> and IP<sub>2</sub> for Cu.

$$\mathbf{2.} \qquad \mathbf{E}^{\mathbf{0}}_{\mathbf{M}^{+3}/\mathbf{M}^{+2}} \qquad \Rightarrow \qquad$$

(a)  $E^0_{Cr^{+3}/Cr^{+2}} = -ve$ 

Reason :  $t_2g^3eg^0 \leftarrow d^3 > d^4$ 

(b) 
$$E^{0}_{Mn^{+3}/Mn^{+2}} = +ve$$
 (high)

Reason :  $d^4 < d^5$ 

(c) 
$$E^{0}_{Fe^{+3}/Fe^{+2}} = \text{less +ve (learn)}$$

Reason :  $d^5 > d^6$ 

**Note :** The SRP of  $E^0_{Fe^{t^3}/Fe^{t^2}}$  is less then expected because of extra stability of  $d^5$  configuration of Fe<sup>+3</sup> ion.

#### (G) TRENDS IN STABILITY OF HIGHER OXIDATION STATES

Standard electrode potential data provide valuable information about the stabilities of different oxidation states shown by an element. The highest oxidation states are shown generally among halides and oxides.

#### Halides of first transition series

- (i) In metal halides. The transition elements react with halogens at high temperatures to form transition metal halides. These reactions have very high heat of reaction. But once the reaction starts, the heat of reaction is sufficient to continue the reaction. The halogens react in the following decreasing order ;  $F_2 > Cl_2 > Br_2 > I_2$
- (ii) In general, the elements of first transition series tend to exist in low oxidation states. Chromium to zinc form stable difluorides and the other chlorides are also known.
- (iii) Since fluorine is the most electronegative element, the transition metals show highest oxidation states with fluorine. The highest oxidation states are found in  $TiX_4$  (tetrahalides, X = F, Cl, Br and I), VF<sub>5</sub> and CrF<sub>6</sub>.

- (iv) The +7 oxidation state for Mn is not shown by simple halides. However,  $MnO_3F$  is known in which the oxidation state of Mn is +7.
- (v) The tendency of fluorine to stabilise the highest oxidation state is due to either higher lattice enthalpy as in case of  $CoF_3$  or higher bond enthalpy due to higher covalent bonds e.g.,  $VF_5$  and  $CrF_6$ .
- (vi) Fluorides are relatively unstable in their low oxidation states. For example, vanadium form only  $VX_2$  (X = Cl, Br or I) and copper can form CuX (X = Cl, I). All copper (II) halides are known except the iodide. This is because, Cu<sup>2+</sup> oxidises I<sup>-</sup> to I<sub>2</sub>.

 $2Cu^{2+} + 4I^{-} \longrightarrow Cu_{2}I_{2}(s) + I_{2}$ 

It has been observed that many copper (I) compounds are unstable in aqueous solution and they undergo disproportionation to Cu(II) and Cu(0) as :

 $2Cu^{+} \longrightarrow Cu^{2+} + Cu$ 

Copper in +2 oxidation state is more stable than in +1 oxidation state. This can be explained on the basis of much larger negative hydration enthalpy ( $\Delta_{hyd}H^{\Theta}$ ) of Cu<sup>2+</sup> (aq) than Cu<sup>+</sup>, which is much more than compensates for the large energy required to remove the second electron i.e., second ionisation enthalpy of copper.

#### (H) IN METAL OXIDES AND OXOCATIONS.

- (i) The ability of oxygen to stabilize the highest oxidation state is demonstrated in their oxides. The highest oxidation states in their oxides concides with the group number. For example, the highest oxidation state of scandium of group 3 is +3 in its oxides,  $Sc_2O_3$  whereas the highest oxidation state of manganese of group 7 is +7, in  $Mn_2O_7$ .
- (ii) Besides the oxides, oxocation of the metals also stabilise higher oxidation states. For example,  $V^{V}$  as  $VO_{2^{+}}$ ,  $V^{IV}$  as  $VO^{2^{+}}$  and  $Ti^{IV}$  as  $TiO^{2^{+}}$ .
- (iii) It may be noted that the ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. For example, manganese forms highest fluoride as  $MnF_4$  whereas the highest oxide is  $Mn_2O_7$ . This is due to the fact that oxygen has great ability to form multiple bonds to metals.
- (iv) The transition elements in the +2 and +3 oxidation states mostly form ionic bonds whereas with higher oxidation states, the bonds are essentially covalent e.g., in  $MnO_4^-$  all bonds are covalent. As the oxidation number of a metal increases, the ionic character of their oxides decrease. For example, in case of Mn,  $Mn_2O_7$  is a covalent. In these higher oxides the acidic character is predominant. Thus  $CrO_3$  gives  $H_2CrO_4$  and  $H_2Cr_2O_7$  and  $Mn_2O_7$  gives  $HMnO_4$ .  $V_2O_5$  is, however amphoteric though mainly acidic and with alkalies as well as acids gives  $VO_4^{3-}$  and  $VO_2^+$  respectively.

#### In general

Oxidation state	Nature of oxide/Hydroxide (d-block)
+1,+2, +3	Basic
+4	Amphoteric
+5, +6, +7, +8	Acidic

Except  $Cr_2O_3$  = Amphoteric

#### (I) FORMATION OF COLOURED IONS : See coordination compound

#### (J) MAGNETIC PROPERTIES

It is interesting to note that when the various substances are placed in a magnetic field, they do not behave in a similar way i.e., they show different behaviour which are known as magnetic behaviour.

These are classified as :

- (i) **Paramagnetic substances.** The substances which are attracted by magnetic field are called paramagnetic substances and this character arises due to the presence of unpaired electrons in the atomic orbitals.
- (ii) Diamagnetic substances. The substances which are repelled by magnetic field are called diamagnetic substances and this character arises due to the presence of paired electrons in the atomic orbitals. Most of the compounds of transition elements are paramagnetic in nature and are attracted by the magnetic field.

The transition elements involve the partial filling of d-sub-shells. Most of the transition metal ions or their compounds have unpaired electrons in d-sub-shell (from configuration  $d^1$  to  $d^9$ ) and therefore, they give rise to paramagnetic character.

(iii) The magnetic moment arise only from the spin of the electrons. This can be calculated from the

relation  $\mu = \sqrt{n(n+2)}$  B.M. n = Number of unpaired electrons

Ion	Configuration	Unpaired	Magnetic	moment
	-	electron(s)	Calculated	Observed
Sc <sup>3+</sup>	3d°	0	0	0
Ti <sup>3+</sup>	$3d^1$	1	1.73	1.75
Ti <sup>2+</sup>	3d <sup>2</sup>	2	2.84	2.76
V <sup>2+</sup>	$3d^3$	3	3.87	3.86
Cr <sup>2+</sup>	$\mathrm{3d}^4$	4	4.90	4.80
Mn <sup>2+</sup>	$\mathrm{3d}^{\mathrm{5}}$	5	5.92	5.96
Fe <sup>2+</sup>	$\mathrm{3d}^6$	4	4.90	5.3 – 5.5
Co <sup>2+</sup>	$3d^7$	3	3.87	4.4 - 5.2
Ni <sup>2+</sup>	$3d^8$	2	2.84	2.9 - 3.4
Cu <sup>2+</sup>	3d <sup>9</sup>	1	1.73	1.8 - 2.2
Zn <sup>2+</sup>	$\mathrm{3d}^{10}$	0	0	
1				

#### Table : Calculated and Observed Magnetic Moments (BM)

(K) FORMATION OF COMPLEXES : See coordination compound

#### (L) FORMATION OF INTERSTITIAL COMPOUNDS

Transition metals form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen. The small atoms of these non-metallic elements (H, B, C, N, etc.) get trapped in vacant spaces of the lattices of the transition metal atoms as shown below.

e.g. WC,  $Fe_{3}C$ ,  $TiH_{1.30-1.80}$ 

#### Properties :

llen

- (1) They are generally non-stoichiometric compound.
- (2) Nither typical ionic nor covalent
- (3) Harder then pure metal
- (4) High melting point then pure metal
- (5) Maleability and ductility less then pure metal
- (6) Chemically inert



Figure showing formation of interstitial compounds

#### **CATALYTIC PROPERTIES** (M)

d-block metals or their compound act as catalyst in many reaction due to :

- Possibility of variable oxidation state (i)
- (ii) Presence of free valencies over metal surface (adsorption power)
- (iii) Presence of vacant d-orbital

e.g.

 $SO_2 + \frac{1}{2}O_2 \xrightarrow{V_2O_5} SO_3$ (1)

 $V_2O_5 + SO_2 \longrightarrow SO_3 + V_2O_4$  (divanadium tetroxide)

 $2V_2O_4 + O_2 \longrightarrow 2V_2O_5$ 

- $2I^- + S_2O_8^{2^-} \xrightarrow{Fe(III)} I_2 + 2 SO_4^{2^-}$ (2)
- (3) Veg oil +  $H_2 \xrightarrow{Ni/pt}$  Veg ghee

#### **ALLOY FORMATION:** (N)

Alloys are homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other metal. The alloys are generally formed by those atoms which have metallic radii within about 15% of each other. Transition metals form a large number of alloys. The transition metals are quite similar in size and therefore the atoms of one metal can substitute the atoms of other metal in its crystal lattice.



Atoms of metal M Atoms of different metal

#### Alloy formation

Note : Fe, Co, Ni do not form amalgam with Hg (Due to large difference in size)

## **BEGINNER'S BOX-1**

1.	The general electro exceptions mainly d	nic configuration of d-block lue to	elements is (n-1)d <sup>1-10</sup> ns	<sup>1–2</sup> . This generalisation has seve	ral ral
	(1) strong shielding	of (n—1) d-electrons			D-BLOCK
	(2) very little energy	difference between (n−1)d	and ns orbitals		JLE-5\2-0
	(3) presence of unp	aired electrons			G/WODI
	(4) high energy diffe	erence between (n-1)d and	ns orbitals		HEM\EN
2.	Select group of tran	nsition elements			ARGET\C
	(1) Pb, Sc, V	(2) Pd, Cd, La	(3) Pd, La, Fe	(4) Zn, Pd, Bi	AI-B0\T
3.	Which element is h	aving lowest melting and bo	piling point :		DE02\BC
	(1) Ti	(2) Cu	(3) Zn	(4) Mn	ON/:Z
72					Ε

4. Density of which of the following element is highest								
	(1) Pt	(2) Hg	(3) Mn	(4) Cu				
5.	Not more than o	ne oxidation state is shown	by <b>:</b>					
	(1) Mn	(2) Cr	(3) Fe	(4) Sc				
6.	Consider the ion	us Fe <sup>2+</sup> , Fe <sup>3+</sup> , Cr <sup>2+</sup> , Cr <sup>3+</sup> , Mr	n <sup>2+</sup> , Mn <sup>3+</sup>					
	(i) Strongest oxid	ising ion is						
	(1) $Fe^{2+}$	(2) Cr <sup>3+</sup>	(3) Mn <sup>3+</sup>	(4) Mn <sup>2+</sup>				
	(ii) Strongest red	ucing ion is						
	(1) $Fe^{2+}$	(2) Mn <sup>2+</sup>	(3) Cr <sup>2+</sup>	(4) Mn <sup>3+</sup>				
7.	Which compoun	d does exist						
	(1) MnO <sub>3</sub> F	(2) K <sub>2</sub> [Cul <sub>4</sub> ]	(3) MnF <sub>7</sub>	(4) CrF <sub>7</sub>				
8.	In the form of dichromate, Cr(VI) is a strong oxidising agent in acidic medium but Mo(VI) in MoO <sub>3</sub> and W(VI) in WO <sub>2</sub> are not because							
	(1) Cr(VI) is more stable than Mo(VI) & W(VI)							
	(2) Mo(VI) and W(VI) are less stable than Cr(VI)							
	(3) H.O.S. of heavier members of group 6 of transition metals are more stable							
	(4) L.O.S. of heavier members of group 6 of transition metals are more stable							
9.	By which of the	following species, a transitio	nal metal can brought ir	n to its highest oxidation state				
	(1) F <sub>2</sub>	(2) Cl <sub>2</sub>	(3) Br <sub>2</sub>	(4) I <sub>2</sub>				
<u> </u>								

#### 2.2 COMPOUNDS OF d-BLOCK ELEMENTS : POTASSIUM PERMANGANATE ( $KMnO_4$ ) :

#### (a) Preparation

This is the most important and well known salt of permanganic acid and is prepared from the pyrolusite ore. It is prepared by fusing pyrolusite ore either with KOH or  $K_2CO_3$  in presence of atmospheric oxygen or any other oxidising agent such as  $KNO_3$ . The fused mass turns green with the formation of potassium manganate,  $K_2MnO_4$ .

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

$$2MnO_2 + 2K_2CO_3 + O_2 \longrightarrow 2K_2MnO_4 + 2CO_2$$

The fused mass is extracted with water and the solution is now treated with a current of chlorine or ozone or carbon dioxide to convert manganate into permanganate.

Commercially it is prepared by fusion of  $MnO_2$  with KOH followed by electrolytic oxidation of manganate.

 $MnO_4^{2-}$  (green)  $\longrightarrow MnO_4^{-}$  (purple) +  $e^-$ 

In the laboratory, a manganese(II) ion salt is oxidised by peroxodisulphate to permanganate

 $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^{-} + 10SO_4^{2-} + 16H^+$ 

**(b) Physical property :** It is purple coloured crystalline compound. It is moderately soluble in water at room temperature.

#### (c) Chemical property:

- Effect of heating  $2KMnO_4 \xrightarrow{750K} K_2MnO_4 + MnO_2 + O_2$
- On treatment with concentrated  $H_2SO_4$  (KMnO<sub>4</sub> is taken in excess), it forms manganese heptoxide via permanganyl sulphate which decomposes explosively on heating.

$$KMnO_4 \xrightarrow{Conc.H_2SO_4} Mn_2O_7$$
 (an explosive)

- Potassium permanganate is a powerful oxidising agent.
   Potassium permanganate acts as an oxidising agent in alkaline, neutral or acidic solutions.
- In alkaline & neutral medium : In strongly alkaline medium KMnO<sub>4</sub> is reduced to manganate.

$$2KMnO_4 + 2KOH (conc.) \longrightarrow 2K_2 MnO_4 + H_2O + [O]$$

 $e^- + MnO_4^- \longrightarrow MnO_4^{2-}$ 

However if solution is dilute then  $\rm K_2MnO_4$  is converted in to  $\rm MnO_2$  which appears as a brownish precipitate.

Preparation : The chromite ore is roasted with sodium carbonate in presence of air in a reverberatory

4FeO.  $Cr_2O_3$  (chromite ore) +  $8Na_2CO_3 + 7O_2 \xrightarrow[in air]{Roasting} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$ 

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

$$2e^{-} + 2H_2O + MnO_4^{2-} \longrightarrow MnO_2 + 4OH^{-}$$

This type of behaviour is shown by  $KMnO_4$  itself in neutral medium

 $3e^{-} + 2H_2O + MnO_4^{-} \longrightarrow MnO_2 + 4OH^{-}$ 

#### (d) Other reactions



Mn<sup>+2</sup> (MnSO<sub>4</sub>) colorless

**POTASSIUM DICHROMATE (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) :** 

furnace



(a)

ALLEN

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

$$2\mathrm{Na}_{2}\mathrm{CrO}_{4} + \mathrm{H}_{2}\mathrm{SO}_{4} \longrightarrow \mathrm{Na}_{2}\mathrm{Cr}_{2}\mathrm{O}_{7} + \mathrm{Na}_{2}\mathrm{SO}_{4} + \mathrm{H}_{2}\mathrm{O}_{4}$$

The solution is concentrated when less soluble  $Na_2SO_4$  crystallises out. The solution is further concentrated when crystals of  $Na_2Cr_2O_7$  are obtained. Hot saturated solution of  $Na_2Cr_2O_7$  is then treated with KCl when orange red crystals of  $K_2Cr_2O_7$  are obtained on crystallisation.

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

•  $K_2Cr_2O_7$  is preferred over  $Na_2Cr_2O_7$  as a primary standard in volumetric estimation because  $Na_2Cr_2O_7$  is hygroscopic in nature but  $K_2Cr_2O_7$  is not.

• 
$$\operatorname{CrO}_{4}^{-2} \xrightarrow{H^{+}} \operatorname{Cr}_{2}O_{7}^{-2}$$

- Solubility of Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is higher than K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>
- (b) Physical property : It is orange-red coloured crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at 398℃.

#### (c) Chemical property :

• **Effect of heating :** On strongly heating, it decomposes with liberating oxygen.

$$2\mathrm{K}_{2}\mathrm{Cr}_{2}\mathrm{O}_{7} \longrightarrow 2\mathrm{K}_{2}\mathrm{Cr}\mathrm{O}_{4} + \mathrm{Cr}_{2}\mathrm{O}_{3} + \frac{3}{2}\mathrm{O}_{2}$$

#### (d) Other reactions



#### 1. Chromyl chloride test :

 $NaCl + K_2Cr_2O_7 + H_2SO_4 \rightarrow CrO_2Cl_2 \text{ (Red orange vapour)} \\ \downarrow NaOH$ 

## Na2CrO4 (Yellow)

**2.** Acidified  $K_2Cr_2O_7$  solution reacts with  $H_2O_2$  in a etheral solution to give a deep blue solution due to the formation of  $CrO_5$ .

$$\operatorname{Cr}_2\operatorname{O}_7^{2-}$$
 +  $2\operatorname{H}^+$  +  $4\operatorname{H}_2\operatorname{O}_2$   $\longrightarrow$   $2\operatorname{CrO}_5$  +  $5\operatorname{H}_2\operatorname{O}$ 

**Note :** Reaction with  $C_2H_5OH$  is used in drunken driver test.

# **f-BLOCK ELEMENTS**

#### 2.3 INNER TRANSITION ELEMENTS

The elements in which the additional electron enters in (n - 2)f orbitals are called **inner transition elements** or **f-block elements**.

#### **Position in The Periodic Table**

The lanthanoids resemble with Yttrium in most of their properties. So it became necessary to accomodate all the fifteen elements together at one place. This has been done by placing the first element, lanthanum below yttrium and placing the remaining fourteen elements separately in the lower part of the periodic table.

Lanthanoid series	( Z = 58 – 71)	(Ce – Lu)
Actinide series	(Z = 90 - 103)	(Th – Lr)

#### 2.4 LANTHANIODS (Rare Earths or Lanthanones)

- (i) Lanthanoids are reactive elements so do not found in free state in nature.
- (ii) Most important minerals for lighter Lanthanoids are Monazite, cerites and orthite and for heavier lanthanoids – Gadolinite and Xenotime

#### (a) Electronic configuration

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

Atomic	Element	Symbol	Outer electronic	c configuration
No.			Atomic	+3 ion
58	Cerium	Ce	$4f^15d^16s^2$	4f <sup>1</sup>
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^2$
60.	Neodymium	Nd	$4f^4 6s^2$	$4f^3$
61.	Promethium	Pm	$4f^5 6s^2$	$4f^4$
62.	Samarium	Sm	$4f^6 6s^2$	$4f^5$
63.	Europium	Eu	$4f^7 6s^2$	$4f^6$
64.	Gadolinium	Gd	$4f^7 5d^1 6s^2$	4f <sup>7</sup>
65.	Terbium	Тb	$4f^9 6s^2$	4f <sup>8</sup>
66.	Dysprosium	Dy	$4f^{10} 6s^2$	4f <sup>9</sup>
67.	Holmium	Ho	$4f^{11} 6s^2$	$4f^{10}$
68.	Erbium	Er	$4f^{12} 6s^2$	$4f^{11}$
69.	Thulium	Tm	$4f^{13} 6s^2$	$4f^{12}$
70.	Ytterbium	Yb	4f <sup>14</sup> 6s <sup>2</sup>	4f <sup>13</sup>
71.	Lutecium	Lu	$4f^{14} 5d^1 6s^2$	4f <sup>14</sup>

(ii) It is to be noted that filling of 4f orbitals in the atoms is not regular. A 5d electron appears in gadolinium (Z = 64) with an outer electronic configuration of  $4f^75d^16s^2$  (and not  $4f^86s^2$ ). This is because the 4f and 5d electrons are at about the same potential energy and that the atoms have a tendency to retain stable half filled configuration.

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

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

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

#### (b) Oxidation states

- (i) In lanthanoids +3 oxidation state is most common.
- (ii) Except Ce, Tb, Nd, Dy, Pr which also exhibit +4.
- (iii) **Sm, Eu, Tm, and Yb,** also exhibit +2 state.

#### (c) Magnetic Properties

- (i) In tripositive lanthanoid ions the number of unpaired electrons regularly increases from lanthanum to Gadolinium (0 to 7) and then continuously decreases up to lutecium (7 to 0).
- (ii) lanthanum and lutecium ions are diamagnetic, while all other tripositive lanthanoid ions are paramagnetic. (Exception – Neodymium is the most paramagnetic lanthanoid).
- (iii)  $Ce^{+4}$  and  $Yb^{+2}$  are also diamagnetic ions.

#### (d) Colour

- (i) The lanthanoid ions have unpaired electrons in their 4f orbitals. Thus these ions absorbs visible region of light and undergo f-f transition and hence exhibit colour.
- (ii) The colour exhibited depends on the number of unpaired electrons in the 4f orbitals.
- (iii) The ions often with  $4f^n$  configuration have similar colour to those ions having  $4f^{14-n}$  configuration.
- (iv) Lanthanoid ions having 4f  $^0$ , 4f  $^{14}$  are colourless.

#### (e) Lanthanoid Contraction

- (i) In the lanthanoid series with increasing atomic number, there is a progressive decrease in the size from lanthanum to lutecium or from  $La^{+3}$  to  $Lu^{+3}$ . This contraction in size is known as lanthanoid contraction.
- (ii) The general electronic configuration of these elements is  $4f^{1-14}5s^2p^6d^{0-1}6s^2$ . In these elements the added electron enters the deep seated f-orbitals and therefore experiences considerable pull by the nucleus.
- (iii) Due to very poor shielding effect of (n-2)f electrons, they exert very little screening effect on the outermost  $6s^2$  electrons.

Hence with increasing atomic number, the enhanced nuclear charge leads to contraction in the size of atoms and ions.

#### APPLICATIONS OF LANTHANOID CONTRACTION

• Atomic size : The ionic radii of  $Zr^{+4}$  is about 9% more than  $Ti^{+4}$ . Similar trend is not maintained on passing from the second to third transition series. The ionic radius of Hf<sup>+4</sup>, instead of increasing (because of inclusion of one more electronic shell), decreases (or is virtually equal to  $Zr^{+4}$ ) as a consequence of the lanthanoid contraction.

This explains the close similarities between the members of the second and third transition series than between the elements of the first and second series.

- **Basic nature of hydroxide :** The effect of lanthanoid contraction basic nature of hydroxide regularly decreases.
- **Similarity in properties of lanthanoid :** Due to small difference in size the chemical properties of lanthanoids are similar and their seperation is difficult.

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#### (e) Important reactions of Lanthanoids



Chemical reactions of the lanthanoids

#### Mish metal is an alloy of lanthanoids (Mainly cerium) and iron.

#### 2.5 ACTINOIDS OR (5f - SERIES)

- (i) The elements in which the extra electron enters 5f-orbitals of (n 2)th main shell are known as actinoids.
- (ii) The man-made eleven elements  $Np_{93} Lr_{103}$  are placed beyond uranium in the periodic table and are collectively called trans-uranium elements.
- (iii) Th, Pa and U first three actinoids are natural elements.

#### (a) Electronic Configuration

The general configuration of actinoids may be given as [Rn]  $5f^{1-14} 6d^{0,1,2}$ ,  $7s^2$ .

Atomic No.	Elements	Symbol	Outer Electronic	Configuration
			Atomic	+3 ion
90	Thorium	Th	$6d^27s^2$	5f <sup>1</sup>
91	Proactenium	Pa	$5f^26d^17s^2$	5f <sup>2</sup>
92	Uranium	U	$5f^36d^17s^2$	5f <sup>3</sup>
93	Neptunium	Np	$5f^46d^17s^2$	$5f^4$
94	Plutonium	Pu	$5f^66d^07s^2$	5f <sup>5</sup>
95	Americium	Am	$5f^66d^17s^2$	5f <sup>6</sup>
96	Curium	Cm	$5f^76d^17s^2$	5f <sup>7</sup>
97	Berkellium	Bk	$5f^96d^07s^2$	5f <sup>8</sup>
98	Californium	Cf	$5f^{10}6d^{0}7s^{2}$	5f <sup>9</sup>
99	Einstenium	Es	$5f^{11}6d^{0}7s^{2}$	5f <sup>10</sup>
100	Fermium	Fm	$5f^{12}6d^07s^2$	5f <sup>11</sup>
101	Mandelevium	Md	$5f^{13}6d^{0}7s^{2}$	5f <sup>12</sup>
102	Nobellium	No	$5f^{14}6d^07s^2$	5f <sup>13</sup>
103	Lowrencium	Lr	$5f^{14}6d^{1}7s^{2}$	5f <sup>14</sup>

#### (b) Oxidation states

- (i) In lanthanoids and actinoids +3 oxidation is the most common for both of the series of elements.
- (ii) This oxidation state becomes increasingly more stable as the atomic number increases in the actinide series.
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- (iii) Highest oxidation states in the actinoids is +7 exhibited by Np<sub>93</sub> & Pu<sub>94</sub>, it is unstable.
- (iv) Highest stable oxidation state is +6 shown by  $U_{92}\,.$

#### **Other Properties**

- **Physical appearance :** Acitinides are silvery white metals. They get tarnished when exposed to the attack of alkalies.
- **Density :** All the actinoids except **thorium** and **americium** have high densities.
- **Colour :** Actinide ions are generally coloured. The colour of actinide ions depends upon the number of 5f-electrons. The ions containing no unpaired 5f-electrons (exactly full filled f-subshell) are colourless, as expected.
- Ionisation energies : Ionisation energies values of actinoids are low.
- **Electropositivie character :** All the known actinide metals are **highly electropositive**. They resemble lanthanoid series in this respect.
- **Melting Boiling properties :** They have **high melting and boiling points.** They do not follow regular gradation of melting or boiling points with increase in atomic number.
- **Magnetic properties :** The actinide elements are paramagnetic due to the presence of unpaired electrons.
- **Radioactive nature :** All the actinoids are radiaoactive in nature.
- Actinide contraction : The size of atom/cation decrease regularly along the actinoids series. The steady decrease in ionic radii with increase in atomic number is referred to as actinide contraction. This is due to poor shielding of 5f-electrons.

#### **Comparison of Lanthanides and Actinoids**

#### Points of Resemblance :

- (i) Both lanthanoids and actinoids show a dominant oxidation state of +3.
- (ii) Both are electropositive and act as strong reducing agents.
- (iii) Cations with unpaired electrons in both of them are paramagnetic.
- (iv) Most of the cations of lanthanoids and actinoids are coloured.
- (v) Both of them show a steady decrease in their ionic radii along the series. Thus, lanthanoids show **lanthanoid contraction** and actinoids show **actinide contraction**.

	Lathanoids	Actinoids
1.	Besides the most common oxidation state of $+3$	Besides the most common oxidation state of $+3$ ,
	lanthanoids show $+2$ and $+4$ oxidation states in	actinoids show +4, +5 and +6 oxidation states
	case of certain elements.	in case of certain elements.
2.	Lanthanoids have less tendency towards	Actinoids have a stronger tendency towards
	complex formation.	complex formation.
3.	Except promethium, they are non radioactive.	All the actinoids are radioactive.
4.	Oxides and hydroxide of lanthanoids are less basic.	Oxides and hydroxides of actinoids are
		more basic

#### POINTS OF DISTINCTION

#### Some important uses of actinoids are as follows -

Thorium : Thorium is used in atomic reactors as fuel rods and in the treatment of cancer.

**Uranium :** Uranium is used as nuclear fuel. Its salts are used in glass industry (for imparting green colour). textile industry and also in medicines.

Plutonium : Plutonium is used as fuel for atomic reactors as well as in atomic bombs.

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		BEGIN	NER'	'S BO)	(–2						
	KMnO₄ can be acidifie	d by									
	(1) Dil. HCl	(2) conc. $H_2SO_4$	(	(3) conc	. HNO	3	(4)	dil. H <sub>2</sub> S	$O_4$		
	NaCl $\xrightarrow{\text{conc. } H_2SO_4}{X}$ ye	llow green gas, X is									
	(1) K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	(2) MnO <sub>2</sub>	(	(3) KMr	$O_4$		(4)	both (2)	& (3)		
•	$X \xrightarrow[K_2Cr_2O_7]{\text{conc.}H_2SO_4} \rightarrow \text{ red br}$	own vapours. X can be									
	(1) Nal	(2) NaBr	(	(3) Both	(1) &	(2)	(4)	None of	f these		
ŀ.	$\underset{ore}{\overset{KOH}{\underset{air}{\longrightarrow}}} Y$	$\xrightarrow{H^+} Z_{\text{an oxidising agent}} + \Sigma$	K								
	True statement is (1) X can't be MnO <sub>2</sub> (3) Z can be K <sub>2</sub> MnO <sub>4</sub>		(	(2) Y ca (4) step	n be Kl (1) is ox	MnO <sub>4</sub> tidation	while st	tep (ii) is	disproj	portiona	atic
•	$X \xrightarrow{H^{+}}_{OH} Y; Y \xrightarrow{SO_2}$	$\rightarrow$ Z + SO <sub>4</sub> <sup>-2</sup>									
	X and Y are oxy anion	ate of	Cr in X,	Y, Z u	vill be re	spective	ely				
	(1) +3, +6, +6	(2) +6, +3, +6		(3) +6,	+6, +6		(4)	+6, +6,	+3		
	When KMnO <sub>4</sub> solution instantaneous after sor	n is added to oxalic acid ne time because	, solutio	on, the	decolo	urisatior	n is slov	v in beg	inning	but bec	om
	(1) $CO_2$ is a by product		(	(2) Mn <sup>24</sup>	acts as	s a catal	yst				
	(3) reaction in exother	nic		(4) $MnO_4^{-}$ catalyzes the reaction							
•	The elements from ce called :	rium (At.No. 58) to lut	tetium	(At.No.	71) in	which	4f ener	rgy leve	ls are t	filled up	a
	(1) lanthanides	(2) rare earths		(3) lanthanones				(4) all the above			
•	Which of the followin (1) Ta	g is a lanthanide : (2) Rh	(	(3) Th			(4)	(4) Gd			
).	The element with the electronic configuraton [Xe]54 4f14 5d16s2 is a(1) representative element(2) transition element(3) lanthanide(4) actinide										
0.	Name the three lantha (1) Sm, Tb, Gd	anides which show +2 (2) Sm, Eu, Yb	oxidat	tion stat (3) La,	e also Gd, Lu	: I	(4)	Yb, Prr	n, Sm		
		ANS	WE	R K	EY						
	BEGINNER'S BOX-1	<b>Que.</b> 1 2	3	4	5	6	7	8	9		ļ
		Ans. 2 3	3	1	4	3,3	1	3	1		i i

Que.

Ans.

**BEGINNER'S BOX-2** 

#### NCERT QUESTIONS (REASONING)

#### Q.1 Why do the transition elements have higher boiling & melting points ?

**Ans.** Because of having larger number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence stronger bonding between atoms. Hence strong metallic bonds between the atoms of these elements attribute to their high melting and boiling points.

#### Q.2 Give the main difference in oxidation states of transition elements & p-block elements.

- Ans. (i) The variation of oxdiation state in transition elements is in such a way that their oxidation state differ from each other by unity e.g. V<sup>+2</sup>, V<sup>+3</sup>, V<sup>+4</sup>, V<sup>+5</sup>. While in p block elements oxidation states normally differ by two due to inert pair effect.
  - (ii) Stability of higher oxidation state in transition elements increase down the group

e.g.  $Pt^{\scriptscriptstyle +4}$  is more stable than  $Pt^{\scriptscriptstyle +2}$ 

While in p block elements lower oxidation state become increasingly stable down the group as result of inert pair effect.

#### Q.3 For the first series of transition metals the $E^{\Theta}$ values are

<b>E</b> <sup>0</sup>	V	Cr	Mn	Fe	Со	Ni	Cu
(M <sup>2+</sup> /M)	-1.18	- 0.91	-1.18	-0.44	-0.28	-0.25	+0.34

#### Explain the irregularity in the above values.

**Ans.** This is because of irregular variation of ionization energies  $(IE_1 + IE_2)$  and also the sublimation energies which are much less for manganese and vanadium

#### Q.4 Zinc does not show variable valency because of :

(A) complete 'd' sub-shell(B) inert pair effect (C)  $4s^2$  sub-shell (D) none.

**Ans.**  $Zn = [Ar]^{18} 3d^{10} 4s^2$ . Zinc has completely filled d-sub-shell so removal of electron from completely filled 4d sub-shell would be quite difficult. Thus it does not show variable valency.

#### Q.5 Explain the blue colour of $CuSO_4.5H_2O$ .

**Ans.** Cu<sup>2+</sup> ion (3d<sup>9</sup>) absorbs red light from the visible region, for the promotion of 3d electrons, the ions reflect blue light and appear blue.

#### Q.6 How iron (III) catalyses the reaction between iodide & persulphate?

**Ans.**  $2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$ 

 $2Fe^{2_{+}} + S_2O_8^{2_{-}} \longrightarrow 2Fe^{3_{+}} + 2SO_4^{2_{-}}$ 

$$2I^- + S_2O_8^{2-} \xrightarrow{Fe(III)} I_2 + 2 SO_4^{2-}$$

#### **EXERCISE-I** (Conceptual Questions) 10. d-BLOCK ELEMENTS medium is : 1. For a catalyst which condition is not essential : (1) $IO_{3}^{-}$ (2) $I_{2}$ (3) IO-(1) Variable valency (2) High ionisation energy (3) Empty orbitals for longer period. (4) Free valency on the surface 2. To which of the following series the transition element from Z = 39 to Z = 48 belong : (1) 3d series (2) 4d series (3) 5d series (4) 6d series 3. $KMnO_4$ on treatment with conc. $H_2SO_4$ forms a (4) (1) and (3) both compound (X) which decomposes explosively on 12. heating forming (Y). The (X) and (Y) are respectively amphoteric in nature (1) $Mn_{2}O_{7}$ , $MnO_{2}$ (2) Mn<sub>2</sub>O, Mn<sub>2</sub>O<sub>2</sub> (3) MnSO<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub> (4) $Mn_{2}O_{3}$ , $MnO_{2}$ 4. Which pair of ions is colourless : 13. (2) Fe<sup>3+</sup>, Cr<sup>3+</sup> (1) Mn<sup>3+</sup>, Co<sup>3+</sup> (3) Zn<sup>2+</sup>, Sc<sup>3+</sup> (4) Ti<sup>2+</sup>, Cu<sup>2+</sup> (1) Is more stable 5. (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Ammonium dichromate) is used in (2) Is equally stable fire works. The green coloured powder blown in (3) Is less stable air is : (2) $CrO_{2}$ (3) $Cr_{2}O_{4}$ (4) $CrO_{3}$ (1) $Cr_2O_3$ 14. Pick out the wrong statement :- $Cr_2O_7^{2-} \xrightarrow{X} 2CrO_4^{2-}$ , X and Y are respectively 6. sulphate (2) Iron do not form amalgam (1) $X = OH^{-}, Y = H^{+}$ (2) $X = H^{+}, Y = OH^{-}$ (3) $X = OH^{-}, Y = H_2O_2$ (4) $X = H_2O_2, Y = OH^{-}$ Alnico 7. During estimation of oxalic acid Vs KMnO<sub>4</sub>, self La<sup>+3</sup> to Lu<sup>+3</sup> indicator is : (2) Oxalic acid (1) $KMnO_{4}$ 15. (4) MnSO<sub>4</sub> (3) $K_2 SO_4$ is :-8. The higher oxidation states of transition elements are found to be the combination with A and B, which are: **16**. (1) F, O (2) O, N by : (3) O, Cl (4) F, Cl (1) KMnO<sub>4</sub> + conc. HCl $\longrightarrow$ 9. Magnetic moment of $x^{n+}$ is $\sqrt{24}$ B.M. Hence No. of unpaired electron and value of 'n' respectively. (3) $MnO_2$ + conc. HCl $\longrightarrow$ (Atomic number = 26) (1)4,3

(2) 3, 5 (4) 4, 1

(3) 4, 2

The product of oxidation of  $I^-$  with  $MnO_4^-$  in alkaline

(4) IO<sub>4</sub>

- **11.** Copper becomes green when exposed to moist air
  - (1) Because of the formation of a layer of cupric oxide on the surface of copper
  - (2) Because of the formation of a layer of basic carbonate of copper on the surface of copper
  - (3) Because of the formation of a layer of cupric hydroxide on the surface of copper.
- Which of the following oxide of chromium is

(1) CrO	(2) Cr <sub>2</sub> O <sub>3</sub>
(3) CrO <sub>3</sub>	(4) CrO <sub>5</sub>

- Compared to Cu<sup>2+</sup> having 3d<sup>9</sup> configuration, Cu<sup>+</sup> having 3d<sup>10</sup> configuration (aq. solution) :-
  - (4) Stability depends upon nature of copper salt
  - (1)  $K_{2}Cr_{2}O_{7}$  reduces ferric sulphate to ferrous
  - (3) Permanent magnet is made by an alloy called
  - (4) In the Lathanides ionic radius decreases from
- $CrO_3$  is red or orange in colour. The nature of oxide

(1) Acidic	(2) Basic
(3) Amphoteric	(4) Neutral

- Cl<sub>2</sub> gas is obtained by various reactions but not
  - (2) KCl +  $K_{2}Cr_{2}O_{7}$  + conc.  $H_{2}SO_{4} \longrightarrow$
  - (4) KCl +  $F_2 \xrightarrow{\Delta}$

## Maximum magnetic moment is shown by : 17. (1) $d^5$ (2) $d^6$ (3) d<sup>7</sup> (4) d<sup>8</sup> **18.** Disproportion can be shown by (1) $MnO_4^{2-}$ in acidic medium (2) Cu<sup>+</sup> in aqueous medium (3) $Cl_2$ in alkaline medium (4) All of these 19. The basic character of the transition metal monoxides follows the order : (Atomic no. Ti = 22, V = 23, Cr = 24, Fe = 26) (1) TiO > FeO > VO > CrO(2) TiO > VO > CrO > FeO(3) VO > CrO > TiO > FeO(4) CrO > VO > FeO > TiO**20.** Which of the following reactions is used to estimate copper volumetrically? (1) $2Cu^{2+} + 4F^- \longrightarrow Cu_2F_2 + F_2$ (2) $Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_d]^{2+}$ (3) $2Cu^{2+} + 2CNS^{-} + SO_2 + 2H_2O \longrightarrow Cu_2(CNS)_2$ $+ H_2 SO_4 + 2H^+$ (4) $2Cu^{2+} + 4I^{-} \longrightarrow Cu_{2}I_{2} + I_{2}$ **21.** Atomic size of gold is almost the same as that of silver. It is due to : (1) the same crystal structure of silver and gold (2) almost the same electropositive character of the two metals (3) transition metals contraction in a series (4) the effect of lanthanide contraction 22 Which among the following statements is incorrect (1) In d-block elements oxidation state differ by unity.

- (2) In p-block metals oxidation state differ by two units.
- (3) In a group of p-block lower oxidation states are favoured by the heavier members.
- (4) In a group of d-block higher oxidation states are favoured by the lighter member.

23	Which among the follow	wing order of oxidising
	(1) C C · M C	
	(1) $\operatorname{Cr}O_3 > \operatorname{MoO}_3$	(2) $K_2 Cr_2 O_7 > KMnO_4$
~ ^	(3) $Fe(CO)_5 > Min(CO)_5$	(4) $V_2 O_3 > V_2 O_5$
24	Which of the following co	ontigurations of 3d series
	metals exhibits the large	est number of oxidation
	states-	
	(1) [Ar] $3d^8 4s^2$	(2) [Ar] $3d^{10} 4s^{1}$
	(3) [Ar] 3d <sup>5</sup> 4s <sup>2</sup>	(4) [Ar] $3d^7 4s^2$
25	Which of the followin	g statement regarding
	interstetial compounds	is incorrect-
	(1) They are chemically	inert
	(2) They are soft and no	onconductive
	(3) They retain metallic	conductivity
	(4) They have high melt	ting point.
26	Which of the following pa	air of ions has same value
	of "spin-only" magnetic	moment
	(1) Cu <sup>+</sup> , Cu <sup>2+</sup>	(2) Co <sup>3+</sup> Fe <sup>2+</sup>
	(3) Ti <sup>2+</sup> , V <sup>2+</sup>	(4) $Sc^{2+}$ , $Zn^{+2}$
f-BLO	OCK ELEMENTS	
97	The elements from the	orium (At No. 90) to
21.	lauroncium (At No. 103)	in which 5f anarou lavals
	are filled up are called	
	(1) lanthanidos	(2) rare carths
	(3) actinides	(4) transuranics
28.	Select the element in th	ne following which does
	not show +4 oxidation	state :
	(1) Ti	(2) Zr
	(3) La	(4) Pt
	(0) Lu	
29.	With increase in atomic	c number the ionic radii
	of actinides :	
	(1) contract slightly	
	(2) increase gradually	
	(3) show no change	
	(d) change irregularly	
	(+) change integularly	
30.	The general electronic co	onfiguration of lanthanide
	is :	
	(1) [Xe] $4f^{14} 5d^{0-1} 6s^2$	
	(2) [Xe] 4f <sup>0-14</sup> 5d <sup>1-2</sup> 6s <sup>1</sup>	
	(3) [Xe] $4f^{0-14}$ $5d^{0-1}$ $6s^{1-1}$	-2
	(d) None of these	
	(T) NOTE OF LIESE	
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31.	Cerium can show the o	xidation state of +4 because	36.	The common oxida	ation state of actinides is :
	(1) it resemble alkali	metals		(1) +4	(2) +3
	(2) it has very low va	lue of I.E.		(3) +5	(4) +6
	(3) of its tendency to at of xenon	tain noble gas configuration	37.	Which of the follo change its group o	wing f - block elements, will n emmitting α-particle (alpha
	(4) of its tendency to	attain $4f^7$ configuration		particle) :	
32.	In aqueus solution Eu	u <sup>+2</sup> acts as :		(1) <sub>58</sub> Ce	(2) <sub>70</sub> Lu
	(1) an oxidising agent			(3) <sub>90</sub> Th	(4) <sub>92</sub> U
	(2) reducing agent			Correct answer is :-	
	(3) can act as redox a	agent		(1) Only 1 and 3	(2) Only 2 and 4
	(4) None of these			(3) All	(4) None
33.	The maximum oxidatio	on state shown by actinides	38.	Which of the follow size	wing pair have almost similar
	1S :			(1) $Ti_{22}$ and $Zr_{40}$	(2) Nb <sub>41</sub> and Ta <sub>73</sub>
	(1) + 6	(2) + 7		(3) $Y_{39}$ and $La_{57}$	(4) $\operatorname{Ca}_{20}$ and $\operatorname{Ir}_{31}$
	(3) +5	(4) +4	39.	An increase in bot	h atomic and ionic radii with
34.	The outer electronic c	onfiguration of gadolinium		atomic number occu	irs in any group of the periodic
	(At. No. 64) is :			table. In accordance	e of this the ionic radii of Ti (IV)
	(1) $4f^{7}5d^{1}6s^{2}$	(2) $4f^85d^06s^2$		and Zr (IV) ions are (	).68 Å and 0.74 Å respectively
	(3) $4f^85d^16s^1$	(4) $4f^{7}5d^{0}6s^{2}$		but for Hf (IV) ion th is almost the same	ne ionic radius is 0.75 Å, which as that for Zr (IV) ion. This is
35.	• The most characteristic oxidation state of lanthanides is :			due to :- (1) greater degree o	of covalency in compounds of
	(1) +2	(2) +3		$Hf^{4+}$	
	(3) +4	(4) none of these		<ul><li>(2) Lanthanide cont</li><li>(3) Difference in the and Hf<sup>+4</sup> in thei</li></ul>	raction e co-ordination number of Zr <sup>+4</sup> r compounds
				(4) Actinide contrac	tion

EX	<b>ERC</b>	ISE-I	(Cone	ceptua	al Que	stions	5)						ANS	WER	KEY
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	2	1	3	1	1	1	1	3	1	2	2	3	1	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	1	4	2	4	4	4	1	3	2	2	3	3	1	4
Que.	31	32	33	34	35	36	37	38	39						
Ans.	3	2	2	1	2	2	1	2	2						
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E	XERCISE-II (Previous Year Questions)	ļ	AIPMT/NEET & AIIMS (2006-2018)
	AIPMT 2006		AIPMT 2010
1.	In which of the following pairs are both the ions coloured in aqueous solution ? (At. no. : Sc= 21, Ti = 22, Ni = 28, Cu = 29, Co = 27) (1) Ni <sup>2+</sup> , Cu <sup>+</sup> (2) Ni <sup>2+</sup> , Ti <sup>3+</sup> (3) Sc <sup>3+</sup> , Ti <sup>3+</sup> (4) Sc <sup>3+</sup> , Co <sup>2+</sup>	7. 8.	Which of the following oxidation states is the most common among the lanthanoids :-(1) 2(2) 5(3) 3(4) 4Which of the following pairs has the same size(1) $Zn^{2+}$ , $Hf^{4+}$ (2) $Fe^{2+}$ , $Ni^{2+}$ (3) $Zr^{4+}$ , $Ti^{4+}$ (4) $Zr^{4+}$ , $Hf^{4+}$
2.	<ul> <li>More number of oxidation states are exhibited by the actinoids than by the lanthanoids. The main reason for this is</li> <li>(1) more active nature of the actinoids</li> <li>(2) more energy difference between 5f and 6d orbitals than that between 4f and 5d orbitals</li> <li>(3) lesser energy difference between 5f and 6d orbitals than that between 4f and 5d orbitals</li> <li>(4) greater metallic character of the lanthanoids than that of the corresponding actinoids</li> </ul>	9.	Which one of the following ions has electronic configuration [Ar]3d <sup>6</sup> ? (At. nos. Mn = 25         Fe = 26, Co = 27, Ni = 28)         (1) Co <sup>3+</sup> (2) Ni <sup>3+</sup> (3) Mn <sup>3+</sup> (4) Fe <sup>3+</sup> Which of the following ions will exhibit colour in aqueous solutions ?         (1) Sc <sup>3+</sup> (z = 21)       (2) La <sup>3+</sup> (z = 57)         (3) Ti <sup>3+</sup> (z = 22)       (4) Lu <sup>3+</sup> (z = 71)
	AIPMT 2007	11.	Uranium can be obtained by the electrolysis of:
3.	Which one of the following ions is the most stable		(1) $UF_6$ (2) $UF_4$ (3) $UCI_6$ (4) $UI_6$
	in aqueous solution (1) $V_{3+}^{3+}$ (2) $T_{3+}^{3+}$ (2) $M_{-3+}^{3+}$ (4) $C_{-3+}^{3+}$		AIPMT Pre. 2011
4.	<ul> <li>(1) V (2) II (3) III (4) CI</li> <li>Identify the incorrect statement among the following</li> <li>(1) Lanthanoid contraction is the accumulation of successive shrinkages.</li> <li>(2) As a result of lanthanoid contraction, the properties of 4d series of the transition elements have no similarities with the 5d series of elements.</li> <li>(3) Shielding power of 4f electrons is quite weak.</li> <li>(4) there is a decrease in the radii of the atoms</li> </ul>	12.	For the four successive transition elements (Cr, Mn Fe and Co), the stability of +2 oxidation state in gaseous state will be there in which of the following order ? (1) Mn > Fe > Cr > Co (2) Fe > Mn > Co > Cr (3) Co > Mn > Fe > Cr (4) Cr > Mn > Co > Fe (At. nos. Cr = 24, Mn = 25, Fe = 26, Co = 27 AIIMS 2011
	or ions as one proceeds from La to Lu.	13.	When $KMnO_4$ reacts with $Br_2$ in weak alkaling
5.	AIPMT 2008 The correct order of decreasing second ionisation		medium gives bromate ion. Then oxidation state of Mn changes from $+7$ to: (1) $+6$ (2) $+4$ (3) $+3$ (4) $+2$
	enthalpy of T1 (22), $V(23)$ , $Cr(24)$ and Mn (25) is: (1) Mn>Cr>Ti>V (2) Ti>V>Cr>Mn		AIPMT Pre. 2012
	(3) $Cr>Mn>V>Ti$ (4) $V>Mn>Cr>Ti$	14.	Which of the statements is not true?
_			(1) $K_2Cr_2O_7$ solution in acidic medium is orange
6.	Which one of the elements with the following outer orbital configurations may exhibit the largest number of oxidation states? (1) 3d <sup>2</sup> 4s <sup>2</sup> (2) 3d <sup>3</sup> 4s <sup>2</sup> (3) 3d <sup>5</sup> 4s <sup>1</sup> (4) 3d <sup>5</sup> 4s <sup>2</sup>		<ul> <li>(2) N<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution becomes yellow on increasing the pH beyond 7</li> <li>(3) On passing H<sub>2</sub>S through acidified K<sub>2</sub>Cr<sub>2</sub>O solution, a milky colour is observed</li> <li>(4) Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is preferred over K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in volumetric analysis</li> </ul>
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#### AIPMT Mains 2012

- **15.** Which one of the following does not correctly represent the correct order of the property indicated against it ?
  - (1) Ti < V < Cr < Mn : increasing melting points
  - (2) Ti < V < Mn < Cr : increasing 2<sup>nd</sup> ionization enthalpy
  - (3) Ti < V < Cr < Mn : increasing number of oxidation states
  - (4)  $Ti^{3+} < V^{3+} < Cr^{3+} < Mn^{3+}$  : increasing magnetic moment
- **16.** The catalytic activity of transition metals and their compounds is ascribed mainly to :-
  - (1) their ability to adopt variable oxidation states
  - (2) their chemical reactivity
  - (3) their magnetic behaviour
  - (4) their unfilled d-orbitals

#### **AIIMS 2012**

- **17.** Magnetic moment of  $Cr^{2+}$  is nearesst to :-(1)  $Fe^{2+}$  (2)  $Mn^{2+}$  (3)  $Co^{+2}$  (4)  $Ni^{2+}$ **AIIMS 2013**
- **18.** Which of the following element has lowest melting point :-(1) Cr (2) Fe (3) Ni (4) Cu
- **19.** Maximum no. of unpaired electrons are present in :-

(1)  $Gd^{+3}$  (2)  $Yb^{+2}$  (3)  $Tb^{+2}$  (4)  $Pm^{+3}$ 

- **20.**  $K_2 Cr_2 O_7$  in acidic medium converts into :-(1)  $Cr^{2+}$  (2)  $Cr^{3+}$  (3)  $Cr^{4+}$  (4)  $Cr^{+5}$
- Which of the following metal ion forms unstable complex with CN<sup>-</sup>:(1) Ag(I)
  (2) Zn (II)
  (3) Cu (II)
  (4) Cr (II)
- **22.** Which of the following ion does not exist ? (1)  $[Cul_{4}]^{2-}$  (2)  $VO_{4}^{3-}$  (3)  $WO_{4}^{2-}$  (4)  $CrO_{4}^{2-}$

#### **AIPMT 2015**

- **23.** Magnetic moment 2.84 B.M. is given by :-(At. no.), Ni = 28, Ti = 22, Cr = 24, Co = 27) (1) Ti<sup>3+</sup> (2) Cr<sup>2+</sup> (3) Co<sup>2+</sup> (4) Ni<sup>2+</sup>
- **24.** Which of the following processes does not involve oxidation of iron ?
  - (1) Decolourization of blue CuSO<sub>4</sub> solution by iron
  - (2) Formation of  $Fe(CO)_5$  from Fe
  - (3) Liberation of H<sub>2</sub> from steam by iron at high temperature
  - (4) Rusting of iron sheets

- **25.** Because of lanthanoid contraction, which of the following pairs of elements have nearly same atomic radii ? (Nubmers in the parenthesis are atomic numbers).
  - (1) Zr (40) and Nb (41)
  - (2) Zr (40) and Hf (72)
  - (3) Zr (40) and Ta (73)
  - (4) Ti (22) and Zr (40)

#### AIIMS 2015

- **26**. Highly unstable species is (1) Sc(II) (2) Ti(II) (3) Co(II) (4) V(II)
- 27. Which of the following is diamagnetic
  (1) Aurum
  (2) Tungsten
  (3) Palladium
  (4) Niobium

#### **NEET-I 2016**

- **28.** Which one of the following statements is correct when SO<sub>2</sub> is passed through acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution ?
  - (1) The solution turns blue
  - (2) The solution is decolourized
  - (3)  $SO_2$  is reduced
  - (4) Green  $Cr_2(SO_4)_3$  is formed
- **29.** The electronic configurations of Eu(Atomic No 63), Gd(Atomic No 64) and Tb (Atomic No. 65) are
  - (1) [Xe]4f<sup>7</sup>6s<sup>2</sup>, [Xe]4f<sup>8</sup> 6s<sup>2</sup> and [Xe]4f<sup>8</sup>5d<sup>1</sup>6s<sup>2</sup>
  - (2) [Xe]4f75d16s2, [Xe]4f7 5d1 6s2 and [Xe]4f96s2
  - (3) [Xe]4f<sup>6</sup>5d<sup>1</sup>6s<sup>2</sup>, [Xe]4f<sup>7</sup>5d16s<sup>2</sup> and [Xe]4f<sup>8</sup>5d<sup>1</sup>6s<sup>2</sup>
  - (4)  $[Xe]4f^{7}6s^{2}$ ,  $[Xe]4f^{7}5d^{1}6s^{2}$  and  $[Xe]4f^{9}6s^{2}$

#### **NEET-II 2016**

- **30.** Which one of the followng statements related to lanthanons is **incorrect** ?
  - (1) All the lanthanons are much more reactive than aluminium
  - (2) Ce(+4) solutions are widely used as oxidizing agent in volumetric analysis
  - (3) Europium shows +2 oxidation state.
  - (4) The basicity decreases as the ionic radius decreases from Pr to Lu.

	AIIMS 2016							
31.	Which of the followin	g is ferromagnetic :-						
	(1) U	(2) Co						
	(3) Cr	(4) Cu						
32.	Aquaregia convert :-							
	(1) Pt to [PtCl <sub>4</sub> ] <sup>-2</sup>	(2) Ag to AgCl						
	(3) Pt to PtCl <sub>2</sub>	(4) Au to [AuCl <sub>4</sub> ] <sup>-</sup>						
33.	Which of the follow	ing can convert Cl- into						
	Cl <sub>2</sub> :-							
	(1) KMnO <sub>4</sub>	(2) $H_2 SO_3$						
	(3) $Fe_2(SO_4)_3$	(4) HIO <sub>3</sub>						
34.	Which of the following Lanthanoid show yell-							
	colour :-							
	(1) La <sup>+3</sup>	(2) Yb <sup>+3</sup>						
	(3) Lu <sup>+3</sup>	(4) Ce <sup>+4</sup>						
	NEET(UG	6) 2017						
35.	Name the gas that can	readily decolourise acidified						
	$KMnO_4$ solution :							
	(1) SO <sub>2</sub> (2) NO <sub>2</sub>	(3) $P_2O_5$ (4) $CO_2$						
36.	$HgCl_2$ and $I_2$ both	when dissolved in water						
	containing $\boldsymbol{I}^{\!-}$ ions the pair of species formed is							
	(1) HgI <sub>2</sub> , I <sup>−</sup>	(2) $HgI_4^{2-}, I_3^-$						
		-						
	(3) Hg <sub>2</sub> I <sub>2</sub> , I <sup>−</sup>	(4) $HgI_2, I_3^-$						
37.	The reason for greate	r range of oxidation states						
	in actinoids is attributed to :-							

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

#### **AIIMS 2017**

38. Gadolinium is :-

- (1) Ferromagnetic
- (2) Anti ferromagnetic
- (3) Ferrimagnetic
- (4) Diamagnetic
- **39**. Which of the following pair contains all diamagnetic ions.

(1) Yb <sup>+2</sup> & Lu <sup>+3</sup>	(2) Ce <sup>+4</sup> & Pr <sup>+4</sup>
(3) Dy <sup>+3</sup> & Lu <sup>+3</sup>	(4) Lu <sup>+3</sup> & Gd <sup>+3</sup>

- Which of the following is incorrect about interstital **40**. compound.
  - (1) they have high melting points in comparison to pure metals.
  - (2) they are very hard
  - (3) they retain metallic conductivity
  - (4) they are chemically very reactive
- **41**. Which of the following does not decolourises acidic KMnO<sub>4</sub> solution.
  - (1) KI & NaNO<sub>2</sub>
  - (2) NaNO<sub>3</sub> & Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>
  - (3)  $Na_2SO_4 \& Na_2C_2O_4$
  - (4) I<sub>2</sub> & NaNO<sub>3</sub>

- 42. Select the incorrect statement about iodide of Millon's base.
  - (1) it is formed by the reaction  $K_0[HgI_4] + KOH +$  $NH_4^+$  solution
  - Hg I (2) its formula Hg
  - (3) it is a brown ppt. but give test of complex cation I<sup>-</sup> ions.
  - (4) it is a Nesler's reagent of alkaines solution of  $K_{2}[HgI_{4}]$
- **43**. Which of the following will not be present in last flask during the iodometric titration of Cu<sup>+2</sup>



(1)  $CrO_4^{2-}$ (2)  $Cr_2O_7^{2-}$ (4) MnO<sub>4</sub><sup>2-</sup> (3) MnO<sub>4</sub>

46.	Match the metal ions given in Column I with the spin magnetic moments of the ions given in Column II and assign the <b>correct</b> code :					th the <b>52</b> . olumn	
	(	Colun	nn I		Column II		
	a. (	Co <sup>3+</sup>			i. $\sqrt{8}$ B.M.	53.	
	b. (	Cr <sup>3+</sup>			ii. $\sqrt{35}$ B.M.		
	c. l	Fe <sup>3+</sup>			iii. $\sqrt{3}$ B.M.		
	d. I	Ni <sup>2+</sup>			iv. $\sqrt{24}$ B.M.		
					v. $\sqrt{15}$ B.M.		
		а	b	С	d		
	(1)	iv	v	ii	i		
	(2)	i	ii	iii	iv		
	(3)	iv 	i	ii	iii 		
	(4)	111	v	1	11	54	
			Α	IIMS	2018	01	
47.	Whi	ch of	the	follov	ving elements have	least	
	diffe	rence	in E <sup>0</sup>	value	of M <sup>+2</sup> /M :-		
	(1) V	/ & Mi	n		(2) Mn & Fe	55	
	(3) F	e & C	0		(4) Co & Ni	55.	
<b>48</b> .	Viole	et colc	or of g	lass is	due to :-		
	(1) K	(I)	(2)	Mn(I\	) (3) $I_2$ (4) (	Cr(III)	
49.	In which compound oxidation state not changed						
	in ac	cidic &	$\lim_{n \to \infty} \frac{1}{2} = \frac{1}{2} \lim_{n \to \infty} \frac{1}{2} $				
	(1)	$V \ln O_4$			(2) $CrO_4^{-2}$		
50	(3) F	$eO_4^2$	diant		(4) $MnO_4^{-2}$	56.	
50.	(1) N	In Call	uspi	acen	(2) Tl		
	(3)	Sc			(2) II (4) In		
51.	Whi	ch sho	ws le:	ast nu	nber of oxidation stat	es?	
	(1)	Mn			(2) Th		
	(3) C	Cr			(4) Np		
					• • •		

Spin only magnetic moment of a divalent metal ion having total 23 electrons :-

(1) 5.9	(2) 5.2

- (3) 4.0(4) 5.0
- In salts of Co, Sb, Sn & Cd,  $H_{2}S$  was added. The colour of the precipitates obtained were as follows



Which set is correct for its colour of its sulphide:-

(1) A-Co	(2) B-Sb
(3) C-Sn	(4) D-Cd

The colour of compound formed when  $KMnO_4$  is fused with KOH :-

(1) Green	(2) Black
-----------	-----------

(3) Brown	(4) Pale Pink
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- In which of the following conversion Blue colour is appeared.
  - (1)  $MnO_4^- + SO_2 \longrightarrow$
  - (2)  $\operatorname{Cr}_{2}O_{7}^{-2} + \operatorname{KI} \longrightarrow$
  - (3)  $K_2Cr_2O_7 + NaCl + conc. H_2SO_4 \longrightarrow$
  - (4)  $CuSO_4 + KI + Starch \longrightarrow$
- Which of the following pair is soluble in excess NH₄OH
  - (1)  $Zn(OH)_2$ ,  $Pb(OH)_2$
  - (2)  $Zn(OH)_2$ ,  $Sn(OH)_2$
  - (3) Cd(OH)<sub>2</sub>, Zn(OH)<sub>2</sub>
  - (4) Be(OH)<sub>2</sub>, Cd(OH)<sub>2</sub>

EXERCISE-II (Previous Year Questions)									ANSWER KEY						KEY
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	3	4	2	3	4	3	4	1	3	2	1	2	4	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	1	1	4	1	2	3	1	4	2	2	1	3	4	4	1
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	2	4	1	4	1	2	2	1	1	4	4	4	3	3	4
Que.	46	47	48	49	50	51	52	53	54	55	56				
Ans.	1	1	2	2	3	2	1	1	1	4	3				
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AL		1	Fre-Medical . Chemisiry
E	XERCISE-III (Analytical Questions)		Check Your Understanding
1.	The correct order of ionic radii of $Y^{3+}$ , $La^{3+}$ , $Eu^{3+}$ and $Lu^{3+}$ is (1) $Lu^{3+} < Eu^{3+} < La^{3+} < Y^{3+}$	10.	Atomic number 21, shows the oxidation states (1) +1 (2) +3 (3) $-1$ (4) +5
	(1) $Lu^{3+} < Lu^{3+} < Lu^{3+} < Y^{3+}$ (2) $La^{3+} < Eu^{3+} < Lu^{3+} < Y^{3+}$ (3) $Y^{3+} < La^{3+} < Eu^{3+} < Lu^{3+}$ (4) $Y^{3+} < Lu^{3+} < Eu^{3+} < La^{3+}$	11.	Transition element makes complex compound due to - (1) Presence of empty d-orbital (2) large size
2.	Among the following series of transition metal ions, the one where all metal ions have $3d^2$ electronic configuration is :-	19	<ul> <li>(2) Mige size</li> <li>(3) Variable valency</li> <li>(4) presence of 2e<sup>-</sup></li> </ul>
	(1) $Ti^{2+}$ , $V^{3+}$ , $Cr^{4+}$ , $Mn^{5+}$ (2) $Ti^{2+}$ , $V^{2+}$ , $Cr^{3+}$ , $Mn^{4+}$ (3) $Ti^+$ , $V^{4+}$ , $Cr^{6+}$ , $Mn^{7+}$ (4) $Ti^{4+}$ , $V^{3+}$ , $Cr^{2+}$ , $Mn^{3+}$	12.	<ul> <li>(1) the same effective nuclear charge from Ce to Lu</li> <li>(2) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge</li> <li>(3) the appreciable shielding on outer electrons by</li> </ul>
3.	The aqueous solution containing which one of the following ions will be colourless :- [Atomic n : Sc = 21, Fe = 26, Ti = 22, Mn = 25] (1) $Fe^{2+}$ (2) $Mn^{2+}$		4f electrons from the nuclear charge (4) the appreciable shielding on outer electrons by 5d electrons from the nuclear charge
	(3) $Ti^{3+}$ (4) $Sc^{3+}$	13.	$KMnO_4$ is a strong oxidizing agent in acid medium. To provide acid medium $H_2SO_4$ is used instead of
4.	The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is (1) + 4 $(2) + 6$ $(3) + 2$ $(4) + 3$		HCl. This is because (1) $H_2SO_4$ is a stronger acid than HCl (2) HCl is oxidized by KMnO <sub>4</sub> to Cl <sub>2</sub> (3) $H_2SO_4$ is a dibasic acid
5.	The lanthanide contraction is responsible for the fact that (1) Zr and Y have about the same radius (2) Zr and Nb have similar oxidation state (3) Zr and Hf have about the same radius (4) Zr and Zn have the same oxidation state	14.	(4) rate is faster in the presence of $H_2SO_4$ When hydrogen peroxide is added to acidified potassium dichromate, a blue colour is produced due to formation of (1) $CrO_3$ (2) $Cr_2O_3$
6.	Which one of the following nitrates will leave behind a metal on strong heating ?(1) Copper nitrate(2) Manganese nitate(3) Silver nitrate(4) Ferric nitrate	15.	(3) $\operatorname{CrO}_5$ (4) $\operatorname{CrO}_4^{2-}$ Identify the incorrect statement among the following (1) 4f and 5f orbitals are equally shielded
7.	Excess of KI reacts with $CuSO_4$ soluiton and then $Na_2S_2O_3$ solution is added to it. Which of the statements is incorrect for this reaction :- (1) $Na_2S_2O_3$ is oxidised (2) $Cul_2$ is formed (3) $Cu_2I_2$ is formed (4) Evolved $I_2$ is reduced	16.	<ul> <li>(1) If and of orbitals are equally shielded.</li> <li>(2) d-Block elements show irregular and erratic chemical properties among themselves.</li> <li>(3) La and Lu have partially filled d orbitals and no other partially filled orbitals.</li> <li>(4) The chemistry of various lanthanoids is very similar.</li> <li>The actinoids exhibit more number of oxidation</li> </ul>
8.	In which of the following oxidation state of Mn is six		states in general than the lanthanoids. This is because
	(1) $K_2MnO_4$ (2) $MnO_2$ (3) $KMnO_4$ (4) $MnO_4^{-1}$		<ul><li>(1) due to less energy difference between 6d &amp; 5f</li><li>(2) the 5f orbitals are more buried than the 4f orbitals</li></ul>
9.	Which has maximum magnetic moment :- (1) $Co^{+2}$ (2) $Mn^{+3}$		<ul><li>(3) there is a similarity between 4f and 5f orbitals in their angular part of the wave function</li><li>(4) the actinoids are more reactive than the</li></ul>
	(3) $Mn^{+2}$ (4) $Cr^{+3}$		lanthanoids. 89

17	$I_{m} \cap O^{-2}$		-2	ati	1	:			•				A .				
17.	In $\operatorname{Cr}_2 \operatorname{O}_7^2$ oxidation n (1) +3	→ CrC umber is (2) –3	, ~ rea :- (3)	ction tl ) 2	ne char (4)	nge in 0	23.	<b>23.</b> A test tube containing a nitrate and a containing a bromide and $MnO_2$ are treat concentrated $H_2SO_4$ . The reddish brown									
18.	Which of th be explaine	e following d due to l	g prope lanthan	erties of ide con	Zr and l tractior	Hf can n :-		evolve be co	ed are p loured	bassed t	4. The hrough	h water.	The w	ater will			
	(1) radius of 2r and HI is same (2) Their EN is same							(1) The nitrate (2) The bromide									
	(3) They are	e f-block	elemen	nts				(3) Bo	oth		(	(4) None	e of the	e two			
	(4) All						24	$Cr^{2+}$	is reduc	ing in	nature	becaus	e-				
19.	Similar sizes can be exp	of second ained on	l and thi the ba	ird trans isis of :	ition ele -	ements		(1) In $Cr^{2+}$ , configuration changes from d <sup>4</sup> to									
	(1) Inert-pai	r effect						(2) Cr	$^{2+}$ gain (	e nali	ron to r	2g <sup>.</sup> Schoive (	1 <sup>5</sup> confi	guration			
	(2) Screenir	ig effect						(2) Cr (3) Cr	yall i פ מונים <sup>+2</sup>	an electi	on to a	acheive (	l <sup>5</sup> confi	guration			
	(3) Lanthan	ide contra	action .					(4) In	$Cr^{2+}$ co	nfigura	tion ch	nanges f	rom $d^4$	to d <sup>3</sup> to			
	(4) Increasi	ng ettectiv	ve nucle	ear cha	rge			ac	heive h	alf filled	d d-sub	shell.	4				
20.	Iron exhibit	s +2 and	+3 oxi	idation	states.	Which	25	Highe	est stable	e Mn flu	oride is	sMnF₄v	vhere as	s highest			
	of the follow	ing statem	nents ab	out iror	is <b>inco</b>	rrect?	_	Mn o	xide is	Mn <sub>2</sub> O <sub>2</sub>	due to	4 · D-		5.00			
	(1) Ferrous ( than the	correspo	is are m nding fe	nore eas erric coi	ny hydr mpouno	olysed ds.		(1) O	atom i	s smalle	er the	F.					
	(2) Ferrous	oxide is n	nore bas	sic in na	ature th	an the		(2) O	xygen ł	nas abil	ity to f	orm mu	ultiple b	onds			
	terric ox	ide. Smpound	s aro rol:	ativolum	nore ion	ic than		(3) M	n <sup>7+</sup> doe	es not e	exist						
	the corre	sponding	g ferric o	compou	inds.			<ul><li>(4) F can not-stabilise higher oxidation states.</li><li>26 Which among the following order of oxidising</li></ul>									
	(4) Ferrous	compoun	ids are	less vol	atile tha	an the	26										
	correspo	naing ter	ric com	pounds	5.			powe	r is cor	rect–							
21.	Four succes	sive memb	pers of t	he first	row trai	nsition		(1) $CrO_4^- < MoO_4^- < WO_4^-$									
	Which one	e listed b of them is	erow w expecte	ed to ha	ve the h	noers. nighest		(2) $VO_2^+ < Cr_2O_7^{-} < MnO_4^-$									
	positive $F^0$		11e ?	-		5		(3) $\text{CrO}_3 < \text{MnO}_2 < \text{Fe}_2\text{O}_3$									
	(1) $Cr(7 = 2)$	<sup>3+</sup> /M <sup>2+</sup> Val 24)	(2)	Mn(7 =	= 25)			(4) Pł									
	(3) Fe (Z = $(Z = Z)$	26)	(2) $(4)$	Co(Z =	= 27)		27	<b>27</b> Cu <sup>+</sup> ion is not stable in aqueous solution, due									
22.	Which of the	e following	g metal o	al cation is reduced from $(1) d^{10}$ configuration													
	its higher o	xidation s	state (+2	2) to (+	1) by b	oth KI		(2) dis	propor	tionatic	n						
	solution and	d excess (	of KCN	l solutic	on ?			(3) less charge									
	(1) Zn <sup>2+</sup>	(2) Hg <sup>2+</sup>	(3)	) Cu <sup>2+</sup>	(4)	None		(4) ps	eudo in	iert gas	config	guration					
E	XERCISE	-III (An	alytic	al Que	estion	s)							NER	KEY			
Que.	1 2	3	4	5	6	7	8	9	10	11	12	13	14	15			
Ans.	4 1	4	4	3	3	2	1	3	2	1	2	2	3	1			
Que.	16 17	18	19	20	21	22	23	24	25	26	27						
Ans.	1   4	1	3	1	4	3	2	1	2	2	2						

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E	XERCISE	-IV (Asse	ertion & R	eason)				Targe	et AIIMS				
			Directio	ons for Asse	rtion	& Reason	questions						
Tł	nese questio these (	ns consist Questions y	of two state you are requ	ments each, j iired to choos	printed se any	as Assertion one of the fo	n and Reaso ollowing fou	on. While an r responses	nswering 5.				
(A)	If both As	sertion & R	leason are Tr	rue & the Rea	son is a	correct expl	anation of th	ne Assertior	1.				
<b>(B)</b>	If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.												
(C)	If Assertic	on is True bu	ut the Reaso	n is False.									
(D)	If both Ass	sertion & R	leason are fa	lse.									
1.	<b>Assertion</b> is greater th	: 1 <sup>st</sup> ionisa nan cadmiu	ation potenti m	al of mercury	<b>8</b> .	<b>Assertion</b> of Fe	: Melting p	oint of Mn l	ess than that				
	<b>Reason</b> configuratio	: Hg ha m (5d <sup>10</sup> 6s <sup>2</sup>	as stable )	electronic		<b>Reason</b> than Fe in a	: Mn has le atomic state	ss number o	f unpaired e−				
	(1) A	(2) B	(3) C	(4) D		(1) A	(2) B	(3) C	(4) D				
2.	Assertion atomic radiu	: Zr and i	Hf have abo	out the same	9.	<b>Assertion</b> intensely co	: Solution loured.	of Na <sub>2</sub> CrO <sub>4</sub>	in water is				
	Reason:	Zr and Hf	lies in the s	same group.		Reason:	Ox. state of	f Cr in Na <sub>2</sub> 0	$CrO_4$ is +6.				
	(1) A	(2) B	(3) C	(4) D		(1) A	(2) B	(3) C	(4) D				
<b>3</b> .	Assertion elements wh	: Zn, Cd, nile Cu, Ag,	, Hg are no Au are trans	on-transition ition element	10.	<b>Assertion :</b> Ce <sup>+4</sup> acts as oxidising agent in aqueous medium							
	Reason: completely t Cu, Ag, Au	In Zn, Cd filled in thei they are in	, Hg (n - 1)a r atomic state ncomplete.	l orbitals are e where as in		<b>Reason</b> lanthanides	: +4 is con	nmon oxida	tion state of				
	(1) A	(2) B	(3) C	(4) D		(1) A	(2) B	(3) C	(4) D				
<b>4</b> .	Assertion Reason:	: Cu <sup>+</sup> is n ΔIP is gro	nore stable t eater than 1	han Cu <sup>+2</sup> 6 eV	11.	Assertion	: Neptuniu	m is transura	nic element.				
	(1) A	(2) B	(3) C	(4) D		Reason	: It is heave	ier than ura	nium				
5.	Assertion	: KMnO <sub>4</sub>	is dark pii	nk coloured		(1) A	(2) B	(3) C	(4) D				
	compound				12.	Assertion	: La(OH) <sub>3</sub> is	s more basic t	han Lu(OH) <sub>3</sub>				
	Reason	: In the l	KMnO <sub>4</sub> cha	rge transfer		Reason	: Lanthanu	m is d-blocł	a element				
	spectrum od	ccurs.		(4) D		(1) A	(2) B	(3) C	(4) D				
6.	(1) A Assertion	(2) B : Hg is the	(3) C e only metal v	(4) D vhich is liquid	13.	<b>Assertion</b> : Actinides show much higher range of oxidation states							
	Reason :	It has very l	high IP and	weak metallic		<b>Reason</b> : Energy difference between 5f and 6d orbitals is large							
	(1) A	(2) B	(3) C	(4) D		(1) A	(2) B	(3) C	(4) D				
7.	<b>Assertion</b> variable	: Valency	of transitior	elements is	14.	Assertion a common	: All the lan oxidation	thanide elem state of -	nents exhibits ⊦3 in their				
	<b>Reason</b> almost same	: Energy ( e.	of ns and (n-	-1)d orbital is		Reason elements con	: The atom ntains three e	ms of the lectron in the	lanthanide eir outermost				
	(1) A	(2) B	(3) C	(4) D		shell. (1) A	(2) B	(3) C	(4) D <b>91</b>				

(1) A

15.	<b>Assertion:</b> - $K_2Cr_2O_7$ is used as a primary standard											
	in volum	etric analysis										
	Reason	:- It has a g	ood solubility	in water.								
	(1) A	(2) B	(3) C	(4) D	00							
16.	Assertio	o <b>n:-</b> Change	in colour of	acidic solution	20.							
	of potass	ium dichroma	ate by breath	is used to test								
	drunk dri	vers.										
	<b>Reason:-</b> Change in colour is due to the											
	complexation of alcohol with potassium											
	dichroma	te.										
	(1) A	(2) B	(3) C	(4) D								
17.	Assertio	on:- Eu <sup>2+</sup> & Y	7b <sup>2+</sup> are reduc	cing agents for								
	their ions	5.										
	<b>Reason:</b> - Both ions have stable half filled configuration											
	(1) A	(2) B	(3) C	(4) D								
18.	Assertic	on :- MnO <sub>2</sub> is	anti ferromag	netic in nature.								
	Reason	:- In MnO <sub>2</sub> , e	egual number	of domain are								

alligned with parallel and antiparallel spin.

(3) C

(4) D

(2) B

**ALLEN19.** Assertion :-  $La_2O_3$  is basic nature.**Reason :-** La in aqueous solution gives  $La(OH)_3$ <br/>(1) A(1) A(2) B(3) C(4) D**20.** Assertion :- FeCl<sub>3</sub> does not affect iodometric<br/>titration of CuSO<sub>4</sub> Solution<br/>**Reason :-** FeI<sub>3</sub> is formed.<br/>(1) A(2) B(3) C(4) D**21.** Assertion :- Actinoids can posses +4 O.S. more

easly then lanthanoid. **Reason :-** 4f, 5d, 6s have almost same energy levels. (1) A (2) B (3) C (4) D

**22.** Assertion :-  $UF_6$  is more covalent than  $UF_4$ .

**Reason** :- Fluorine is smaller in size.

(1) A (2) B (3) C (4) D

EX	(ERC	ISE-I	V (As	sertio	n & R	eason	)						ANS	WER	KEY
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	2	3	4	1	1	1	3	2	3	1	2	3	3	3
Que.	16	17	18	19	20	21	22								
Ans.	3	3	1	1	4	2	2								
~~															