

d & f-BLOCK ELEMENTS

INTRODUCTION

- (i) The element lying between s- and p-block elements of the periodic table are collectively known as transition or transitional elements. (T.E'.S.)
- (ii) Their properties are transitional between the highly electropositive s- block element to least electropositive p-block element.
- (iii) In d- block elements, the last electron is accommodated to the penultimate shell.
- (iv) The general electronic configuration of transition element is $(n-1)d^{1-10} ns^{0, 1 \text{ or } 2}$
- (v) These elements either in their atomic state or in any of their common oxidation state have partially filled $(n-1)d$ orbitals of $(n-1)^{\text{th}}$ shell.

Classification of Transition Elements

- (i) **1st Series** : They are classified in fourth period and are called as '3d' series of elements. Their atomic numbers are 21(Sc) to 30 (Zn).
- (ii) **2nd Series** : They are classified in fifth period and are called as '4d' series of elements. Their atomic numbers are 39(Y) to 48(Cd).
- (iii) **3rd series** : They are classified in sixth period and are called as '5d' series of elements. Their atomic numbers are 57(La), 72(Hf) to 80(Hg)
- (iv) **4th Series** : They are classified in the seventh period and are called as '6d' series of elements. This is an incomplete series. Their atomic numbers are 89(Ac) 104(Ku) to 112 (Uub).

Electronic Configuration

note

- Compared to Cu⁺² having 3d⁹ configuration, Cu⁺ having 3d¹⁰ configuration is less stable.

1st Series										
Z	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

2nd Series										
Z	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

3rd Series										
Z	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

POINTS

Cu²⁺

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- The irregularities in the observed configuration of Cr ($3d^5 4s^1$ instead of $3d^4 4s^2$), Cu ($3d^{10} 4s^1$), Mo ($4d^5 5s^1$), Pd ($[Kr] 4d^{10} 5s^0$), Au ($[Xe] 4f^{14} 5d^{10} 6s^1$), Ag ($[Kr] 4d^{10} 5s^1$) are explained on the basis of the concept that half-filled and completely filled d-orbitals are relatively more stable than partially filled d-orbitals.
- For explaining the irregularities found in the observed electronic configuration, one has to consider the net effect of so many other factors such as :
 - Nuclear electronic attraction ✓
 - Screening effect ✓
 - Inter- electronic repulsion ✓
 - The exchange energy force ✓
- Zn (30) is $[Ar] 3d^{10} 4s^2$ Cd (48) is $[Kr] 4d^{10} 5s^2$ Hg (80) is $[Xe] 4f^{14} 5d^{10} 6s^2$
 - These three elements do not have any unpaired electrons in their 'd' orbitals in atomic as well as in their common oxidation states. Therefore they are only classified as 'd' block elements and not as transition elements.
 - Copper, Silver and Gold, the elements of IB group i.e., coinage metals, have $ns^1 (n-1)d^{1-10}$ configuration. They are transition elements as in their higher oxidation state they have an unpaired electron in their 'd' orbitals.
- In 3d transitional series Mn^{+2} has maximum para magnetic behaviour.
 $25 Mn^{+2} \rightarrow 3d^5 4s^2$

GENERAL PROPERTIES OF d-BLOCK ELEMENTS

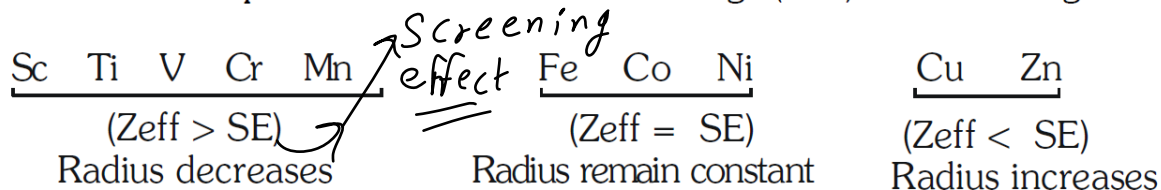
- (i) The properties of d-block elements of any given period are not so much different from one another as those of the same period of non transition elements.
- (ii) It is due to the fact that, in transition series, there is no change in number of electrons of outermost shell and only change occur in (n-1)d electron from member to member in a period.

Metallic Character

- (i) All the d-block elements are metals as the numbers of electrons in the outer most shell are one or two.
- (ii) They are hard, malleable and ductile (except Hg). IB group elements Cu, Ag and Au are most ductile and soft.
- (iii) These are good conductor of heat and electricity (due to free e^-) Elements of IB group are most conductive in nature. Their order of conductivity is $Ag > Cu > Au > Al$
- (iv) Covalent and metallic bonding both exist in the atom of transition metals.
- (v) The presence of unfilled of d-subshell favour covalent bonding and metallic bonding is due to possession of one or two electron in outermost energy shell.

Atomic Size

- (i) In the same period order of atomic and ionic radii. $s > d > p$
- (ii) Atomic radii depends on effective nuclear charge (Z_{eff}) and screening effect (SE). **In 3d series**



- (iii) In dipositive ions of 3d series Cu^{+2} is the smallest in size.
- (iv) Due to **Lanthanide contraction** elements of 4d and 5d series belong to a particular group have almost same atomic radii. **Ex.** $Zr \simeq Hf$, $Tc \simeq Re$, $Nb \simeq Ta$, $Ru \simeq Os$ etc.
- (v) **In d-block elements** - Largest atomic radii – La, Smallest atomic radii – Ni
- (vi) In IIIB group order of atomic radii is – $Sc < Y < La$ To $To < Lu$.

Ionisation Potential

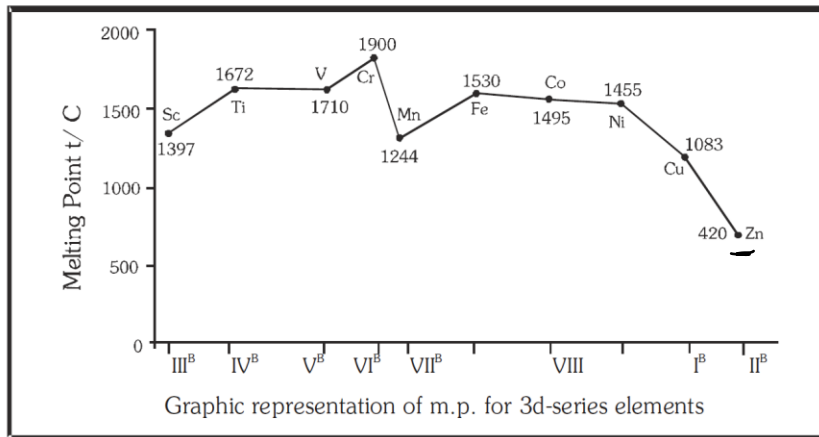
- (i) Along a period I.P. increases but in 3d series it is not regular.
- (ii) However the third member (5d series) has higher value than second member (4d-series) due to lanthanide contraction.

Reducing Power

- Reducing power of d-block elements depends on their electrode potential agent.
- Standard oxidation potential (SOP) of Cu is minimum in the 3d series so it is least reducing.
- Au is the least reducing element in the d-block because of minimum +ve value of Standard oxidation potential.
- The poor reducing capacity of the transition metal is due to high heats of vaporization, high ionization potential and low heat of hydration of their ions.

Melting and Boiling Points

- Melting and boiling point of d-block > s-block
- There is no regular trend of m.p. in 3d series. First increases up to Cr then decreases upto Mn and further increase and decrease upto Cu.



Characteristic properties of transition elements :

- | | | |
|------------------------------|-------------------------|---|
| (a) Variable oxidation state | (b) Coloured ions | (c) Paramagnetic properties |
| (d) Catalytic properties | (e) Formation of alloys | (f) Formation of interstitial compounds |
| (g) Formation of complexes. | | |

Variable Valency or Variable Oxidation States

(i) They exhibit variable valency due to involvement of (ns) and (n-1)d electrons. Due to less energy difference between these electrons.

(ii) MnO^{+2} $\text{Mn}_2^{+3}\text{O}_3$ MnO_2^{+4} $\text{Mn}_2^{+5}\text{O}_5$ $\text{Mn}_2^{+7}\text{O}_7$

(iv) The transition metal ions having stable configuration like d^0 d^5 or d^{10} are more stable.

Ex. Sc^{+3} , Ti^{+4} , V^{+5} , Fe^{+3} , Mn^{+2} , Zn^{+2} etc.

(v) In aqueous medium Cr^{+3} is stable due to half filled try set.

(vi) Co^{+3} and Ni^{+2} are stable in complexes..

(vii) In aqueous medium due to disproportionation Cu^{+1} is less stable than Cu^{+2} while its configuration is $3d^{10}$

(viii) Most common oxidation state among the transition elements is +2.

(ix) Highest oxidation state shown by transition elements of '4d' and '5d' series is +8 by Ru (44) and Os (76).

Note : **Ex.** Sc^{+2} , Ti^{+2} , V^{+2} , Fe^{+2} , Co^{+2} etc are reducing agents

Cr^{+6} , Mn^{+7} , Mn^{+6} , Mn^{+5} , Mn^{+4} etc are oxidising agents.

The relative stability of various oxidation states

- (i) The relative stabilities of various oxidation states of 3d-series element can be correlated with the extra stability of $3d^0, 3d^5$ & $3d^{10}$ configuration to some extent.

Ex. Stability of $Ti^{4+} (3d^0) > Ti^{3+} (3d^1) Mn^{2+} (3d^5) > Mn^{3+} (3d^4)$

- (ii) The higher oxidation state of 4d and 5d series element are generally more stable than the elements of 3d series.

Ex. (a) $Mo^{VI} O_4^{2-}$, (4d series) & $W^{VI} O_4^{2-}$, $Re^{VII} O_4^-$ (5d series) are more stable due to their maximum oxidation state.

(b) $Cr^{VI} O_4^{2-}$ & $Mn^{VII} O_4^-$ (3d-series) are strong oxidizing agents. Down the group stability of higher ox. state increases hence oxidizing character decreases.

- (iii) Strong reducing states probably do not form fluorides or oxides, but may well form the heavier halides. Conversely, strong oxidizing state form oxides & fluoride, but not Bromide and Iodide.

Ex. (a) V react with halogens to form VF_5 , VCl_5 , VBr_3 , but doesn't form VBr_5 and VI_5 because in +5 oxidation state V is strong oxidizing agent thus convert Br^- & I^- to Br_2 & I_2 respectively, So VBr_3 & VI_3 are formed but not VBr_5 & VI_5

(b) On the other hand VF_5 is formed because V^{5+} ion unable to oxidize highly electronegative & small anion F^- .

(c) Similarly highly electronegative and small O^{2-} ion formed oxides **Ex.** VO_4^{3-} , CrO_4^{2-} & MnO_4^- etc.

Diffrent oxidation state of chloride & oxides compound

+2	+3	+4	+5	+6	+7
TiCl ₂	TiCl ₃	TiCl ₄			
VCl ₂	VCl ₃	VCl ₄	VOCl ₃		
(Ionic, basic)	Less ionic (Amphoteric)	Covalent and Acidic (Strong lewis acid)			
TiO	Ti ₂ O ₃	TiO ₂			
VO	V ₂ O ₃		V ₂ O ₅	Amphoteric or less acidic	
CrO	Cr ₂ O ₃			CrO ₃	
MnO	Mn ₂ O ₃	MnO ₂		MnO ₃	Mn ₂ O ₇
Ionic, basic	Less Ionic (Amphoteric)			Acidic, covalent	

Colour Property

- (i) Most of the transition metal ions exhibit colour property.
- (ii) This is due to d-d transition of unpaired electrons in their t_{2g} and e_g sets of 'd' orbitals.
- (iii) They require less amount of energy to undergo excitation of electrons. Hence they absorb visible region of light exhibiting colour.

Ex. Sc⁺² [Ar]3d¹, Ti⁺² [Ar]3d², V⁺² [Ar]3d³

- (iv) Transition metal ions which do not have any unpaired electrons in their 'd' orbitals like 3d⁰ and 3d¹⁰ configurations, hence they do not exhibit any colour property.

Ex. Sc⁺³ [Ar]3d⁰, Cu⁺¹ [Ar]3d¹⁰, Ti⁺⁴ [Ar]3d⁰ etc are colourless ions.

Factors affecting the colour of complex

The colour of a transition metal complex depends on-

- The magnitude of energy difference Δ_0 between the two d-levels t_{2g} and e_g .
- An increase in the magnitude of Δ_0 decreases the wave length (λ) of the light absorbed by the complexes.

$$\Delta_0 \propto \frac{1}{\lambda(\text{Wavelength of light absorb})}$$

Δ_0 = Crystal field splitting energy for octahedral complex.

- Thus with a decrease in the λ the colour of complex changes from Red to Violet.
- KMnO_4 (dark pink), $\text{K}_2\text{Cr}_2\text{O}_7$ (orange) having d^0 configuration but they are coloured due to charge transfer spectrum and charge is transferred from anion to cation.

Example of Some coloured metal ions :

Ti^{+3}	Purple	Cr^{+3}	Green	Mn^{+2}	Light pink	Fe^{+2}	Green
Fe^{+3}	Yellow	Co^{+3}	Pink	Ni^{+2}	Green	Cu^{+2}	Blue

Magnetic Properties

- If there there is any one unpaired electron in metal or metal ion behave as paramagnetic.
- If unpaired electrons are zero then metal or metal ion is diamagnetic.

$\mu = \sqrt{n(n+2)}$ Where 'n' is the number of unpaired electrons in the metal ion. $\mu \propto n$ \propto unpaired electrons

μ = Magnetic moment in Bohr Magnetons (B.M.)

$$1\text{BM} = \frac{eh}{4\pi mc}$$

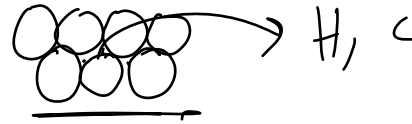
Catalytic Property

- (i) Transition elements and their compounds exhibit catalytic properties. This is due to their variable valency as well as due to the free valencies on their surface.
- (ii) When transition elements and their compounds are in powdered state, their catalytic property exhibited will be to a greater extent. This is due to greater surface area available in the powdered state.

<i>Catalyst</i>	<i>Used</i>
Fe	Haber's process for manufacture of NH_3 .
V_2O_5	Contact process for H_2SO_4 manufacture.
Pt	Ostwald's process of nitric acid.
Ni	Hydrogenation of oils.
FeSO_4 & H_2O_2	Fenton's reagent for oxidising alcohol to aldehyde.
Cu	Dehydrogenation of alcohols
TiCl_4	Ziegler-Natta catalyst in the production of Polyethene.
FeCl_3	For making CCl_4 from CS_2 and Cl_2 .
Pt/Platinumoxide	Adams catalyst, used for reduction.

SOME IMPORTANT ALLOY

- | | |
|-------------------|----------------------------------|
| (a) Bronze | Cu (75 - 90 %) + Sn (10 - 25 %) |
| (b) Brass | Cu (60 - 80 %) + Zn (20 - 40 %) |
| (c) Gun metal | (Cu + Zn + Sn) (87 : 3 : 10) |
| (d) German Silver | Cu + Zn + Ni (2 : 1 : 1) |
| (e) Bell metal | Cu (80 %) + Sn (20 %) |



Formation of Interstitial Compounds

- (i) Transition elements form interstitial compounds with smaller sized non metal elements like hydrogen, carbon, boron, nitrogen etc.
- (ii) The smaller sized atoms get entrapped in between the interstitial spaces of the metal lattices.
These interstitial compounds are nonstoichiometric in nature and hence cannot be given any definite formula.
- (iii) The smaller sized elements are held in interstitial spaces of transition elements by weak Vander Waals forces of attractions.
- (iv) The interstitial compounds have essentially the same chemical properties as the parent metals but they differ in physical properties such as density and hardness.
The process of adsorption of excess of H atom by the transition metals like Pd, Pt, Co etc is called occlusion.

Nonstoichiometry

- (i) The transition elements sometimes form nonstoichiometric compounds due to variable valency.
- (ii) These are the compounds of indefinite structure & proportion.
- (iii) For example, Iron (II) Oxide FeO should be written as a bar over the formula $\overline{\text{FeO}}$ to indicate the ratio of Fe & O atom is not exactly 1:1 ($\overline{\text{Fe}_{0.94}\text{O}}$ & $\overline{\text{Fe}_{0.84}\text{O}}$), $\overline{\text{VSe}}$ ($\overline{\text{VSe}_{0.98}\text{VSe}_{1.2}}$), $\overline{\text{TiO}}$

POINTS

- Complex forming tendency of metals is due to small size and high nuclear charge.
- Fe and Pt can not form Amalgam
- Colour of species without unpaired electron is due to charge transfer spectrum.

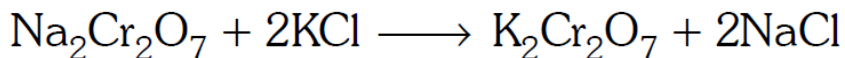
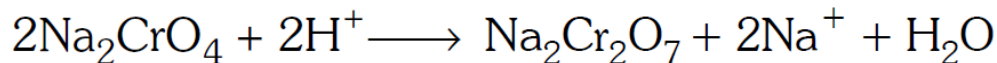
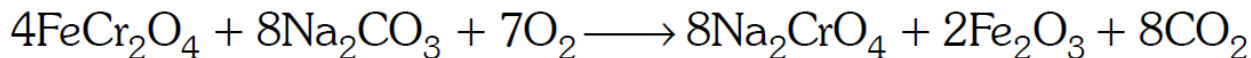
Na - Hg

POTASSIUM DICHROMATE ($K_2Cr_2O_7$)

- It is orange red due to charge transfer.

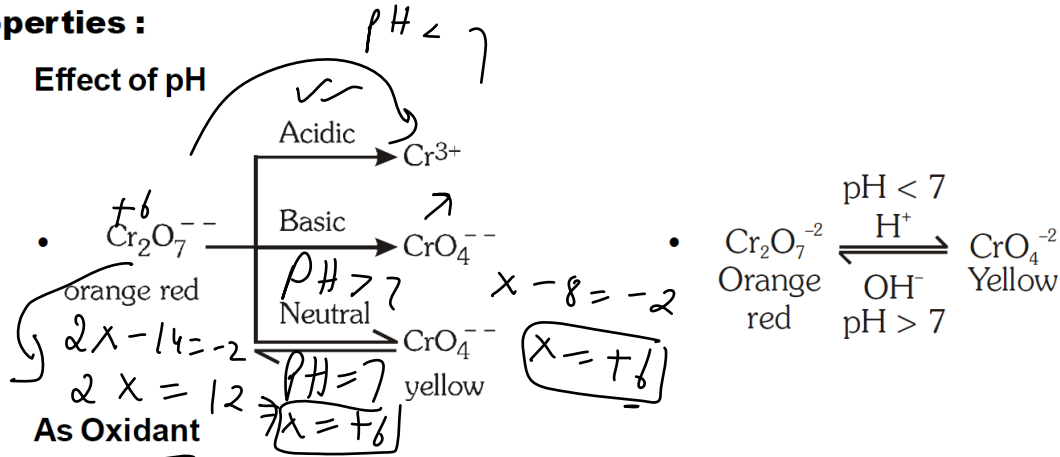
Preparation

It is prepared by fusion of iron chromite ($FeCr_2O_4$) with sodium carbonate in presence of air

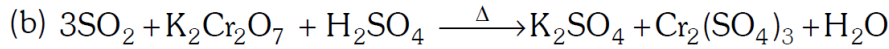
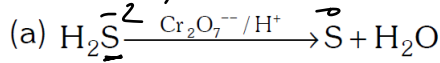


Properties :

Effect of pH



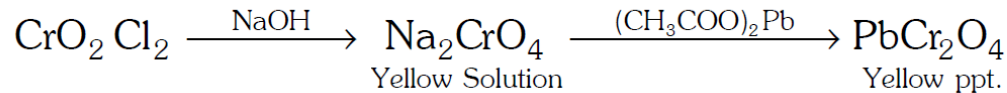
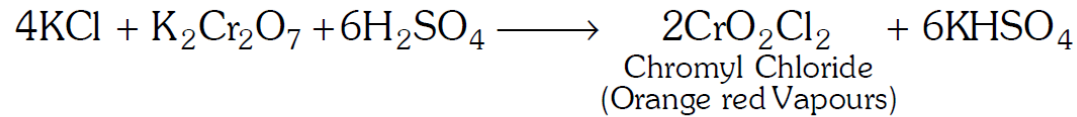
As Oxidant



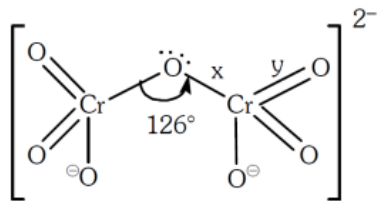
Green

Chromyl chloride Test

It is for ionic chlorides



Structure of Dichromate Ion



* 6 Cr-O bond lengths are equal

* All Cr-O bond lengths are not equal

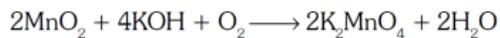
* Bond length $x > y$

POTASSIUM PERMANGANATE (KMnO₄)

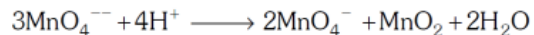
- It is purple coloured due to charge transfer.

Preparation

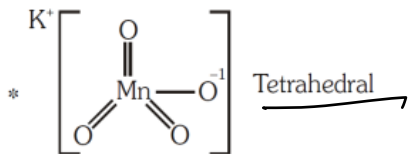
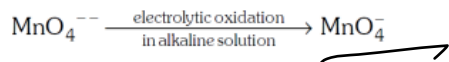
It is prepared by fusion of MnO₂ with an alkali metal hydroxide and on oxidising agent like KNO₃ followed by acidification.



Pyrolusite



Commercial conversion of MnO_4^{--} in the MnO_4^- by the electrolytic oxidation.



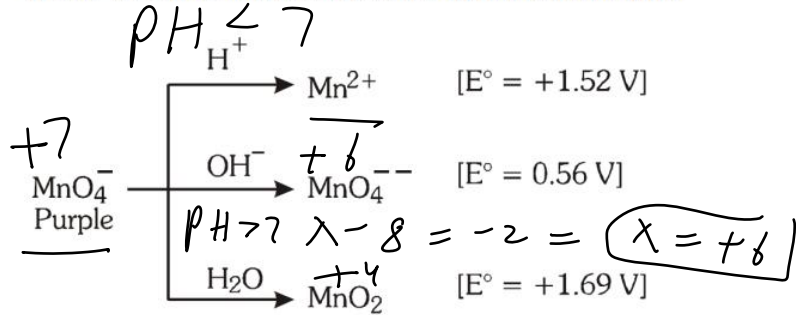
* All Mn-O bond lengths are equal

* Colour of KMnO₄ is due to charge transfer

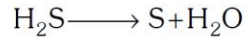
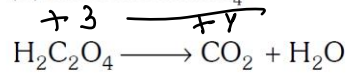
Properties

As Oxidant

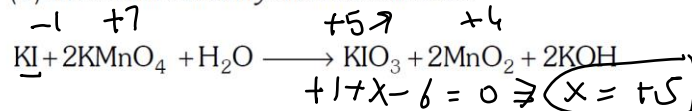
It acts as oxidant in acidic basic and neutral medium.



(a) In Acidic KMnO_4 $\text{pH} = 7$



(b) In neutral or faintly alkaline solutions



POINTS

- Sodium dichromate is more soluble than potassium dichromate.
- Chromyl chloride test is not give by covalently bonded chloride like HgCl_2 , CHCl_3 etc.
- Potassium permanganate titrations in presence of HCl and HNO_3 in unsatisfactorily since HCl is oxidised and HNO_3 is itself oxidant.

f-BLOCK ELEMENTS

F-Block Elements

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

These are divided in two series of 14-14 elements are known as Lanthanoids and actinoids which are placed in bottom of periodic table

Lanthanoids-58-71 → [Rare earth metals]

Actinoids-90-109 → [Radioactive elements]

Lanthanoides

(1) E.C. [Electronic configuration]

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

Atomic Number	Element	Symbol	Outer electronic configuration	
			Atomic	+3 ion
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^1$
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^2$
60.	Neodymium	Nd	$4f^4 6s^2$	$4f^3$
61.	Promethium	Pm	$4f^5 6s^2$	$4f^4$
62.	Samarium	Sm	$4f^6 6s^2$	$4f^5$
63.	Europium	Eu	$4f^7 6s^2$	$4f^6$
64.	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7$
65.	Terbium	Tb	$4f^9 6s^2$	$4f^8$
66.	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^9$
67.	Holmium	Ho	$4f^{11} 6s^2$	$4f^{10}$
68.	Erbium	Er	$4f^{12} 6s^2$	$4f^{11}$
69.	Thulium	Tm	$4f^{13} 6s^2$	$4f^{12}$
70.	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{13}$
71.	Lutecium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14}$

Note :- [In lanthanoide series only Pm(Z=6) is synthetic radioactive element]

(2) Oxidation states :- Common oxidation state is (+3) but some element show less or more oxidation state to attain stable E.C as f^0 or f^4 or f^{14}

Ex. $Ce^{+4}(f^0)$, $Yb^{+2}(f^{14})$, $Eu^{+2}(f^7)$

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

(3) Magnetic properties

- Elements having unpaired e^- are paramagnetic in nature
- Elements having zero unpaired electrons are diamagnetic in nature. Eg. Ce^{+4} $4f^0$
- Those elements or ions having unpaired electrons are coloured.

(4) Lanthanoids contraction

Regular decrease in atomic radius of elements in series is known as lanthanoide contraction.

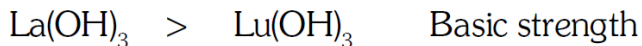
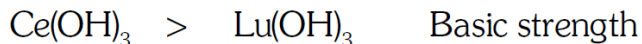
Consequence of lanthanoide contraction

(a) Similar chemical properties

Due to similar properties these are not easily separated but by ion exchange method.

(b) Basic strength of hydroxides

Decrease along series



Radius of $\begin{pmatrix} Zr \approx Hf \\ Nb \approx Ta \\ Mo \approx W \end{pmatrix}$ is similar.

- Density increases along the group density of 3rd $>$ density of 2nd transition series.
- Ionisation potential of III series $>$ II series
I.P. of Hg $>$ Cd

(5) Ionisation Energy

Highly electro positive & due to large radius, I.E. is low as comparable to alkaline earth metals, so they are good reducer.

(6) Having less complex formation property

Note :- These are used in formation of misch metal = 95% (Lanthanides) + 5% (Fe) flints of lighter, jet engine parts.

ACTINIDES (5f-BLOCK ELEMENT)

Electronic Configuration

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

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

(2) Oxidation states

Common oxidation state is +3 but these elements show more oxidation states due to less energy difference between 5f and 6d orbitals and maximum O.S. is +7 (Np, Pu)

(3) Actinides contraction

Due to poor screening of f-electrons radius of actinides gradually dec. along series is K/as actinide contraction.

Note :- Elements after uranium are K/as trans uranium elements.

(4) They have more complex formation property than lanthanides.

(5) Mostly elements are paramagnetic and their compounds are coloured.

Elements → compounds

Paramagnetic - Coloured Exam. U^{+3} , Np^{+3}

Diamagnetic - Colour less Exam. Th^{+4}

(6) There are more reactive than lanthanides and form oxo compounds

As UO_2^{+2} , UO_2^{+1} and are more electro positive.

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

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

Note : Actinoids represents more oxidation state due to less energy difference between 4f and 5d subshell.

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

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

Points of Distinction

Lanthanides

Actinides

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

1. Besides the most common oxidation state of +3, actinides show +4, +5 and +6 oxidation states in case of certain elements.
2. Actinides have a stronger tendency towards complex formation.
3. All the actinides are radioactive.
4. Oxides and hydroxides of actinides are more basic.

POINTS

- **Alloy** : Alloys of lanthanides with Fe are called ***mish metals***.
- **Basic Nature** : $\text{La}(\text{OH})_3$ is most basic in nature while $\text{Lu}(\text{OH})_3$ least basic.
- **Carbide** : Lanthanides form MC_2 type carbide with carbon, which on hydrolysis gives C_2H_2 .

d AND f-BLOCK ELEMENTS

1. In the form of dichromate, Cr(VI) is a strong oxidising agent in acidic medium but Mo(VI) in MoO_3 and W(VI) in WO_3 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

2. Which compound does exist

- | | |
|----------------------------|--------------------------------|
| (1) MnO_3F | (2) $\text{K}_2[\text{CuI}_4]$ |
| (3) MnF_7 | (4) CrF_7 |

3. Which of the element have highest density –

- | | | | |
|-------|--------|--------|--------|
| (1) W | (2) Os | (3) Tc | (4) Mo |
|-------|--------|--------|--------|

EXERCISE

4. Which catalyst is used in conact process ?

- | | |
|--------|-------------------------------------|
| (1) Ni | (2) V_2O_5 |
| (3) Fe | (4) $\text{AlCl}_3 + \text{TiCl}_4$ |

5. $\text{X} \xrightarrow[\text{K}_2\text{Cr}_2\text{O}_7]{\text{conc. H}_2\text{SO}_4}$ red brown vapours. X can be

- | | |
|--------------------|-------------------|
| (1) NaI | (2) NaBr |
| (3) Both (1) & (2) | (4) None of these |

6.
$$\begin{array}{ccccc} \text{X} & \xrightarrow[\text{air}]{\text{KOH}} & \text{Y} & \xrightarrow{\text{H}^+} & \text{Z} + \text{X} \\ \text{black coloured} & & \text{dark green} & & \text{an oxidising agent} \\ \text{ore} & & & & \end{array}$$

True statement is

- (1) X can't be MnO_2
- (2) Y can be KMnO_4
- (3) Z can be K_2MnO_4
- (4) X is MnO_2 and Y is K_2MnO_4



X and Y are oxy anion of Cr than oxidation state of Cr in X, Y, Z will be respectively

- (1) +3, +6, +6 (2) +6, +3, +6
 (3) +6, +6, +6 (4) +6, +6, +3

8. When KMnO_4 solution is added to oxalic acid, solution, the decolourisation is slow in beginning but become instantaneous after some time because

- (1) CO_2 is a by product
 (2) Mn^{2+} acts as a catalyst
 (3) reaction is exothermic
 (4) MnO_4^- catalyzes the reaction

9. Which type of hydroxide generally formed by Lanthanoids ?

- (1) $\text{Ln}(\text{OH})_3$ (2) $\text{Ln}(\text{OH})_2$
 (3) $\text{Ln}(\text{OH})_4$ (4) $\text{Ln}(\text{OH})_6$

10. 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

11. KMnO_4 on treatment with conc. H_2SO_4 forms a compound (X) which decomposes explosively on heating forming (Y). The (X) and (Y) are respectively

- (1) $\text{Mn}_2\text{O}_7, \text{MnO}_2$ (2) $\text{Mn}_2\text{O}, \text{Mn}_2\text{O}_3$
 (3) $\text{MnSO}_4, \text{Mn}_2\text{O}_3$ (4) $\text{Mn}_2\text{O}_3, \text{MnO}_2$

12. $\text{Cr}_2\text{O}_7^{2-} \xrightleftharpoons[\text{Y}]{\text{X}} 2\text{CrO}_4^{2-}$, X and Y are respectively

- (1) $\text{X} = \text{OH}^-, \text{Y} = \text{H}^+$ (2) $\text{X} = \text{H}^+, \text{Y} = \text{OH}^-$
 (3) $\text{X} = \text{OH}^-, \text{Y} = \text{H}_2\text{O}_2$ (4) $\text{X} = \text{H}_2\text{O}_2, \text{Y} = \text{OH}^-$

19. The electronic configuration of gadolinium (At. No. 64) is :
- (1) $[\text{Xe}] 4f^7 5d^1 6s^2$ (2) $[\text{Xe}] 4f^8 5d^0 6s^2$
 (3) $[\text{Xe}] 4f^8 5d^1 6s^1$ (4) $[\text{Xe}] 4f^7 5d^0 6s^2$
20. Which oxidation state is not shown by lanthanoids?
- (1) +2 (2) +3
 (3) +4 (4) +6
21. Which of the following species acts as a reducing agent ?
- (1) Ce^{+4} (2) Lu^{+3} (3) Eu^{+2} (4) Ce^{+3}
22. An increase in both atomic and ionic radii with atomic number occurs in any group of the periodic table. In accordance of this the ionic radii of Ti (IV) and Zr (IV) ions are 0.68 Å and 0.74 Å respectively but for Hf (IV) ion the ionic radius is 0.75 Å, which is almost the same as that for Zr (IV) ion. This is due to :-
- (1) greater degree of covalency in compounds of Hf^{4+}
 (2) Lanthanide contraction
 (3) Difference in the co-ordination number of Zr^{+4} and Hf^{+4} in their compounds
 (4) Actinide contraction
23. When lanthanoid element is heated with sulphur then compound obtained is :-
- (1) LnS_2 (2) Ln_2S_3
 (3) Ln_2S (4) Ln_3S_4
24. 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) $\text{Ni}^{2+}, \text{Cu}^+$ (2) $\text{Ni}^{2+}, \text{Ti}^{3+}$
 (3) $\text{Sc}^{3+}, \text{Ti}^{3+}$ (4) $\text{Sc}^{3+}, \text{Co}^{2+}$
25. Which one of the following ions is the most stable in aqueous solution
- (1) V^{3+} (2) Ti^{3+} (3) Mn^{3+} (4) Cr^{3+}
26. Identify the incorrect statement among the following
- (1) Lanthanoid contraction is the accumulation of successive shrinkages.
 (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.
 (3) Shielding power of 4f electrons is quite weak.
 (4) there is a decrease in the radii of the atoms or ions as one proceeds from La to Lu.

27. The correct order of decreasing second ionisation enthalpy of Ti (22), V(23), Cr(24) and Mn (25) is:-

- (1) $Mn > Cr > Ti > V$
- (2) $Ti > V > Cr > Mn$
- (3) $Cr > Mn > V > Ti$
- (4) $V > Mn > Cr > Ti$

28. Which one of the following ions has electronic configuration $[Ar]3d^6$? (At. nos. Mn = 25, Fe = 26, Co = 27, Ni = 28)

- (1) Co^{3+}
- (2) Ni^{3+}
- (3) Mn^{3+}
- (4) Fe^{3+}

29. 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)

30. Which of the statements is not true?

- (1) $K_2Cr_2O_7$ solution in acidic medium is orange
- (2) $K_2Cr_2O_7$ solution becomes yellow on increasing the pH beyond 7
- (3) On passing H_2S through acidified $K_2Cr_2O_7$ solution, a milky colour is observed
- (4) $Na_2Cr_2O_7$ is preferred over $K_2Cr_2O_7$ in volumetric analysis

31. Magnetic moment 2.84 B.M. is given by :-

(At. no.), Ni = 28, Ti = 22, Cr = 24, Co = 27)

- (1) Ti^{3+}
- (2) Cr^{2+}
- (3) Co^{2+}
- (4) Ni^{2+}

32. The electronic configurations of Eu(Atomic No 63), Gd(Atomic No 64) and Tb (Atomic No. 65) are

- (1) $[Xe]4f^76s^2$, $[Xe]4f^8 6s^2$ and $[Xe]4f^85d^16s^2$
- (2) $[Xe]4f^75d^16s^2$, $[Xe]4f^7 5d^1 6s^2$ and $[Xe]4f^96s^2$
- (3) $[Xe]4f^65d^16s^2$, $[Xe]4f^75d^16s^2$ and $[Xe]4f^85d^16s^2$
- (4) $[Xe]4f^76s^2$, $[Xe]4f^75d^16s^2$ and $[Xe]4f^96s^2$

33. HgCl_2 and I_2 both when dissolved in water containing I^- ions the pair of species formed is :



34. Match the metal ions given in Column I with the spin magnetic moments of the ions given in Column II and assign the **correct** code :

Column I

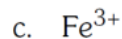
Column II



i. $\sqrt{8}$ B.M.



ii. $\sqrt{35}$ B.M.



iii. $\sqrt{3}$ B.M.

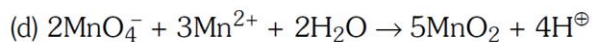
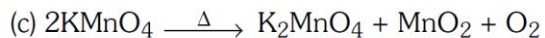
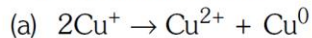


iv. $\sqrt{24}$ B.M.

v. $\sqrt{15}$ B.M.

	a	b	c	d
(1)	iv	v	ii	i
(2)	i	ii	iii	iv
(3)	iv	i	ii	iii
(4)	iii	v	i	ii

35. Which of the following reactions are disproportionation reaction ?



Select the **correct** option from the following :-

(1) (a) and (b) only (2) (a), (b) and (c)

(3) (a), (c) and (d) (4) (a) and (d) only

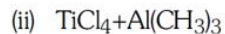
36. Match the catalyst with the process :-

Catalyst

Process



(a) The oxidation of ethyne to ethanal



(b) Polymerisation of alkynes



(c) Oxidation of SO_2 in the manufacture of H_2SO_4

(iv) Nickel complexes (d) Polymerisation of ethylene

Which of the following is the correct option ?

(1) i-c, ii-d, iii-a, iv-b (2) i-a, ii-b, iii-c, iv-d

(3) i-a, ii-c, iii-b, iv-d (4) i-c, ii-a, iii-d, iv-b

37. When neutral or faintly alkaline KMnO_4 is treated with potassium iodide, iodide ion is converted into 'X'. 'X' is-

- | | |
|---------------------|---------------------|
| (1) I_2 | (2) IO_4^- |
| (3) IO_3^- | (4) IO^- |

38. The oxidation state of Cr in CrO_5 is :

- | | |
|--------|---------|
| (1) -6 | (2) +12 |
| (3) +6 | (4) +4 |

d AND f-BLOCK ELEMENTS

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	1	2	2	2	4	4	2	1	2	1	1	3	1	3
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	4	3	2	1	4	3	2	2	2	4	2	3	1	1	4
Que.	31	32	33	34	35	36	37	38							
Ans.	4	4	2	1	1	1	3	3							