

d - BLOCK ELEMENTS

TRANSITION ELEMENTS AND COMPLEXES

They are often called 'transition elements' because

- (i) They show's variable oxidation state in their compounds.
- (ii) Their outermost (n^{th}) and as well as penultimate ($n - 1$) shell is incomplete.
- (iii) Their position in the periodic table is between s-block and p-block elements

Typically, the transition elements have an incompletely filled d-level. Since Zn group has d^{10} configuration and are not considered as transition elements but they are d-block elements.

- (i) **The first transition series : (3d series)** involves the filling of 3d orbitals and has 10 elements from scandium ($Z = 21$) to zinc ($Z = 30$)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$

- (ii) **The second transition series : (4d series)** involves the filling of 4d orbitals and has 10 elements from yttrium ($Z = 39$) to cadmium ($Z = 48$).

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
$4d^1 5s^2$	$4d^2 5s^2$	$4d^4 5s^1$	$4d^5 5s^1$	$4d^5 5s^2$	$4d^6 5s^1$	$4d^7 5s^1$	$4d^9 5s^1$	$4d^{10} 5s^1$	$4d^{10} 5s^2$

- (iii) **The third transition series : (5d series)** involves the filling of 5d orbitals and has 10 elements. The first element of this series is lanthanum ($Z = 57$). It is followed by 14 elements (lanthanides, involving filling of 4f orbitals). The next nine elements are from hafnium ($Z = 72$) to mercury ($Z = 80$)

La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
$5d^1 6s^2$	$5d^2 6s^2$	$5d^3 6s^2$	$5d^4 6s^2$	$5d^5 6s^2$	$5d^6 6s^2$	$5d^7 6s^2$	$5d^9 6s^1$	$5d^{10} 6s^1$	$5d^{10} 6s^2$

- (iv) **The fourth transition series** is incomplete and contains only three elements $_{89}\text{Ac}$, $_{104}\text{Rf}$, $_{105}\text{Ha}$.

Zn (30) is $[\text{Ar}] 4s^2 3d^{10}$

Cd (48) is $[\text{Kr}] 5s^2 4d^{10}$

Hg (80) is $[\text{Xe}] 6s^2 4f^{14} 5d^{10}$

These elements have completely filled $(n-1)d$ subshell in their elementary as well as ionic state and so are not true transition metals. Their properties are quite different from those of transition metals.

Zn is used in galvanizing, in making alloys, in making white pigment and in rubber industry (ZnO acts as filler). Cd is used in nuclear reactors as moderators, in making NiCd storage cells and in making paints. Mercury is used in scientific equipments and in electrolytic cells. Several compounds of Hg are used in making antiseptics.

GENERAL CHARACTERISTICS

(ii) Electronic configuration: $(n-1)d^{1-10}ns^{1-2}$

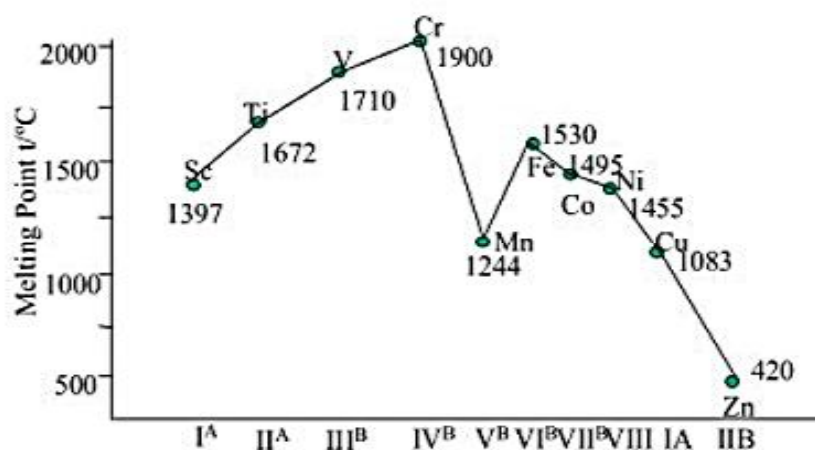
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
others are				$4s^1$					$4s^1$	
as usual				$3d^5$					$3d^{10}$	

(a) Metallic Character

- All the transition elements are metals, since the number of electrons in the outermost shell is very small being equal to 2.
- They are hard, malleable and ductile, except Hg which is liquid and soft.
- They exhibit all the three types of structures. Face Centred Cubic (fcc), Hexagonal Close packed (hcp) and Body Centred Cubic (bcc).
- Covalent and Metallic bonding both exist in the atom of transition metals.
- The presence of unfilled d- subshell favour covalent bonding, and metallic bonding is due to possession of one or two electron in outermost energy shell.
- These metals are good conductors of heat and electricity.

(b) Melting and Boiling Points :

- The transition elements have very high melting & boiling points as compared to those of s & p block elements.
- The high melting and boiling point of transition metals are attributed to the stronger force that bind their atoms together.
- As the number of d- electron increases the number of covalent bond between the atoms are expected to increase up to Cr- Mo- W family where each of the d- orbital has only unpaired electrons and the opportunity for covalent sharing is greatest.
- In spite of presence of five unpaired electrons in Mn, the unexpected low melting and boiling is due to its complex structure it is unable to form metallic and covalent bonds.
- The absence of unpaired electron [$(n-1)d^{10}4s^2$] in Zn, Cd, & Hg is responsible for its low melting & boiling point.



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

(c) **Atomic and Ionic Radii**

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic Radii (Å°)	1.44	1.32	1.22	1.18	1.14	1.17	1.16	1.15	1.27	1.25
Ionic radii (Å°) for M^{2+}	0.95	0.90	0.88	0.74	0.80	0.76	0.74	0.72	0.69	0.74
for M^{3+}	0.81	0.68	0.73	0.69	0.66	0.64	0.63	0.62	-	-
Metallic radii (Å°)	1.62	1.47	1.34	1.27	1.26	1.26	1.25	1.24	1.28	1.38

The value of these radii decreases generally, on moving from left to right in the period.

Reason :

- This is due to the fact that an increase in the nuclear charge tends to attract the electron cloud inwards.
- The radii for the elements from Cr to Cu are however very close to one another.
- The simultaneous addition of electron of 3d-level exercises the reverse effect by screening the outer 4s-electron from the inward pull of the nucleus.
- As a result of these two opposing effects, the atomic radii do not alter much on moving from Cr to Cu.
- The radii of M^{2+} ions, although some what smaller than that of Ca^{2+} ion ($= 0.99 \text{ Å}^\circ$) are comparable with it.

Oxides :

- Thus Mo oxides of transition element should be similar to CaO in many ways, although some what less basic and less soluble in water.
- Similarly the Hydration energy of M^{2+} ion [$Ti^{2+} \rightarrow Cu^{2+}$] are between 446 KCal to 597 KCal is some what greater than that of Ca^{2+} ion [395 K cal].

Oxides of first row transition metals

- Basic Oxides : Sc_2O_3 , TiO_2 , Ti_2O_3 , VO , V_2O_3 , MnO , FeO , Fe_2O_3 , Fe_3O_4 , CoO , NiO , Cu_2O .
- Acidic oxides : V_2O_5 , CrO_3 , Mn_2O_7 .
- Amphoteric oxides : TiO_2 , VO_3 , Cr_2O_3 , CrO_2 , Mn_2O_3 , Mn_3O_4 , MnO_2 , CuO .

(d) **Ionisation Potential**

- The first ionisation potential of transitional elements lie between those of s & p block elements.
- The first ionization potential of all the transition elements lie between 6 to 10 ev.
- In case of transition elements the addition of the extra electron in the ($n-1$) d provides a screening effect which shields the outer ns electron from the inward pull of positive nucleus.
- Thus the effect of increasing nuclear charge & the shielding effect created due to the expansion of ($n-1$) d orbital oppose each other.
- On account of these counter affects, the ionisation potentials increases rather slowly on the moving in a period of the first transition series.
- The IE_1 for the first four 3d - block elements (Sc, Ti, V & Cr) differ only slightly from one another.
- Similarly the value of Fe, Co, Ni & Cu also are fairly close to one another.

Ionisation Potential (ev.)	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
IE ₁	6.56	6.83	6.74	7.43	7.43	7.90	7.86	7.63	7.72	9.39
IE ₂	12.91	13.69	14.26	16.95	15.69	16.21	17.08	18.21	20.34	18.00
IE ₃	24.79	27.52	29.35	31.0	23.34	30.69	33.54	35.21	36.88	39.78

(e) Oxidation State

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			+1					+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3		
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

Colour: (aquated)

Sc³⁺ → colourless

Ti⁴⁺ → colourless

Ti³⁺ → purple

V⁴⁺ → blue

V³⁺ → green

V²⁺ → violet

Cr²⁺ → blue

Cr³⁺ → green

Mn³⁺ → violet

Mn²⁺ → light pink

Fe²⁺ → light green

Fe³⁺ → yellow

Co²⁺ → pink

Ni²⁺ → green

Cu²⁺ → blue

Zn²⁺ → colourless

(f) 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 3d⁰, 3d⁵ & 3d¹⁰ configuration to some extent.

Example- Ti⁴⁺ (3d⁰) is more stable than Ti³⁺ (3d¹)

Mn²⁺ (3d⁵) is more stable than Mn³⁺ (3d⁴).

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

Example -

- (a) Mo^{vi}O₄²⁻, Te^{vii}O₄²⁻ (4d-series element) & W^{vi}O₄²⁻, Re^{vii}O₄²⁻ (5d-series elements) are more stable and in which the transition element concerned show their maximum oxidation state.
- (b) Cr^{vi}O₄²⁻ & Mn^{vii}O₄²⁻ (3d-series) are strong oxidizing agents.
- (iii) Strongly 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.

Example -

- (a) V react with halogens to form VF_5 , VCl_4 , VBr_3 , but doesn't form VBr_5 or 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 eg. VO_4^{3-} , CrO_4^{2-} & MnO_4^- etc.
- (iv) All transition elements in their lower oxidation state like to form ionic compounds. Whereas in their higher oxidation state they generally formed covalent compound.

Example-

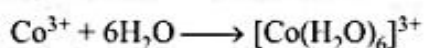
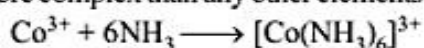
+2	+3	+4	+5	+6	+7
TiCl_2	TiCl_3	TiCl_4			
VCl_2	VCl_3	VCl_4	VOCl_3		
(Ionic, Less ionic basic) Amphoteric Covalent & Acidic, (Strong Lewis acid)					
TiO	Ti_2O_3		TiO_2		
VO	V_2O_3		V_2O_5		
CrO	Cr_2O_3		CrO_3		
MnO	Mn_2O_3	MnO_2	MnO_3	Mn_2O_7	
Ionic	Less Ionic			Acidic	
(Basic)	(Amphoteric)			(Covalent)	

Formation of Complexes :

By virtue of their small size, comparatively high nuclear or ionic charge and availability of vacant d-orbitals of suitable energy, these metals exert strong electrostatic attraction on the ligands. The species formed on interaction of metal and the ligand (or ligands) is known as a complex.

The transition metal ions form complexes because of the following reasons :

- (a) Their small cation size
- (b) High effective nuclear charge
- (c) Availability of vacant (n-1) d-orbitals of appropriate energy
- (d) The structure commonly found in such complex are linear (i.e. co-ordination number, C.N.=2), square planer (C.N.=4), tetrahedral (CN = 4) or octahedral (CN = 6).
- (e) Cobalt form more complex than any other elements



Metal ion	Ligand	C.N.	Complex ion
Ag^+	NH_3	2	$[\text{Ag}(\text{NH}_3)_2]^+$
Ni^{+2}	CN^-	4	$[\text{Ni}(\text{CN})_4]^{-2}$
Cu^{2+}	NH_3	4	$[\text{Cu}(\text{NH}_3)_4]^{+2}$
Fe^{+2}	CN^-	6	$[\text{Fe}(\text{CN})_6]^{-4}$

(g) Magnetic properties

- * Matter, in general is associated with magnetic properties. Majority of substances are either paramagnetic or diamagnetic. A paramagnetic substance is one which is attracted into a magnetic field. Paramagnetism is mainly due to the presence of unpaired electrons in atoms or ions or molecules. Diamagnetic substance is one which is slightly repelled by a magnetic field.
- * $Ti^{+2} [Ar]3d^2$, $Ti^{+3} [Ar]3d^1$, $V^{+2} [Ar]3d^3$, $Cr^{+3} [Ar]3d^3$
As is evident most of the transition metal ions have unpaired electrons in their 'd' orbitals. Hence most of the transition metal ions are paramagnetic in nature. Transition metal ions having $3d^0$ and $3d^{10}$ configuration exhibit diamagnetic nature.
- * An unpaired electron spins and as it is a charged particle, magnetic field is created due to its spinning.
- * Each electron may, in fact, be considered as a micro magnet having a certain value of magnetic moment. The total magnetic moment of a substance is the resultant of the magnetic moments of all the individual electrons. Thus substances containing unpaired electrons get attracted towards the magnets exhibiting paramagnetic nature.
- * The magnetic moment (μ) created due to spinning of unpaired electrons can be calculated by using

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

$$\mu = \text{Magnetic moment in Bohr Magnetons (B.M.)}$$
- * The magnetic moment of diamagnetic substances will be zero.
- * As the number of unpaired electrons increase the magnetic moment created goes on increasing and hence the paramagnetic nature also increases.
- * Transition metal ions having d^5 configuration will have maximum number of unpaired electrons therefore they will be maximum paramagnetic in nature.

Variation of Magnetic moment of 3d- series

Ions with configuration	Outer most configuration	Number of unpaired electron	Magnetic Moment μ B.M.
Sc^{3+}	$3d^0$	0	0
Ti^{3+}, V^{4+}	$3d^1$	1	1.75
Ti^{2+}, V^{3+}	$3d^2$	2	2.86
V^{2+}, Cr^{3+}	$3d^3$	3	3.86
Cr^{3+}, Mn^{3+}	$3d^4$	4	4.80
Mn^{2+}, Fe^{3+}	$3d^5$	5	5.95
Fe^{2+}, Co^{3+}	$3d^6$	4	5.0 – 5.5
Co^{2+}	$3d^7$	3	4.0 – 5.2
Ni^{2+}	$3d^8$	2	2.9 – 3.4
Cu^{2+}	$3d^9$	1	1.4 – 2.2
Zn^{2+}	$3d^{10}$	0	0

(h) Formation of Coloured Compounds :

The transition metal ions have unpaired d-electrons, which on absorbing visible light can jump from one d-orbital to another i.e. intra d-d- transition take place. Thus when light falls certain visible wavelengths are absorbed. The reflected light appears coloured and gives the colour of compound. The ions having no d-d transitions are colourless.

A - Factors affecting the colour of complex.

The colour of a transition metal complex depend on-

- (i) The magnitude of energy difference between the two d- levels (Δ_0),
- (ii) An increase in the magnitude of Δ_0 decreases the wave length (λ) of the light absorbed by the complexes.
- (iii) Thus with a decrease in the λ the colour of complex changes from Red \longrightarrow Violet.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Oxidation Potential value (v) for $M \rightarrow M^{2+} + 2e^-$	-	1.60	1.20	0.91	1.18	0.44	0.28	0.25	0.34	0.76
$M \rightarrow M^{3+} + 3e^-$	2.10	-	-	0.74	-	-	-	-	-	-

(i) Formation of interstitial compounds

- (i) Small non metallic atom such as H, B, C, N etc. are able to occupy interstitial space of the lattice of the d-block elements to form combinations which are termed interstitial compounds.
- (ii) These are non-stoichiometric in nature and do not follow the common rule of valency.
- (iii) These interstitial compounds have similar chemical properties as the parent metal but differ appreciably in their physical properties such as density, hardness and conductivity.

(j) Catalytic properties

Many transition metals & their compounds have catalytic properties. Some common examples are-

- (a) In some cases the transition metals with their variable valency may form unstable intermediate compounds.
- (b) In other cases the transition metal provide a suitable reaction surface.
- (c) Enzymes are catalyst that enhance the rate of specific reactions. Some enzymes require the presence of metal ions as cofactors and these are called metalloenzymes.
 - (i) $TiCl_3$ - Used as Ziegler - Natta catalyst in the production of polyethene.
 - (ii) V_2O_5 - Convert SO_2 to SO_3 in the contact process for making H_2SO_4 .
 - (iii) MnO_2 - Used as a catalyst to decompose $KClO_3$ to give O_2 .
 - (iv) Fe - promoted iron is used in Haber- Bosch process for making NH_3 .
 - (v) $FeCl_3$ - Used for making CCl_4 from CS_2 & Cl_2 .
 - (vi) $FeSO_4$ & H_2O_2 - Used as Fenton's reagent for oxidizing alcohol to aldehyde.
 - (vii) Pt.- used as a catalyst in the manufacture of H_2SO_4 .
 - (viii) Ni - used as a catalyst in the hydrogenation of oils.
 - (ix) $PdCl_2$ - Wacker process for converting $C_2H_4 + H_2O + PdCl_2$ to $CH_3CHO + 2HCl + Pd$.
 - (x) Pt/ PtO- Adams catalyst, used for reduction.

(k) Alloy formation

- (i) Transition metals form a large number of alloys.
- (ii) d- block elements are quite similar in atomic size, the atom of one metal can substitute the atoms of other metal in its crystal lattices.
- (iii) Thus, on cooling a mixture solution of two or more transition metals, smooth solid, alloys are formed.
- (iv) Alloy containing mercury as one of the constituent elements are called amalgams.
- (v) The purpose of making alloy is to develop some useful properties which are absent in constituent element

COMPOUNDS OF TRANSITION ELEMENTS

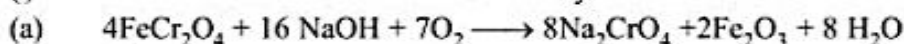
(I) Potassium Dichromate ($K_2Cr_2O_7$)

(a) Preparation :

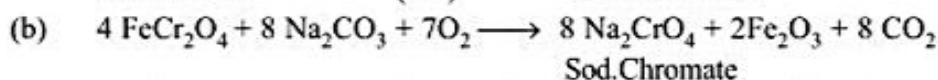
- (i) It is prepared from Chromite ore ($FeCr_2O_4$).
- (ii) The preparation of $K_2Cr_2O_7$ from chromite ore involve the following steps :

(A) Conversion of Chromite ore to Sodium Chromate :

- (i) The Chromite ore is fused with Sodium hydroxide or Sodium Carbonate in the presence of air.



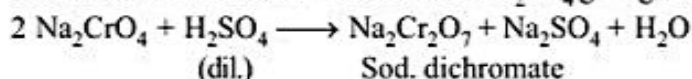
Chromite ore (Air) Sod. Chromate



Sod. Chromite is extracted with water & ferric oxide is left behind.

(B) Conversion of Sodium chromate to Sodium dichromate :

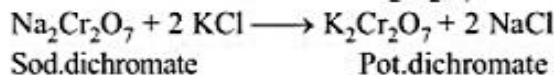
- (i) The Sod. chromite is acidified with dilute H_2SO_4 giving its dichromate



- (ii) On concentration, the less soluble sulphate crystallises and is filtered out. The resulting solution contains Sod. dichromate.

(C) Conversion of Sod. dichromate to Pot. dichromate :

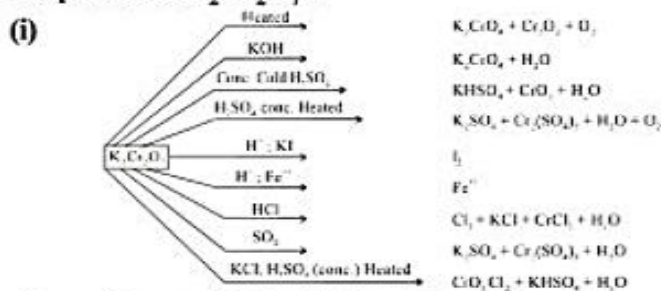
- (i) Hot concentrated solution of $Na_2Cr_2O_7$ with KCl in equimolar proportion



Properties :

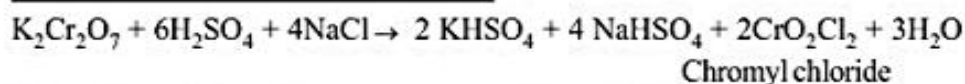
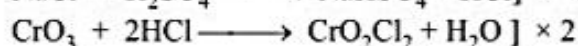
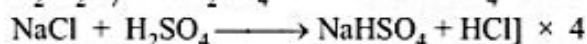
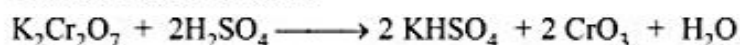
It is orange- red crystalline compound having melting point 670 K.

Properties of $K_2Cr_2O_7$:

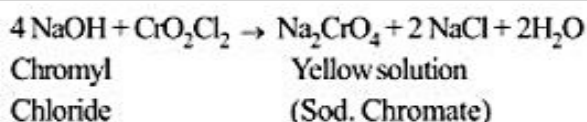
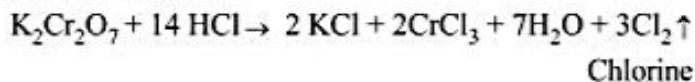


(ii) Chromyl Chloride Test :

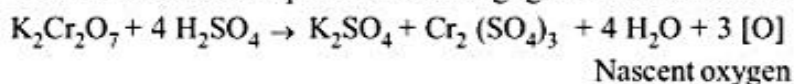
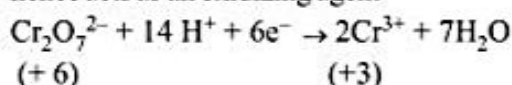
- (a) This is the test of Chloride



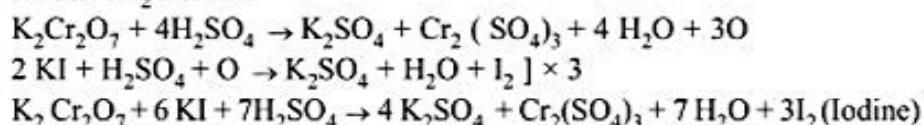
- (b) When Chromyl Chloride vapours are passed through NaOH solution, yellow coloured solution is obtained.

(iii) **Action with HCl :**(iv) **Oxidising character :**

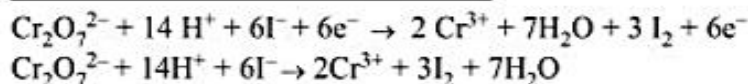
(A) The dichromates act. as powerful oxidizing agent in acidic medium.

(B) In term of electronic concept, the $\text{Cr}_2\text{O}_7^{2-}$ ion take up electron in Acidic medium and hence acts as an oxidizing agent

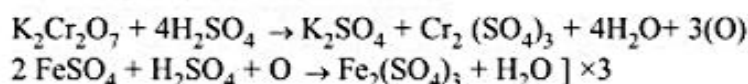
Note : Both $\text{Na}_2\text{Cr}_2\text{O}_7$ & $\text{K}_2\text{Cr}_2\text{O}_7$ are oxidizing agents but $\text{K}_2\text{Cr}_2\text{O}_7$ is preferred since it is not hygroscopic and can be used as primary standard.

(C) Some oxidizing reactions of $\text{K}_2\text{Cr}_2\text{O}_7$ are :(a) It liberate I_2 from KI

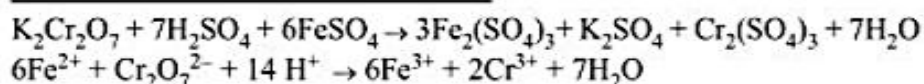
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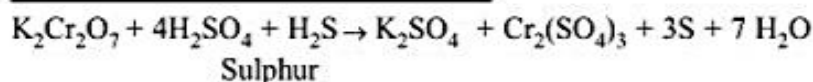
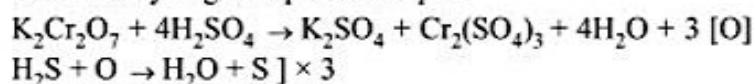
(b) It oxidises ferrous salts to ferric salts.



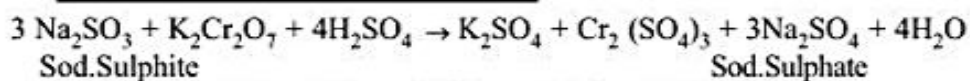
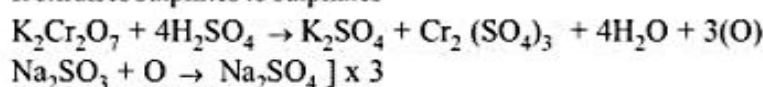
or

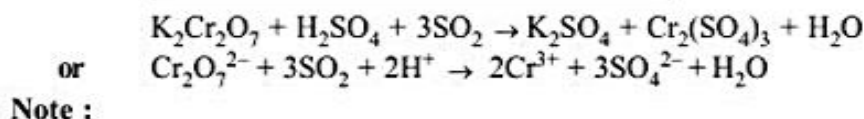
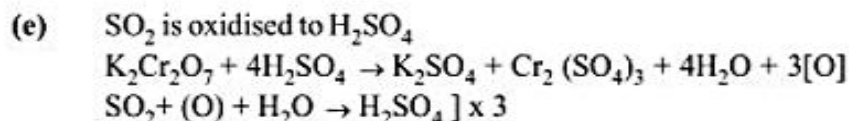


(c) It oxidises hydrogen sulphide to sulphur

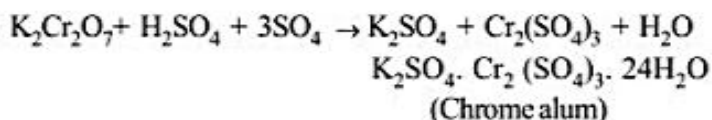
or $\text{H}_2\text{S} + \text{Cr}_2\text{O}_7^{2-} + 8 \text{H}^+ \rightarrow 2 \text{Cr}^{3+} + 3 \text{S} + 7 \text{H}_2\text{O}$

(d) It oxidises sulphites to sulphates

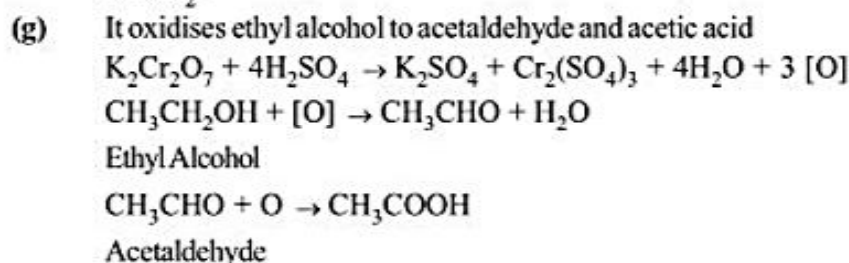
or $3 \text{SO}_3^{2-} + \text{Cr}_2\text{O}_7^{2-} + 8 \text{H}^+ \rightarrow 3 \text{SO}_4^{2-} + 2 \text{Cr}^{3+} + 4 \text{H}_2\text{O}$



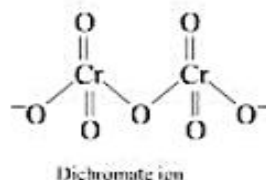
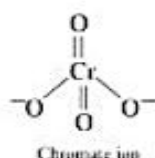
Note :



(f) Similarly, it oxidises, chlorides to chlorine, nitrites to nitrates, arsenites to arsenates thiosulphate to sulphate and sulphur ($\text{S}_2\text{O}_3^{2-} + \text{O} \rightarrow \text{SO}_4^{2-} + \text{S}$), HBr to Br_2 , HI to I_2 .



Structure of Chromate and dichromate ions :



Uses : Potassium dichromate is used :

- As a volumetric reagent in laboratory for the estimation of ferrous ions, iodide ions etc.
- For the preparation of chrome yellow (PbCrO_4), Chrome red ($\text{PbCrO}_4 \cdot \text{PbO}$), Zinc yellow (ZnCrO_4), Guignets green ($\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$), chromic acid (CrO_3 - orange), $\text{K}_3[\text{CrO}_8]$ (Red brown).
- In organic chemistry as oxidising agents.
- In photography for hardening gelatine films.

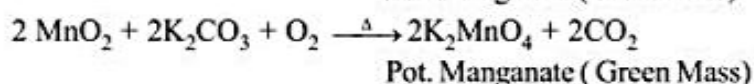
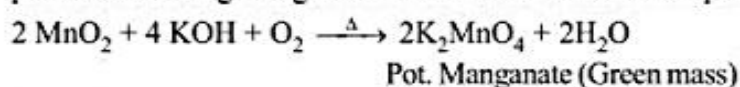
2. Potassium Permanganate (KMnO_4) :

Preparation : Potassium Permanganate is prepared from mineral pyrolusite (MnO_2).

The preparation involves the following steps.

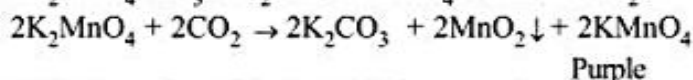
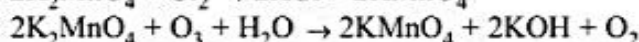
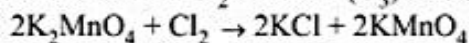
(A) Conversion of Pyrolusite ore to Potassium Manganate

- (a) The pyrolusite (MnO_2) is fused with caustic potash (KOH) or potassium carbonate in presence of air to give a green mass due to the formation of potassium manganate.

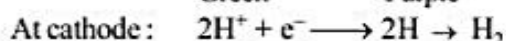
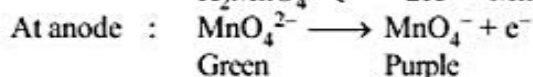
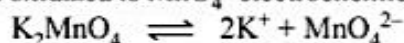


(B) Oxidation of Potassium Manganate to Potassium permanganate :

- (a) The fused mass is extracted with water and the solution is green (MnO_4^{2-}). The solution is treated with Cl_2 or ozone (O_3) or CO_2 to oxidize K_2MnO_4 to KMnO_4 .



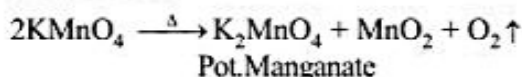
- (b) MnO_4^{2-} can be oxidized to MnO_4^- electrochemically at anode.

**Properties :**

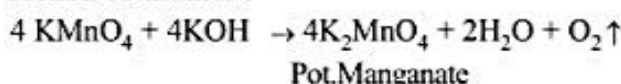
- (A) It is a dark violet crystalline solid having a metallic lustre. It has M.P. 523 K.

- (B) It is fairly soluble in water giving a purple solution.

- (C) Action of heat

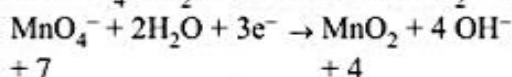


- (D) Action of alkalis :

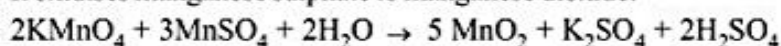


- (E) **Oxidising character :** Potassium permanganate act as an oxidizing agent in neutral, alkaline and acidic solutions.

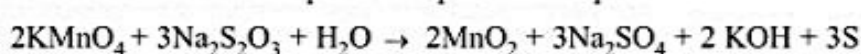
- (a) **In Neutral Medium :** MnO_2 is formed

**Important reactions of Neutral KMnO_4** 

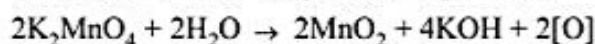
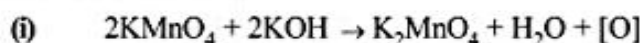
- (ii) It oxidises manganese sulphate to manganese dioxide.



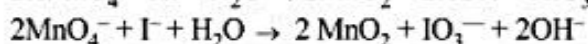
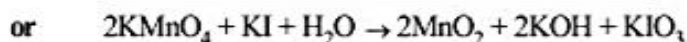
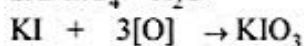
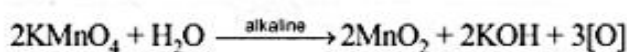
- (iii) It oxidises sodium thiosulphate to sulphate and Sulphur



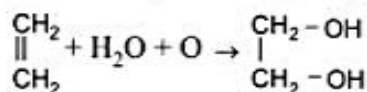
- (b) **Alkaline medium :**

**Important reactions of alkaline KMnO_4 :**

- (i) It oxidises iodides to iodates in alkaline medium

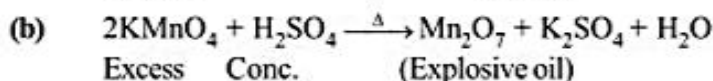
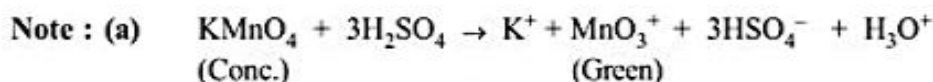


- (ii) Oxidises ethylene to ethylene glycol :

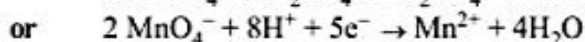
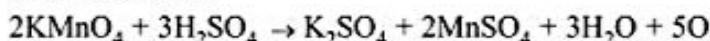


Ethylene Glycol

In alkaline medium it is called **Bayer's Reagent**

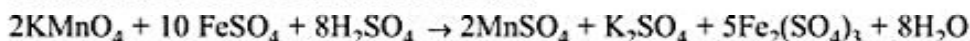


- (c) **Acidic solution :**

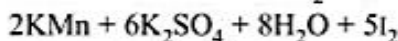


Some of the important reactions of acidified KMnO_4 are

- (i) It oxidises acidified ferrous salt to ferric salts.



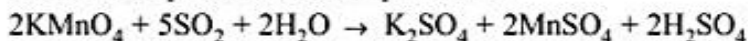
- (ii) It oxidises acidified KI to I_2



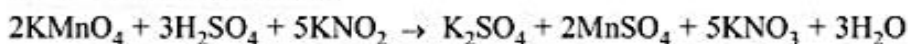
- (iii) It oxidises H_2S to Sulphur



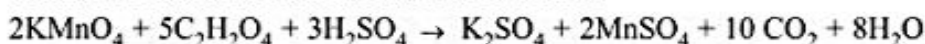
- (iv) It oxidises sulphur dioxide to sulphuric acid



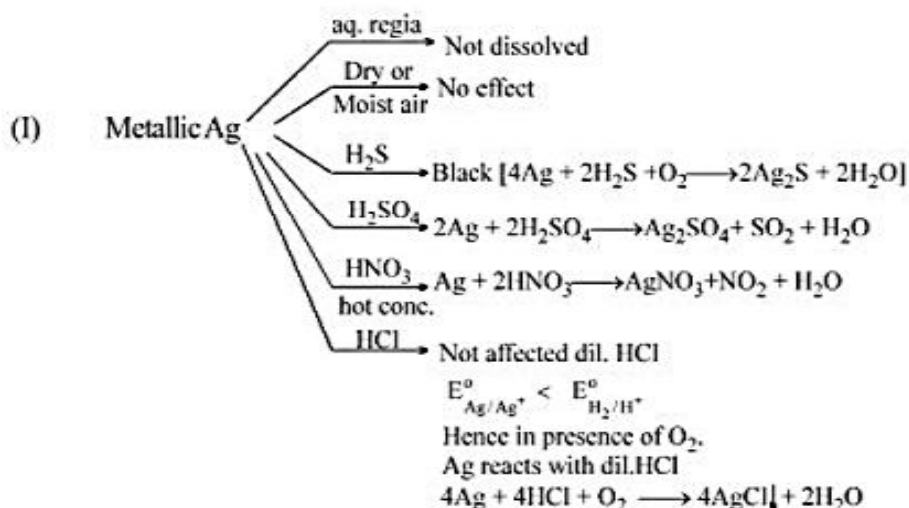
- (v) It oxidises nitrites to nitrates



- (vi) It oxidises oxalates or oxalic acid to carbon dioxide



COMPOUNDS OF SILVER



In the same way in presence of O_2 , Ag complexes with NaCN / KCN.
 $4Ag + 8KCN + 2H_2O + O_2 \longrightarrow 4K[Ag(CN)_2] + 4KOH$

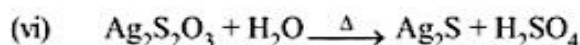
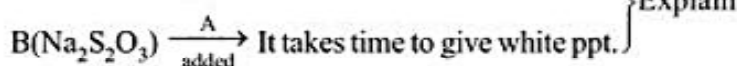
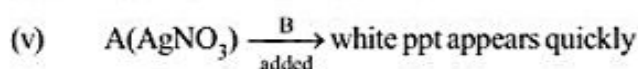
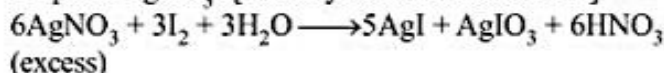
$AgNO_3$

Prepⁿ.: already done.

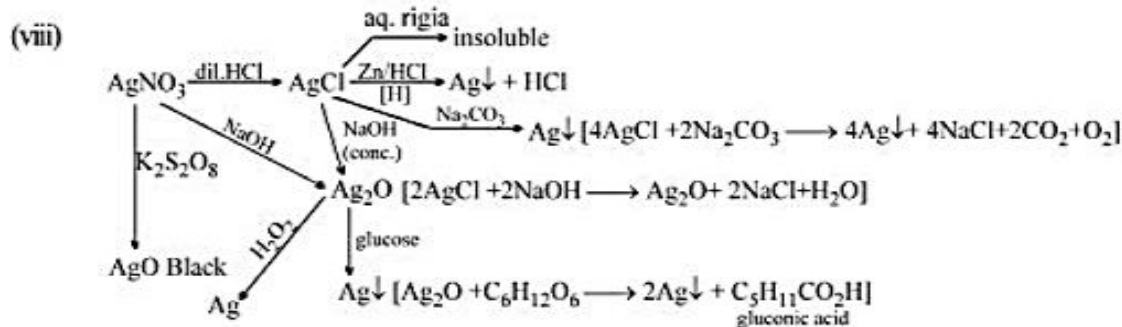
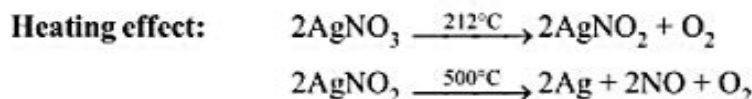
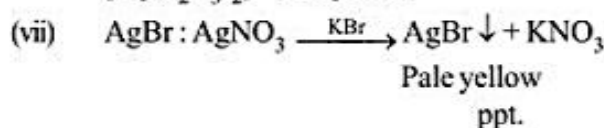
Properties.: (i) It is called as lunar caustic because in contact with skin it produces burning sensation like that of caustic soda with the formation of finely divided silver (black colour)

(ii) Thermal decomposition:

(iii) Props. of $AgNO_3$: [Already done in basic radical]

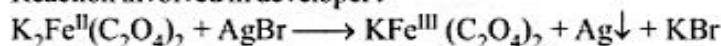


$AgCl$, $AgBr$, AgI (but not Ag_2S) are soluble in $Na_2S_2O_3$ forming $[Ag(S_2O_3)_2]^{-3}$ complexes



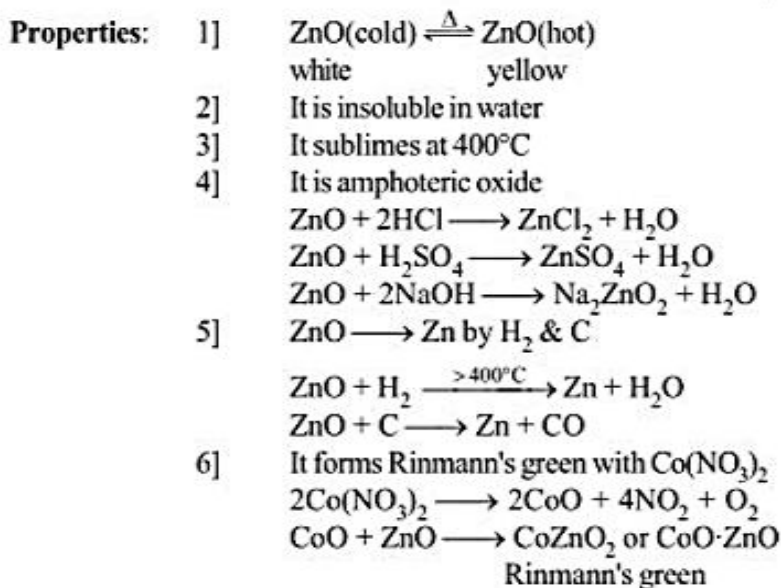
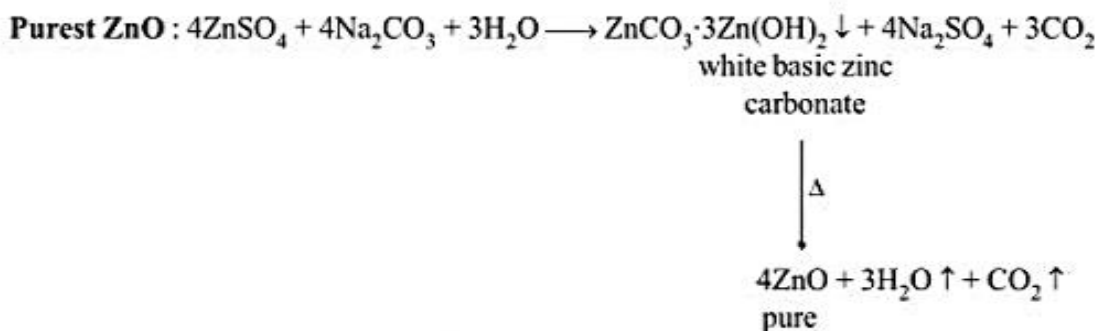
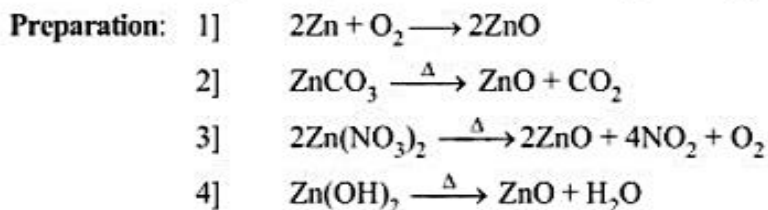
* AgO supposed to be paramagnetic due to d^9 configuration. But actually it is diamagnetic and exists as $Ag^I [Ag^{III}O_2]$

* Reaction involved in developer :



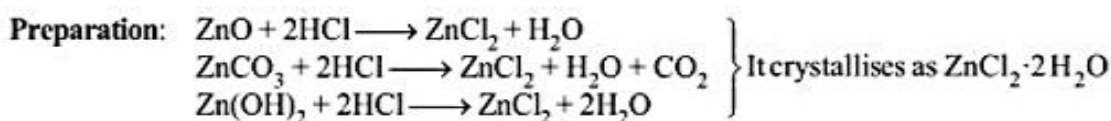
COMPOUNDS OF ZINC

ZnO: It is called as phillospher's wool due to its wooly flock type appearance

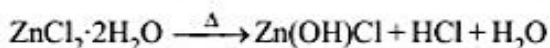


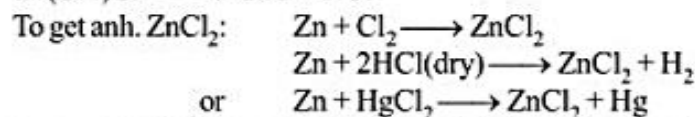
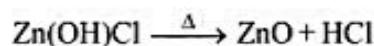
- Uses:**
- (1) As white pigment. It is superior than white lead because it does not turn into black
 - (2) Rinmann's green is used as green pigment
 - (3) It is used as zinc ointment in medicine

ZnCl₂



Anh. ZnCl_2 cannot be made by heating $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ because



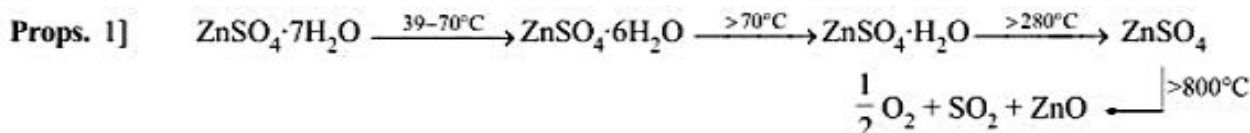
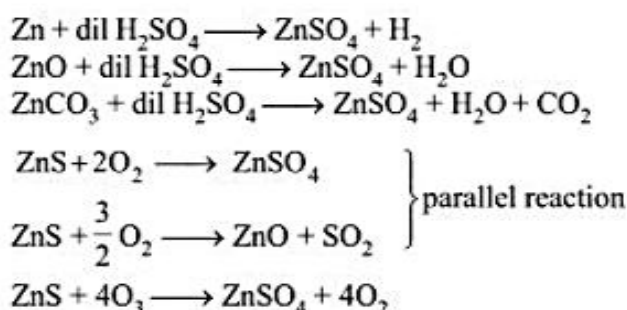


- Properties:**
- (i) It is deliquescent white solid (when anhydrous)
 - (ii) $\text{ZnCl}_2 + \text{H}_2\text{S} \longrightarrow \text{ZnS}$
 - " $+ \text{NaOH} \longrightarrow \text{Zn(OH)}_2 \xrightarrow{\text{excess}} \text{Na}_2[\text{Zn(OH)}_4]$
 - " $+ \text{NH}_4\text{OH} \longrightarrow \text{Zn(OH)}_2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

- Uses:**
- 1] Used for impregnating timber to prevent destruction by insects
 - 2] As dehydrating agent when anhydrous
 - 3] $\text{ZnO} \cdot \text{ZnCl}_2$ used in dental filling

ZnSO_4 :

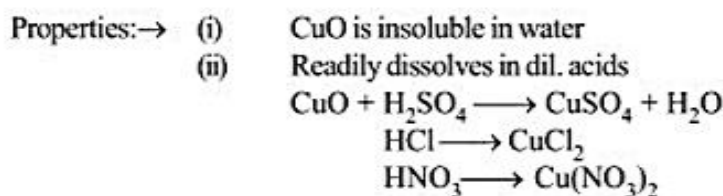
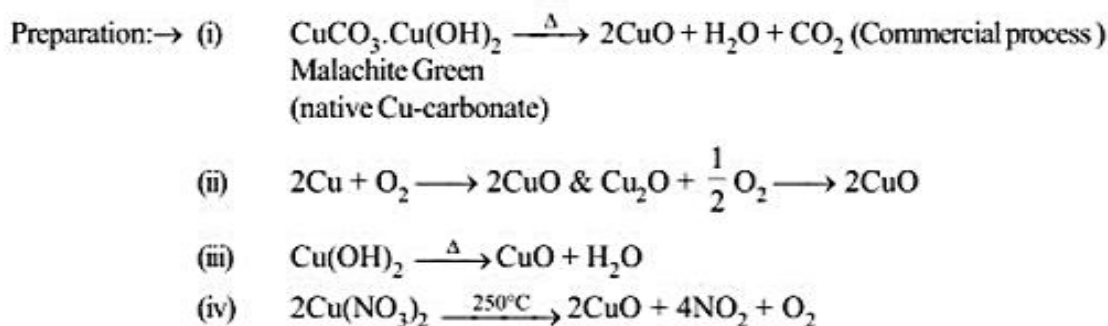
Preparation: \rightarrow



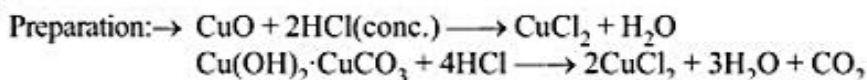
- Uses:**
- 1] in eye lotion
 - 2] Lithophone making ($\text{ZnS} + \text{BaSO}_4$) as white pigment

COMPOUNDS OF COPPER

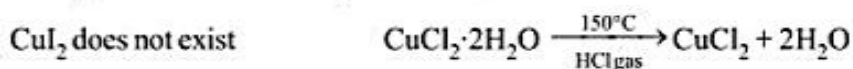
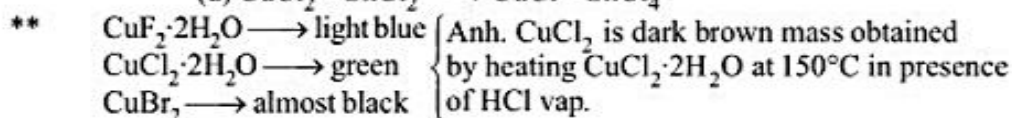
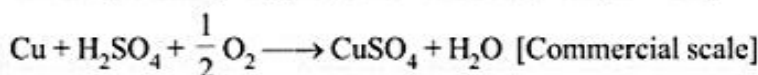
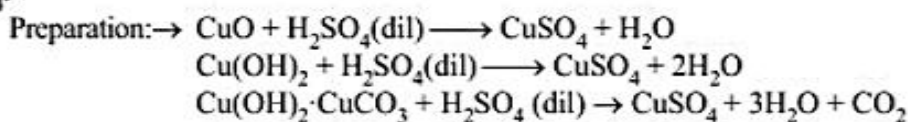
CuO :



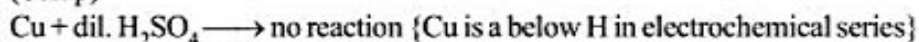
- (iii) It decomposes when, heated above 1100°C
 $4\text{CuO} \longrightarrow 2\text{Cu}_2\text{O} + \text{O}_2$
- (iv) CuO is reduced to Cu by H_2 or C under hot condition
 $\text{CuO} + \text{C} \longrightarrow \text{Cu} + \text{CO} \uparrow$
 $\text{CuO} + \text{H}_2 \longrightarrow \text{Cu} + \text{H}_2\text{O} \uparrow$

 CuCl_2 :

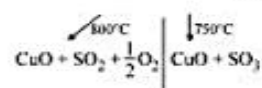
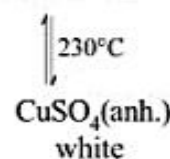
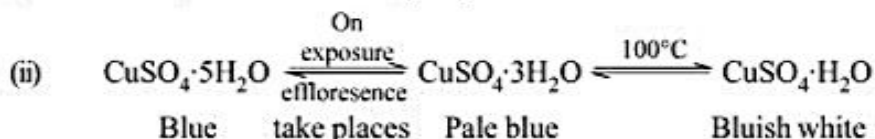
- Properties: \rightarrow
- (i) It is crystallised as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ of Emerald green colour
 - (ii) dil. solution in water is blue in colour due to formation of $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ complex.
 - (iii) conc. HCl or KCl added to dil. solution of CuCl_2 the colour changes into yellow, owing to the formation of $[\text{CuCl}_4]^{2-}$
 - (iv) The conc. aq. solution is green in colour having the two complex ions in equilibrium $2[\text{Cu}(\text{H}_2\text{O})_4]\text{Cl}_2 \rightleftharpoons [\text{Cu}(\text{H}_2\text{O})_4]^{2+} + [\text{CuCl}_4]^{2-} + 4\text{H}_2\text{O}$
 - (v) $\text{CuCl}_2 \longrightarrow \text{CuCl}$ by no. of reagents
 - (a) $\text{CuCl}_2 + \text{Cu-turnings} \xrightarrow{\Delta} 2\text{CuCl}$
 - (b) $2\text{CuCl}_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \longrightarrow 2\text{CuCl} + 2\text{HCl} + 2\text{H}_2\text{SO}_4$
 - (c) $2\text{CuCl}_2 + \text{Zn}/\text{HCl} \longrightarrow 2\text{CuCl} + \text{ZnCl}_2$
 - (d) $\text{CuCl}_2 + \text{SnCl}_2 \longrightarrow \text{CuCl} + \text{SnCl}_4$

 **CuSO_4 :**

(Scrap)



- Properties: \rightarrow (i) It is crystallised as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$



- (iii) Revision with all others reagent

COMPOUNDS OF IRON

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

- Preparation:→ (i) $\text{Scrap Fe} + \text{H}_2\text{SO}_4 \longrightarrow \text{FeSO}_4 + \text{H}_2\uparrow$
(dil.)
- (ii) From Kipp's waste
 $\text{FeS} + \text{H}_2\text{SO}_4(\text{dil}) \longrightarrow \text{FeSO}_4 + \text{H}_2\text{S}\uparrow$
- (iii) $\text{FeS}_2 + 2\text{H}_2\text{O} + \frac{7}{2}\text{O}_2 \longrightarrow \text{FeSO}_4 + \text{H}_2\text{SO}_4$
- Properties:→ (i) It undergoes aerial oxidation forming basic ferric sulphate
 $4\text{FeSO}_4 + \text{H}_2\text{O} + \text{O}_2 \longrightarrow 4\text{Fe}(\text{OH})\text{SO}_4$
- (ii) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{300^\circ\text{C}} \text{FeSO}_4 \xrightarrow[\text{temp.}]{\text{high}} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$
anh. white
- (iii) Aq. solution is acidic due to hydrolysis
 $\text{FeSO}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2 + \text{H}_2\text{SO}_4$
weak base
- (iv) It is a reducing agent
(a) $\text{Fe}^{2+} + \text{MnO}_4^- + \text{H}^+ \longrightarrow \text{Fe}^{3+} + \text{Mn}^{2+} + \text{H}_2\text{O}$
(b) $\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + \text{H}^+ \longrightarrow \text{Fe}^{3+} + \text{Cr}^{3+} + \text{H}_2\text{O}$
(c) $\text{Au}^{3+} + \text{Fe}^{2+} \longrightarrow \text{Au} + \text{Fe}^{3+}$
(d) $\text{Fe}^{2+} + \text{HgCl}_2 \longrightarrow \text{Hg}_2\text{Cl}_2\downarrow + \text{Fe}^{3+}$
white ppt.
- (v) It forms double salt. Example $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$

FeO (Black):

- Prepⁿ: $\text{FeC}_2\text{O}_4 \xrightarrow[\text{in absence of air}]{\Delta} \text{FeO} + \text{CO} + \text{CO}_2$
- Props:→ It is stable at high temperature and on cooling slowly disproportionates into Fe_3O_4 and iron
 $4\text{FeO} \longrightarrow \text{Fe}_3\text{O}_4 + \text{Fe}$

FeCl_2 :

- Prepⁿ: $\text{Fe} + 2\text{HCl} \xrightarrow[\text{a current of HCl}]{\text{heated in}} \text{FeCl}_2 + \text{H}_2$
OR
 $2\text{FeCl}_3 + \text{H}_2 \xrightarrow{\Delta} 2\text{FeCl}_2 + 2\text{HCl}$
- Props:→ (i) It is deliquescent in air like FeCl_3
- (ii) It is soluble in water, alcohol and ether also because it is sufficiently covalent in nature
- (iii) It volatilises at about 1000°C and vapour density indicates the presence of Fe_2Cl_4 . Above 1300°C density becomes normal
- (iv) It oxidises on heating in air
 $12\text{FeCl}_2 + 3\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3 + 8\text{FeCl}_3$
- (v) H_2 evolves on heating in steam
 $3\text{FeCl}_2 + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$
- (vi) It can exist as different hydrated form
 $\text{FeCl}_2 \cdot 2\text{H}_2\text{O} \longrightarrow \text{colourless}$
 $\text{FeCl}_2 \cdot 4\text{H}_2\text{O} \longrightarrow \text{pale green}$
 $\text{FeCl}_2 \cdot 6\text{H}_2\text{O} \longrightarrow \text{green}$

FeCl_3 :	Prep ⁿ :	Anhydrous ferric chloride is prepared by heating metallic iron in a stream of dry chlorine gas.
	(i)	FeCl_3 solid is almost black. It sublimes at about 300°C , giving a dimeric gas.
	(ii)	FeCl_3 dissolves in both ether and water, giving solvated monomeric species.
	(iii)	Iron (III) chloride is usually obtained as yellow-brown lumps of the hydrate $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.
	(iv)	This is very soluble in water and is used both as an oxidizing agent, and as a mordant in dyeing.
	(v)	FeCl_3 is also used in the manufacture of CCl_4 .

Illustration

Q.1 The ions of d-block elements are mostly paramagnetic-

- (A) Because their d-orbitals are complete
- (B) Because they have mostly paired electrons
- (C) Because they have mostly unpaired electrons
- (D) Because they form coloured ions.

Ans. [C]

Sol. All atomic and molecular species which contains one or more unpaired electrons are paramagnetic. Most of the ions of transition elements have unpaired electrons. Hence they are all paramagnetic. Some ions of d-block elements with no unpaired electrons are Sc^{+3} , Ti^{+4} , Zn^{+2} and Cu^{+1} . These ions are not paramagnetic and they are also without colour.

Q.2 Silver jewelry can be made to retain its silvery white appearance by-

- (A) Coating the silver with a film of oxide by dipping the silver in conc. HNO_3
- (B) Coating with a film of the insoluble chloride by dipping the silver in conc. HNO_3
- (C) Plating with Palladium
- (D) Plating with gold

Ans. [C]

Sol. Silver jewelry easily gets blackened when exposed to sulphur compounds. In order to prevent this blackening of silver jewelry, it is coated with Pd.

Q.3 The order of stability of complexes of ion Cu^{+2} , Ni^{+2} , Mn^{+2} and Fe^{+2} decreases in the order-

- (A) $\text{Cu}^{+2} > \text{Ni}^{+2} > \text{Fe}^{+2} > \text{Mn}^{+2}$
- (B) $\text{Mn}^{+2} > \text{Ni}^{+2} > \text{Cu}^{+2} > \text{Fe}^{+2}$
- (C) $\text{Ni}^{+2} > \text{Cu}^{+2} > \text{Fe}^{+2} > \text{Mn}^{+2}$
- (D) $\text{Fe}^{+2} > \text{Ni}^{+2} > \text{Cu}^{+2} > \text{Mn}^{+2}$

Ans. [A]

Sol. The order of stability of the complexes of some of the ions carrying the same charge but differing in ionic radii decrease as the ionic radii increase.

ion	Cu^{+2} ,	Ni^{+2} ,	Fe^{+2} ,	Mn^{+2}
Ionic radii	0.69	0.78	0.83	0.91

The complexes of Cu^{+2} are most stable while Mn^{+2} is least stable.

- Q.4** The elements which exhibit both vertical and horizontal similarities are –
(A) Inert gas elements (B) Representative elements
(C) Rare elements (D) Transition elements

Ans. [D]

Sol. It is a characteristic of transition elements. Vertical relationship is due to similar electronic configuration in a gp and horizontal relationship due to shielding effect being more predominant in last five elements in a period.

Exercise

- Q.1** Transition metals and their oxides are used in industrial processes as –
(A) Detergents (B) Insecticides (C) Catalysts (D) None

Ans. [C]

- Q.2** A blue solution of copper sulphate becomes darker when treated with excess of ammonia. This is because –
(A) ammonia molecules replace water molecules in the solution
(B) ammonia is stronger ligand than water
(C) ammonia forms a stable complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$ with Cu^{2+} ions
(D) All are correct

Ans. [D]

- Q.3** A metal gives two chlorides 'A' and 'B'. 'A' gives black precipitate with NH_4OH and 'B' gives white. With KI 'B' gives a red precipitate, soluble in excess of KI. 'A' and 'B' are respectively –
(A) HgCl_2 and Hg_2Cl_2 (B) Hg_2Cl_2 and HgCl_2 (C) HgCl_2 and HgCl (D) None of these

Ans. [B]

f-Block Elements

They were earlier called as rare earth metals as it was believed that they exist in earth's crust to a very less extent for e.g. : Pm, does not exist in the earth's crust. But this terminology is now not applicable as they exist in earth's crust to a sufficient extent.

(A) 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**.

(a) Position in the periodic table

The lanthanides resemble yttrium in most of their properties. So it became necessary to accommodate 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.

Lanthanide series	(Z = 58 - 71)	(Ce - Lu)
Actinide series	(Z = 90 - 103)	(Th - Lw)

(b) Lanthanides (4f - block elements)

Lanthanides are reactive elements so do not found in free state in nature. Most important minerals for lighter Lanthanides are - Monazite, cerites and orthite and for heavier lanthanides - Gadolinite and Xenotime

(c) Electronic configuration

The general configuration of lanthanides may be given as $4f^{2-14}5s^25p^65d^{0/1}6s^2$. Lanthanides have outer three shells incomplete.

Some properties of Lanthanoids

Element (pm)	Symbol	Atomic number	Outer configuration	Oxidation states	M ³⁺ radius
Lanthanum	La	57	[Xe] 5d ¹ , 6s ²	+3	106
Cerium	Ce	58	[Xe] 4f ² , 6s ²	+3, +4	103
Praseodymium	Pr	59	[Xe] 4f ³ , 6s ²	+3, +4	101
Neodymium	Nd	60	[Xe] 4f ⁴ , 6s ²	+2, +3, +4	100
Promethium	Pm	61	[Xe] 4f ⁵ , 6s ²	+3	98
Samarium	Sm	62	[Xe] 4f ⁶ , 6s ²	+2, +3	96
Europium	Eu	63	[Xe] 4f ⁷ , 6s ²	+2, +3	95
Gadolinium	Gd	64	[Xe] 4f ⁷ , 5d ¹ , 6s ²	+3	94
Terbium	Tb	65	[Xe] 4f ⁹ , 6s ²	+3, +4	92
Dysprosium	Dy	66	[Xe] 4f ¹⁰ , 6s ²	+3, +4	91
Holmium	Ho	67	[Xe] 4f ¹¹ , 6s ²	+3	89
Erbium	Er	68	[Xe] 4f ¹² , 6s ²	+3	88
Thulium	Tm	69	[Xe] 4f ¹³ , 6s ²	+2, +3	87
Ytterbium	Yb	70	[Xe] 4f ¹⁴ , 6s ²	+2, +3	86
Lutetium	Lu	71	[Xe] 4f ¹⁴ , 5d ¹ , 6s ²	+3	85

- (i) It is to be noted here 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 $4f^7 5d^1 6s^2$ (and not $4f^8 6s^2$). 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.
- (ii) On the other hand, the filling of f orbitals is regular in tripositive ions.
- (iii) After losing outer electrons, the f orbitals shrink in size and became more stable. Pm is the only synthetic radioactive lanthanide.

(d) Oxidation states

Lanthanides	Ce ₅₈	Pr ₅₉	Nd ₆₀	Pm ₆₁	Sm ₆₂	Eu ₆₃	Gd ₆₄	Tb ₆₅	Dy ₆₆	Ho ₆₇	Er ₆₈	Tm ₆₉	Yb ₇₀	Lu ₇₁
Oxidation	+3	+3	+3	+3	(+2)	+2	+3	+3	+3	+3	(+2)	(+2)	+2	+3
States	+4	(+4)			+3	+3		+4	(+4)		+3	+3	+3	

- (i) Oxidation states in brackets are unstable states
- (ii) The lanthanides contains two s electrons in the outermost shell, they are therefore expected to exhibit a characteristic oxidation state of +2. But for the lanthanides, the +3 oxidation is common.
- (iii) This corresponds to the use of two outermost electrons ($6s^2$) alongwith one inner electron. The inner electron used is a 5d electron (in La, Gd and Lu), or one of the 4f electron if no 5d electrons present.
- (iv) All the lanthanides attains +3 oxidation state and only cerium, Praseodymium, and terbium exhibit higher oxidation state (+4).

Oxidation states + 2 and +4 occur particularly when they lead to

- (i) A noble gas configuration e.g. Ce^{4+} (f^0)
- (ii) A half filled 'f' orbital e.g. Eu^{2+} , Tb^{4+} , (f^7)
- (iii) A completely filled 'f' orbital e.g. Yb^{2+} (f^{14})

Therefore, in higher oxidation state, they act as oxidising while in lower state as reducing agents.

(e) Magnetic properties

In tripositive lanthanide ions the number of unpaired electrons regularly increases from lanthanum to Gadolinium (0 to 7) and then continuously decreases upto lutecium (7 to 0). So lanthanum and lutecium ions which are diamagnetic, all other tripositive lanthanide ions are Paramagnetic.

Colour - The lanthanide ions have unpaired electrons in their 4f orbitals. Thus these ions absorb visible region of light and undergo f-f transition and hence exhibit colour. The colour exhibited depends on the number of unpaired electrons in the 4f orbitals. The ions often with $4f^n$ configuration have similar colour to those ions having $4f^{14-n}$ configuration.

Lanthanide ions having $4f^0$, $4f^7$, $4f^{14}$ are colourless. Lanthanide ions $4f^1$ and $4d^{13}$ are also colourless.

(f) Other Properties :

- (a) Highly dense metals with high m.pt. (do not show any regular trend).
- (b) **Ionisation Energies** - Lanthanides have fairly low ionisation energies comparable to alkaline earth metals.
- (c) **Electro positive Character** - High due to low I.P.
- (d) **Complex formation** - Do not have much tendency to form complexes due to low charge density because of their large size.
- Lu^{+3} is smallest in size can only form complex.

- (e) **Reducing Agent** - They readily lose electrons so are good reducing agent.
- (i) In +3 oxidation states, nitrates, perchlorates and sulphates of lanthanides and actinides are water soluble, while their hydroxides, fluorides and carbonates are water insoluble.
 - (ii) Alloys of lanthanides with Fe are called misch metals.
 - (iii) $\text{La}(\text{OH})_3$ is most basic in nature while $\text{Lu}(\text{OH})_3$ least basic.
 - (iv) Lanthanides form MC_2 type carbide with carbon, which on hydrolysis gives C_2H_2 .

(B) LANTHANIDE CONTRACTION

- (i) In the lanthanide series with increasing atomic number, there is a progressive decrease in the size from lanthanum to lutetium or from La^{+3} to Lu^{+3} . This contraction in size is known as lanthanide contraction.
- (ii) The general electronic configuration of these elements is $4f^{0-14}5s^2p^6d^{0-1}6s^2$. In these elements the added electron enters the deep seated f-orbitals and therefore experiences considerable pull by the nucleus.
- (iii) Such an electron cannot add to the size of the element and also because the intervening $5s^2p^6d^1$ electronic shells, it is 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.
- (iv) The atomic volumes of europium and ytterbium are unexceptedly large. The large atomic size of Eu and Yb suggest weaker bonding in the solid elements. Both these elements have only two electrons extra than the stable configurations (half filled, f^7 , and completely filled, f^{14}), hence they utilise two electrons in metallic bonding as in the case with barium.

(C) EFFECTS OF LANTHANIDE CONTRACTION

- (i) **Close resemblace of Lanthanides :-** The general decrease in the sizes of the lanthanides with an increase in their nuclear charges result in a small increase in their ionisation energies. Hence their basic and ionic nature gradually decreases from La to Lu. This also explains the variations in properties such as increased tendency for hydrolysis and formation of complex salts and decreased thermal stability. solubility of their salts.
- (ii) **Similarity of yttrium with lanthanides :-** The properties of yttrium are so similar to the lanthanides that it is considered more a member of the lanthanide series than a congener of scandium.
- (iii) **Anomalous behaviour of post-lanthanides :-** The following anomalies may be observed in the behaviour of post-lanthanide elements.
 - (a) **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^{+4} , instead of increasing (because of inclusion of one more electronic shell). decreases (or is virtually equal to Zr^{+4}) as a consequence of the lanthanide 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.
 - (b) **Ionisation potential and electronegativity :-** The effect of lanthanide contraction is also seen in the increase in the ionisation potential values and electronegativities of the elements of the third transition series, contrary to the general trend.

Because of the lanthanide contraction, the post-lanthanide elements have stronger positive field and thus the electrons are held more tightly.

The greater effective nuclear charge of the former make them more electronegative than the latter.

(c) **High density** :- Because of lanthanide contraction the atomic sizes of the post lanthanide elements become very small. consequently, the packing of atoms in their metallic crystals become so much compact that their densities are very high.

The densities of the third transition series elements are almost double to those of the second series elements.

(D) APPLICATION OF LANTHANIDES

Cerium is most useful element in the lanthanides

- Ceramic application - CeO_2 , La_2O_3 , Nd_2O_3 and Pr_2P_3 are used as decolourizing agents for glasses.
- CeS (m.p. - 2000°C) is used in the manufacture of a special type of crucibles and refractories.
- Lanthanide compounds like cerium molybdate, cerium tungstate are used as paints and dyes.
- In textile and leather industries (Ce salts).

(E) ACTINIDES (5f - BLOCK ELEMENTS)

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

(a) **Electronic configuration** :-

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

Some properties of actinoids				
Element	Symbol	Atomic number	Configuration	Oxidation states
Actinium	Ac	89	$[\text{Rn}] 6d^1, 7s^2$	+3
Thorium	Th	90	$[\text{Rn}] 6d^2, 7s^2$	+3, +4
Protactinium	Pa	91	$[\text{Rn}] 5f^2, 6d^1, 7s^2$	+3, +4, +5
Uranium	U	92	$[\text{Rn}] 5f^3, 6d^1, 7s^2$	+3, +4, +5, +6
Neptunium	Np	93	$[\text{Rn}] 5f^4, 6d^1, 7s^2$	+3, +4, +5, +6, +7
Plutonium	Pu	94	$[\text{Rn}] 5f^6, 7s^2$	+3, +4, +5, +6, +7
Americium	Am	95	$[\text{Rn}] 5f^7, 7s^2$	+2, +3, +4, +5, +6
Curium	Cm	96	$[\text{Rn}] 5f^7, 6d^1, 7s^2$	+3, +4
Berkelium	Bk	97	$[\text{Rn}] 5f^8, 6d^1, 7s^2$	+3, +4
Californium	Cf	98	$[\text{Rn}] 5f^{10}, 7s^2$	+2, +3
Einsteinium	Es	99	$[\text{Rn}] 5f^{11}, 7s^2$	+2, +3
Fermium	Fm	100	$[\text{Rn}] 5f^{12}, 7s^2$	+2, +3
Mendelevium	Md	101	$[\text{Rn}] 5f^{13}, 7s^2$	+2, +3
Nobelium	No	102	$[\text{Rn}] 5f^{14}, 7s^2$	+2, +3
Lawrencium	Lr	103	$[\text{Rn}] 5f^{14}, 6d^1, 7s^2$	+3

SOLVED EXAMPLES

- Q.1** Which of the following statements is correct?
 (A) Iron belongs to third transition series of the periodic table
 (B) Iron belongs to f-block of the periodic table
 (C) Iron belongs to first transition series
 (D) Iron belongs to group VIII of the periodic table

Ans. [C]

Sol. The correct statement is that iron belongs to first transition series of elements. It is called 3d series. The members of this series are

Sc Ti V Cr Mn Fe Co Ni Cu Zn

The electronic config of Fe^{2+} is $3d^6, 4s^2$

- Q.2** Zn and Hg do not show variable valency like d-block elements because-
 (A) They are soft
 (B) Their d-shells are complete
 (C) They have only two electrons in the outermost subshell
 (D) Their d-shells are incomplete

Ans. [B]

Sol. Zn and Hg do not show variable valency like d-block elements because their d-shell are complete their electronic config are

$\text{Zn}^{30} \quad 3d^{10}, 4s^2$

$\text{Hg}^{48} \quad 4d^{10}, 5s^2$

The variable valency is shown by those elements which have got incompletely filled 'd' orbitals

- Q.3** A metal ion from the first transition series has a magnetic moment (calculated) of 2.83 BM. How many unpaired electrons are expected to be present in the ion?

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

Ans. [B]

Sol. A metal ion from the first transition series has a magnetic moment (calculated) of 2.83 BM. The no. of unpaired electrons are expected to be present in the ion are 2

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

$$= 2 \cdot \sqrt{2} = 2 \times 1.414 = 2.828 \text{ B.M} = 2.83 \text{ B.M}$$

- Q.4** Out of the compounds K_2SO_4 , MgCl_2 , FeSO_4 , NiCl_2 and ZnO which of the following pair will show paramagnetism-

(A) K_2SO_4 , MgCl_2 (B) ZnO , MgCl_2 (C) K_2SO_4 , ZnCl_2 (D) FeSO_4 , NiCl_2

Ans. [D]

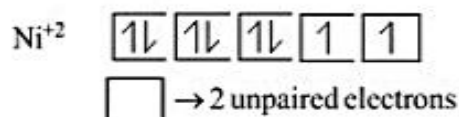
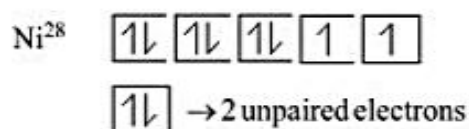
Sol. The pair which shows paramagnetism is FeSO_4 and NiCl_2 . It consist of Fe^{+2} and Ni^{+2} ions which have got unpaired electrons. Their electronic configs. are as given below.

$\text{Fe}^{26} \quad \boxed{1\downarrow} \boxed{1} \boxed{1} \boxed{1} \boxed{1}$

$\boxed{1\downarrow} \rightarrow 4 \text{ unpaired electrons}$

$\text{Fe}^{+2} \quad \boxed{1\downarrow} \boxed{1} \boxed{1} \boxed{1} \boxed{1}$

$\boxed{} \rightarrow 4 \text{ unpaired electrons}$



Q.5 Variable valency is generally shown by-

- (A) s-block elements
(B) p-block elements
(C) Transition elements
(D) All elements in periodic table

Ans. [C]

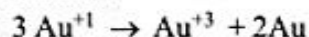
Sol. One of the most striking features of the transition elements, is that they exhibit variable valency. The variable valency occurs to some extent in the p-block elements also. In this case the valency changes usually in units of two. Some example are SnCl_2 , SnCl_4 , PCl_3 , PCl_5 etc. But in transition elements the valency changes in one unit e.g Cu^+ , Cu^{+2} , Fe^{+2} , Fe^{+3} etc.

Q.6 The common oxidation states of gold are-

- (A) 1, 2 and 3 (B) 1, 3 (C) 2 and 3 (D) 3, 4

Ans. [B]

Sol. The common oxidation states of gold are +1 and +3. The +3 state is more stable. This is explained on the basis that +1 ion gets disproportionate.



Q.7 The d-block elements easily form alloys because-

- (A) Their d-block are only partly filled
(B) They have very widely differing atomic sizes.
(C) They are very similar in their atomic sizes
(D) They are highly electronegative in character

Ans. [C]

Sol. In the case of the transition metals the atomic radii have values which are very close, that is they are of very similar size. Hence the atom of an element in a crystal lattice can easily be replaced by a metal atom of another transition elements. This makes metals form alloys very easily.

Q.8 Wilkinson's catalyst used as a homogenous catalyst in the hydrogenation of alkene contains-

- (A) Fe (B) Al (C) Rh (D) Co

Ans. [C]

Sol. Wilkinson's catalyst contains Rh. The formula is $(\text{Ph}_3\text{P})_3\text{RhCl}$. It is used as homogeneous catalyst in the hydrogenation of alkenes.

Q.9 Which of the following is the softest metals-

- (A) Sc (B) Zn (C) Ti (D) V

Ans. [B]

Sol. The softest metal is Zn, while remaining all other metal are comparatively harder metals.

Q.10 In which of the following transition metal ions d-d transition is possible-

- (A) Cu^+ (B) Zn^{+2} (C) Ti^{+3} (D) Sc^{+3}

Ans. [C]

Sol. The d-d transition is possible in Ti^{+3} because it has got $3d^1$ configuration, hence one electron can easily go from one orbital to another in degenerate levels.

Q.11 Which of the following cuprous compounds is not stable-

- (A) CuCl_2 (B) $\text{Cu}_2(\text{CNS})_2$ (C) Cu_2Cl_2 (D) Cu_2SO_4

Ans. [D]

Sol. The compound Cu_2SO_4 is not stable because Cu is stabilized only in Cu^{+2} state in its compounds with SO_4^{-2} ions hence Cu_2SO_4 is not stable while CuSO_4 is stable.

Q.12 A developer used in photography is—

- (A) A weak acid (B) A weak base
(C) A mild reducing agent (D) An oxidizing agent

Ans. [C]

Sol. A developer is a weak reducing agent, e.g., Ferrous oxalate; the parts affected by light on photographic plate are reduced to the maximum extent whereas part not affected by light remains unaffected.