D & F-BLOCK ELEMENTS
&
THEIR IMPORTANT COMPOUNDS
CONTENTS

JEE(ADVANCED) SYLLABUS

Transition elements (3d series) : Definition, general characteristics, oxidation states and their stabilities, colour (excluding the details of electronic transitions) and calculation of spin-only magnetic moment. **Preparation and properties of the following compounds :** Oxides, chlorides and sulphates of Fe^{2+}, Cu^{2+} and Zn^{2+}; Potassium permanganate, potassium dichromate, silver oxide, silver nitrate, silver thiosulphate.

JEE (MAIN) SYLLABUS

Transition Elements
General introduction, electronic configuration, occurrence and characteristics, general trends in properties of the first row transition elements-physical properties, ionization enthalpy, oxidation states, atomic radii, colour, catalytic behaviour, magnetic properties, complex formation, interstitial compounds, alloy formation; Preparation, properties and uses of $K_2Cr_2O_7$ and $KMnO_4$. Inner Transition Elements
Lanthanoids - Electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction.
Actinoids - Electronic configuration and oxidation states.

d & f-block elements & their important compounds

Element		**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Atomic number		21	22	23	24	25	26	27	28	29	30
Electronic configuration											
	M	$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$
	M^+	$3d^24s^0$	$3d^34s^0$	$3d^44s^0$	$3d^5$	$3d^64s^0$	$3d^74s^0$	$3d^84s^0$	$3d^94s^0$	$3d^{10}$	$3d^{10}4s^1$
	M^{2+}	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
	M^{3+}	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	–	–
Enthalpy of atomisation, $\Delta_aH^\oplus$ / kJ mol^{-1}											
		326	473	515	397	281	416	425	430	339	126
Ionisation enthalpy / Δ_iH^- / kJ mol^{-1}											
$\Delta_iH^\oplus$	I	631	656	650	653	717	762	758	736	745	906
$\Delta_iH^\oplus$	II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
$\Delta_iH^\oplus$	III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829
Metallic/ionic	M	164	147	135	129	137	126	125	125	128	137
radii/pm	M^{2+}	–	–	79	82	82	77	74	70	73	75
	M^{3+}	73	67	64	62	65	65	61	60	–	–
Standard electrode		–	–1.63	–1.18	–0.90	–1.18	–0.44	–0.28	–0.25	+0.34	–0.76
Potential $E^\oplus$ / V	M^{3+}/M^{2+}	–	–0.37	–0.26	–0.41	+1.57	+0.77	+1.97	–	–	–

d-block Elements

Last electron enters in (n – 1)d subshell. d-block elements lie in middle of periodic table.

General Introduction

1.	**Occurrence**	Three of transition metals are very abundant in the earth's crust.
		Fe → 4th most abundant elements in earth's crust by weight. Ti → 5th most abundant elements in earth's crust by weight. Mn → 12th most abundant elements in earth's crust by weight.
	First row	Element with even atomic no. are in general more abundant than their neighbours with odd atomic no. except for Mn (Z = 25) but still 12th most abundant element by weight.
	2nd and 3rd row	Less abundant than 1st d- series elements. Tc → does not occur in nature. Last six members of 2nd and 3rd row occur less than 0.16 ppm in earth's crust.
	Coinage metals	Cu, Ag and Au are called coinage metals.
	Noble metals	Cu, Ag, Au, Hg and Pt.
2.	**No. of elements**	Total d-block elements – (40) Total transition elements – (36). If 112 elements are included in periodic table. (Except Zn, Cd, Hg and Uub)
3.	**Groups**	IIIB to VIIB, VIII, IB, IIB or group 3 to 12 (IUPAC).
4.	**Period**	4th to 7th 4th period — 3d- series (Sc - Zn) 5th period — 4d- series (Y - Cd) 6th period — 5d- series (La - Hg) 7th period — 6d- series (Ac - Uub)

Periodic trends and chemical properties

S.N.	Properties	DISCRIPTION
1	**Metallic character**	All the transition elements are metals, therefore they are showing all the metallicproperties. Good conductor of heat and electricity. Metallic lustre, strong and ductile. With the exception of Zn, Cd, Hg, Mn all the transition metals have one or more regular metallic structure. The transition metals are hard and have low volatility (except Zn, Cd and Hg).
2	**Electronic configuration**	$(n-1)d^{1-10}\ ns^{1 \text{ or } 2}$

	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIII	10	11 IB	12 IIB
3d Series	21 Sc $3d^14s^2$	22 Ti $3d^24s^2$	23 V $3d^34s^2$	24 Cr $3d^54s^1$	25 Mn $3d^54s^2$	26 Fe $3d^64s^2$	27 Co $3d^74s^2$	28 Ni $3d^84s^2$	29 Cu $3d^{10}4s^1$	30 Zn $3d^{10}4s^2$
4d Series	39 Y $4d^15s^2$	40 Zr $4d^25s^2$	41 Nb $4d^45s^1$	42 Mo $4d^55s^1$	43 Tc $4d^55s^2$	44 Ru $4d^75s^1$	45 Rh $4d^85s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10}4s^1$	48 Cd $4d^{10}4s^2$
5d Series	57 La* $5d^16s^2$	72 Hf $4f^{14}5d^26s^2$	73 Ta $5d^36s^2$	74 W $5d^46s^2$	75 Re $5d^56s^2$	76 Os $5d^66s^2$	77 Ir $5d^76s^2$	78 Pt $5d^96s^1$	79 Au $5d^{10}6s^1$	80 Hg $5d^{10}6s^2$
6d Series	89 Ac** $6d^17s^1$	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn

S.N.	Properties	DISCRIPTION
		Electrons are being filled penultimate shells, thus outer electronic configuration remains same , with exception in some cases, e.g.Cr and Cu.
		Cr and Cu attain extra stability of half-filled and full-filled electronic configuration by changing the expected pattern of electronic configuration.
		The electronic structure of 2nd and 3rd rows do not always follow the pattern of the first row, e.g. Group 10

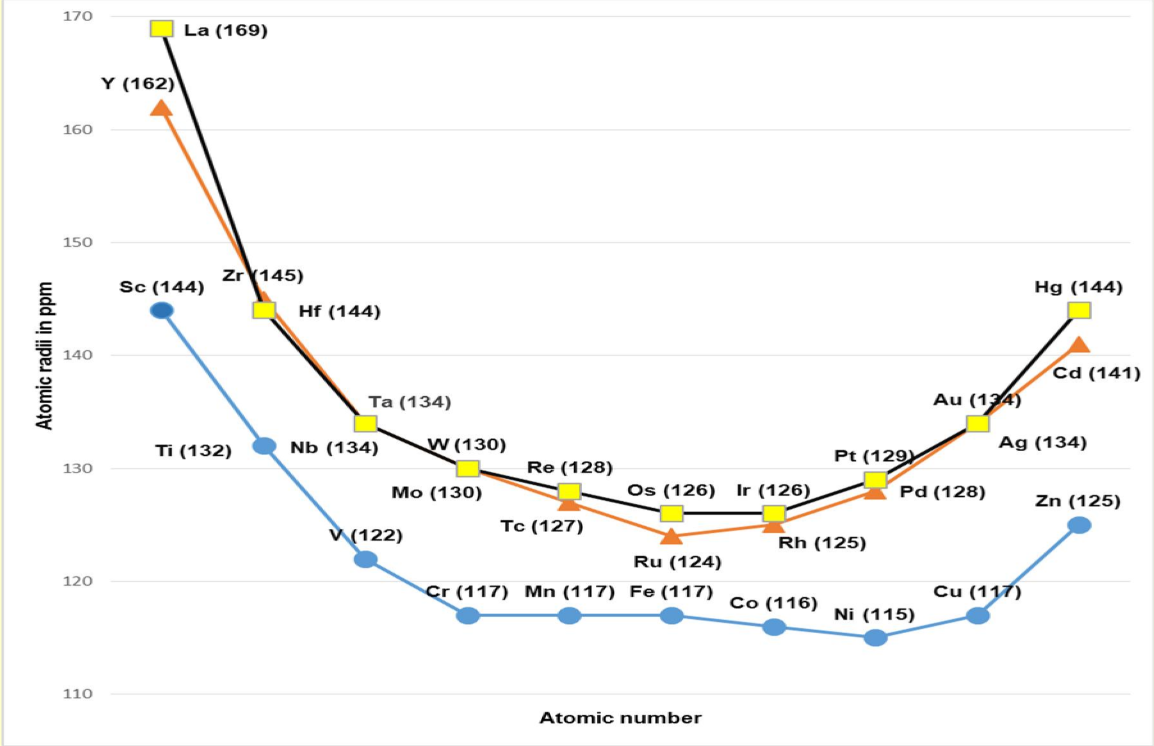
Ni	$3d^8\ 4s^2$
Pd	$4d^{10}5s^0$
Pt	$5d^9\ 6s^1$

S.N.	Properties	DISCRIPTION
		d-orbitals are complete at Cu, Pd, Ag, Au.

Ni $(3d^8\ 4s^2)$	Cu$(3d^{10}4s^1)$	Zn$(3d^{10}4s^2)$
Pd$(4d^{10}5s^0)$	Ag$(4d^{10}5s^1)$	Cd$(4d^{10}5s^2)$

Even though ground state of the atom has a d^{10} configuration Pd and coinage metals behaves as typical transition elements, as in their most common oxidation states they have incomplete d-orbital.

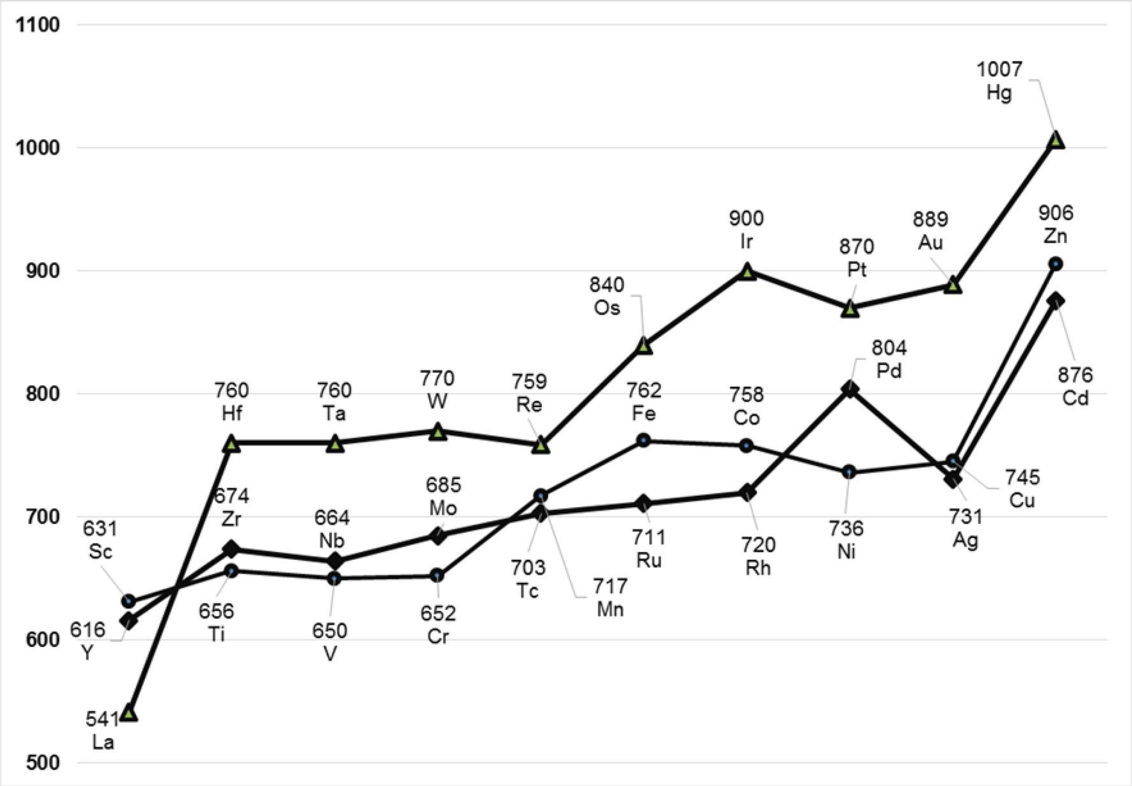
S.N.	Properties	DISCRIPTION
	Transition elements	A transition element is defined as the one which has incompletely filled *d* orbitals in its ground state or in any one of its oxidation states. Zinc, Cadmium and Mercury of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states and hence, they are some times not regarded as transition metals. All transition elements are d-block elements but all d-block elements are not transition elements. (as per NCERT)

<table>
<tr><td>3</td><td>Size of atoms and ions</td><td>In the transition series (e.g. in the first transition series), the covalent radii of the elements decrease from left to right across a row until near the end when the size increases slightly.</td></tr>
<tr><td></td><td>d-orbital contraction</td><td>On moving from left to right, extra protons are placed in the nucleus and the extra electron are added. The orbital electron shield the nuclear charge incompletely. Thus the nuclear charge attracts all the electrons more strongly, hence a contraction in size occurs. The radii of the elements from Cr to Cu, are very close to one another because the extra electron being added increases the repulsion between the electrons and counter balances the increased nuclear charge on the outer electrons (4s). As a result of this, the size of the atom does not change much in moving from Cr to Cu and for zinc this repulsion even dominates the nuclear charge so size slightly increases.
<table>
<tr><td>Element</td><td>Sc</td><td>Ti</td><td>V</td><td>Cr</td><td>Mn</td><td>Fe</td><td>Co</td><td>Ni</td><td>Cu</td><td>Zn</td></tr>
<tr><td>Atomic radius (pm)</td><td>144</td><td>132</td><td>122</td><td>117</td><td>117</td><td>117</td><td>116</td><td>115</td><td>117</td><td>125</td></tr>
</table></td></tr>
<tr><td></td><td>Lanthanide Contraction</td><td>As we move along the lanthanide series, the nuclear charge increases by one unit at each successive element. The new electron is added into the same subshell (4f). As a result, the attraction on the electrons by the nucleus increases and this tends to decrease the size. Further, as the new electron is added into the f-subshell, there is imperfect shielding of one electron by another in this subshell due to the shapes of these f-orbitals. This imperfect shielding in unable to counter balance the effect of the increased nuclear charge. Hence, the net result is a contraction in the size though the decrease is very small.
Thus covalent and ionic radii of Nb (5th period) and Ta (6th period) are almost same due to poor shielding of f-orbitals electrons.</td></tr>
<tr><td></td><td colspan="2">


Ti < Zr ≈ Hf (Lanthanide Contraction)
Sc < Y < La
Due to Lanthanide contraction elements of 4d and 5d series belong to a particular group have almost same atomic radii. Ex. Zr ≈ Hf, Tc ≈ Re, Nb ≈ Ta, Ru ≈ Os etc.</td></tr>
<tr><td>4</td><td>Ionization energies of</td><td>Ionization energy normally increases from left to right in the period.
Ionization energy values of third transition series is greater than ionization</td></tr>
</table>

transition metals energy values of first and second transition series.

Memory warning : Need not memorise the graph.



First ionization energies of the d-block elements (Numerical values are given in kJ mol^{-1}).

(i)The first ionisation potential for the first four 3d-block elements (Sc,Ti,V & Cr) differ only slightly from one another.

(ii) Similarly the value first ionisation energy of Fe, Co, Ni & Cu also are fairly close to one another.

(iii) The value of first ionisation energy for Zn is considerably higher due to the extra stability of $3d^{10}4s^2$ level which is completely filled in Zn atom.

(iv) The first ionization energy of Mn is slightly higher than adjacent elements in 3d series due to half-filled stable configuration.

(v) Second ionisation energy value for Cr & Cu are higher as the Cr^+ & Cu^+ ion are extra stable due to $3d^5$ and $3d^{10}$ Configuration.

(vi) In vertical columns, the ionisation energy decrease from first member to the second member.

(vii) However the third member (5d series) has higher value than second member (4d-series) due to lanthanide contraction. I.E.(3rd T.S.) > I.E.(2nd T.S.) > I.E.(1st T.S.)

5 **Oxidation-State** They show variable oxidation–state.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			+1					**+1**	
	+2	**+2**	**+2**	+2 $^{(a)}$	+2	+2	+2	+2	+2
+3	+3	+3	+3	**+3**	**+3**	**+3**	**+3**		
	+4	**+4**	**+4**	+4$^{(b)}$	**+4**	**+4**	**+4**		
		+5	**+5**	**+5**					
			+6	**+6**	**+6**				
				+7					

(a) Acidic medium (b) Basic medium

* Shaded states are popular ones.

* Underlined states are the most stable ones.

The oxidation states change in units of 1, unlike that in p-block elements, where generally oxidation state differs by units of 2.

Trends of Oxidation state

Highest oxidation state of 3d-series elements can be calculated by n + 2 (where n = number of unpaired electrons) **It is not applied for Cr and Cu.**

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.

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

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

The highest oxidation states (+4, +5, +6, +7, +8) are found in compounds of oxide and oxyfluoride because fluorine and oxygen are most electronegative elements and good oxidants.

e.g. $\overset{+7}{Mn}O_4^-, \overset{+6}{Cr_2}O_7^{2-}, \overset{+6}{Cr}O_4^{2-}, \overset{+4}{Mn}O_2, \overset{+6}{Mn}O_4^{2-}, \overset{+6}{Cr}O_2F_2$

Lower oxidation states even negative (-2, -1, 0, +1) is stabilised by π-bonding ligands such as carbon monoxide and dipyridine due to phenomena of synergic bonding $Ni(CO)_4$ and $Fe(CO)_5$, oxidation state of Ni and Fe is zero.

They form ionic compounds in low oxidation states and covalent compounds in Higher oxidation state.

Formulas of Oxides of 3d Metals (* mixed oxides)

OXIDATION NUMBER	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+7					Mn_2O_7					
+6				CrO_3						
+5			V_2O_5							
+4		TiO_2	V_2O_4	CrO_2	MnO_2					
+3	Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_2O_3				
					Mn_3O_4*	Fe_3O_4*	Co_3O_4*			
+2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO
									Cu_2O	

6 **Colour**

Ionic and covalent compounds of many transition elements are coloured. They form different coloured compounds. The compounds in which metal ion has an unpaired electron that compound may be coloured. When an electron from a lower energy d-orbital is exited to a higher energy d-orbital, if the energy of excitation lies in visible range, complimentary colour is observed. MnO_4^- is coloured inspite of d^0 configuration of Mn. It is not due to d-d transition but it occurs due to charge transfer between Mn and O.

Memory warning : Memorize the table completely.

Oxidation State	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
(I)									**Colurless**	
(II)				**Blue**	**Pink**	**Green**	**Pink**	**Green**	**Blue**	**Colurless**
(III)	**Colurless**	**Purple**	**Green**	**Green**	**Violet**	**Yellow**	**Blue**			
(IV)		**Colurless**	**Blue**							

7 **Electrode potential**

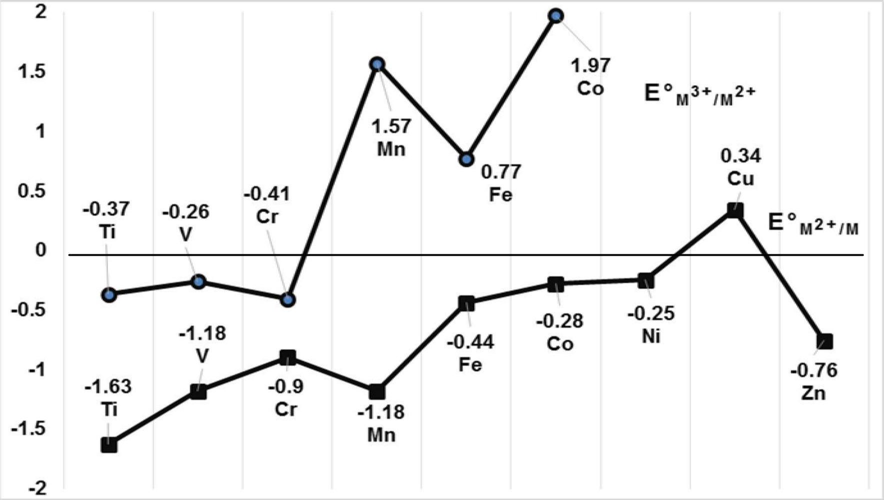
$E^0_{M^{2+}/M}$

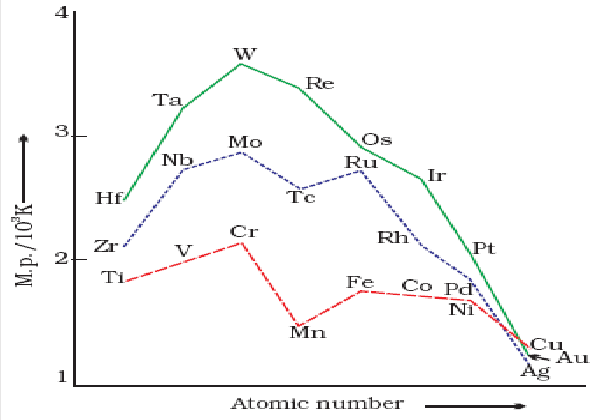
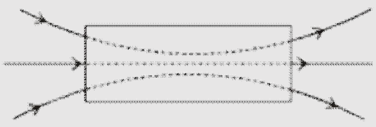
There is no regular trend in these values. This is attributed to the irregular variation of ionisation enthalpies ($IE_1 + IE_2$) , hydration energies and the sublimation energies in the period.

Memory warning : Need not memorize the table but remember the comments.

Element (M)	$E^0_{M^{3+}/M^{2+}}$	$E^0_{M^{2+}/M}$	Comments

Ti	–0.37	–1.63	+3 Oxidation states is more stable
V	–0.26	–1.18	+3 Oxidation states is more stable
Cr	–0.41	–0.9	+3 Oxidation states is more stable
Mn	1.57	–1.18	+2 Oxidation states is more stable
Fe	0.77	–0.44	+2 Oxidation states is more stable
Co	1.97	–0.28	+2 Oxidation states is more stable
Ni	–	–0.25	+3 Oxidation states does not exist for Ni
Cu	–	0.34	+3 Oxidation states does not exist for Cu. 0 Oxidation states is more stable
Zn	–	0.76	+3 Oxidation states does not exist for Zn

	Comparative graph of $E^0_{M^{2+}/M}$ and $E^0_{M^{3+}/M^{2+}}$	 The stability of the half-filled *d* sub-shell in Mn^{2+} and the completely filled d^{10} configuration in Zn^{2+} are related to their $E^{\ominus}$ values, whereas $E^{\ominus}$ for Ni is related to the highest negative hydration energy. It may be noted that the electrode potentials of transition metals are low in comparison to elements of group 2 (e.g., Ca = –2.87 V, the transition elements have fairly large ionisation enthalpies and very large enthalpies of atomisation). Compared to group 2 elements. These reduce their electrode potentials though their hydration enthalpies are large.

8	**Density**	Elements with highest densities are Osmium (Os) = 22.51 g/cm^3 , Iridium (Ir) = 22.61 g/cm^3
9	**Melting and Boiling point**	High melting points are attributed to involvement of greater number of electrons from (n–1)d in addition to the ns electrons in inter atomic metallic bonding thus highest for d^5, except for anamolous value for Mn, and Tc fall regularly. m.p. and b.p. are generally very high exceptions  → Zn (420ºC) → Cd (321ºC) → Hg liquid at room temperature. last of each d-series element behave a typically because the d-shell is complete and d-electrons do not participate in metallic bonding. They have high enthalpies of atomization, which are maximum at middle of each series , indicates that one unpaired e$^-$ per d-orbital is particularly favorable for strong interatomic interaction. Metals of 2nd and 3rd transition series has higher melting pt. bonding pt. as well as enthalpy of atomization, than corresponding elements of the 1st series this is due to metal-metal bonding of heavy transition metals.
10	**Magnetic character**	Metals, which have unpaired electrons show paramagnetism. Spin only magnetic moment $\mu = \sqrt{n(n + 2)}$ here n = no. of unpaired electron. Diamagnetic substance is one which is slightly repelled by a magnetic field. A paramagnetic substance is one which is attracted into a magnetic field. In paramagnetic substance the magnetic field lines of force travel easier than they travel in vacuum. Thus it can be seen that a paramagnetic material attracts lines of force, if it is free to move, a paramagnetic material will move from a weaker to a stronger part of the field.  Paramagnetic material
	Ferromagnetism	Ferromagnetic materials may be regarded as special case of paramagnetism in which the moments of individual domains becomes aligned and all points in the same direction. Ferromagnetic materials ⇒ Fe, Co, Ni.

<table>
<tr>
<td>11</td>
<td>NCERT
Catalytic Properties</td>
<td>The transition metals and their compounds are known for their catalytic activity. This is due to ability to adopt multiple oxidation states and to form complexes.
<table>
<tr><th>Catalyst</th><th>Used</th></tr>
<tr><td>Fe</td><td>Haber's process for manufacture of NH_3.</td></tr>
<tr><td>V_2O_5</td><td>Contact process for H_2SO_4 manufacture.</td></tr>
<tr><td>Pt</td><td>Ostwald's process of nitric acid.</td></tr>
<tr><td>Ni</td><td>Hydrogenation of oils.</td></tr>
<tr><td>$FeSO_4$ & H_2O_2</td><td>Fenton's reagent for oxidising alcohol to aldehyde.</td></tr>
<tr><td>Cu</td><td>Dehydrogenation of alcohols</td></tr>
<tr><td>$Al_2(C_2H_5)_6 + TiCl_4$</td><td>Ziegler-Natta catalyst in the production of Polyethene.</td></tr>
<tr><td>$FeCl_3$</td><td>For making CCl_4 from CS_2 and Cl_2.</td></tr>
<tr><td>Pt/PtO</td><td>Adams catalyst, used for reduction.</td></tr>
</table>
</td>
</tr>
<tr>
<td>12</td>
<td>FORMATION OF INTERSTITIAL COMPOUNDS</td>
<td>Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic nor covalent, for example, TiC, Mn_4N, Fe_3H, $VH_{0.56}$ and $TiH_{1.7}$, etc. The formulas quoted do not, of course, correspond to any normal oxidation state of the metal. Because of the nature of their composition, these compounds are referred to as interstitial compounds. The principal physical and chemical characteristics of these compounds are as follows:
(i) They have high melting points, higher than those of pure metals.
(ii) They are very hard, some borides approach diamond in hardness.
(iii) They retain metallic conductivity.
(iv) They are chemically inert.</td>
</tr>
<tr>
<td>13</td>
<td>FORMATION OF ALLOYS</td>
<td>(i) Transition elements have maximum tendency to form alloys.
(ii) The reactivity of transition elements is very less and their sizes are almost similar. Due to this a transition metal atom in the lattice can be easily replaced by other transition metal atom and hence they have maximum tendency to form alloys.
(iii) In the alloys, ratio of component metals is fixed.
(iv) These are extremely hard and have high melting point.</td>
</tr>
</table>

SOME IMPORTANT ALLOY

Note- Memorize the * marked alloys

*(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 %)
(f)	Nichrome	(Ni + Cr + Fe)
(g)	Alnico	(Al, Ni,Co)
(h)	Type Metal	Pb + Sn + Sb
(i)	Alloys of steel	
	• Vanadium steel	V (0.2 - 1 %)
	• Chromium steel	Cr (2 - 4 %)
	• Nickel steel	Ni (3 -5 %)
	• Manganese steel	Mn (10 -18 %)
	• Stainless steel	Cr (12 - 14 %)& Ni (2 - 4 %)
	• Tunguston steel	W (10 - 20 %)
(j)	14 Carat Gold	54 % Au + Ag (14 to 30 %) + Cu (12 - 28 %)
(k)	24 Carat Gold	100 %Au
*(l)	Solder	Pb + Sn
(m)	Magnellium	Mg (10%) + Al (90%)
(n)	Duralumin	(Al + Mn + Cu)
*(o)	Artificial Gold	Cu (90 %) + Al (10%)
(p)	Constantan	Cu(60%) + Ni (40%)
% of Carbon in different type of Iron		
	Name	% of C
(a)	Wrought Iron	0.1 to 0.25
(b)	Steel	0.25 to 2.0
(c)	Cast Iron/Pig Iron	2.6 to 4.3

Preparations and properties of some important d-Block metal compounds

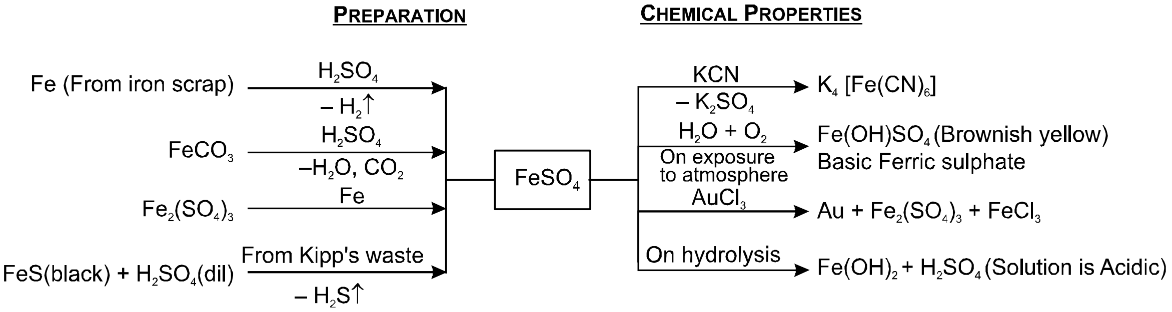
Sulphates (SO_4^{2-})

1. FeSO4.7H2O (Green Vitriol)

Ferrous sulphate.
Commonly known as harkasis.

Physical properties

- Hydrated ferrous sulphate is a green coloured compound.
- Effloresces on exposure to air.
- Anhydrous $FeSO_4$ is colourless.



Heating effect :

$$FeSO_4.7H_2O \xrightarrow{140°C} FeSO_4.H_2O \xrightarrow{300°C} 2FeSO_4 \xrightarrow[\text{Temp.}]{\text{High}} Fe_2O_3 + SO_2\uparrow + SO_3\uparrow$$

Uses : It is used

(i) for making Blue - Black ink.
(ii) as mordant in dyeing.
(iii) as insecticide in agriculture.
(iv) for making laboratory reagents like Mohr's salt etc.

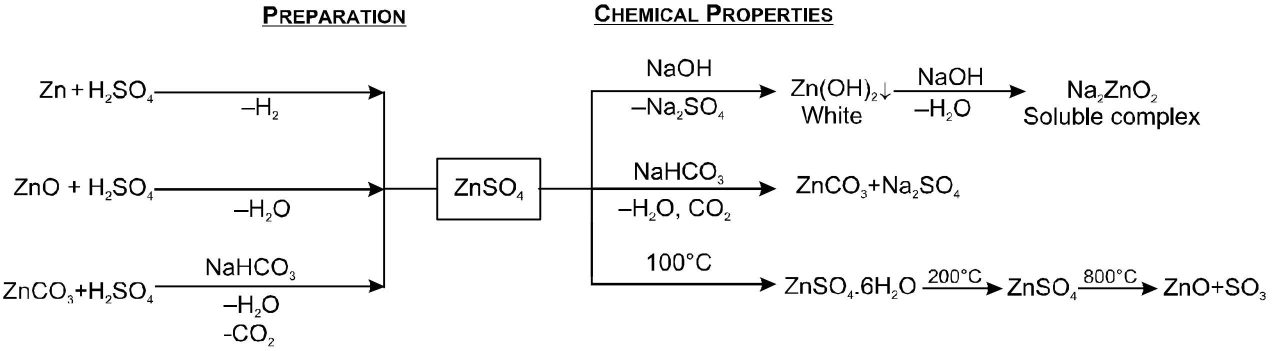
$$FeSO_4 + (NH_4)_2\,SO_4 + 6H_2O) \longrightarrow FeSO_4\,(NH_4)_2SO_4.6H_2O \text{ (Mohr's salt)}$$

(v) $FeSO_4 + H_2O_2$ known as Fenton's reagent is used as catalyst.

2. Zinc Sulphate, ZnSO4. 7H2O (white Vitriol)

Physical Properties

- Colourless, crystalline solid, soluble in water.
- It slowly effloresces when exposed to air.
- It is isomorphos with Epsom salt ($MgSO_4.7H_2O$).



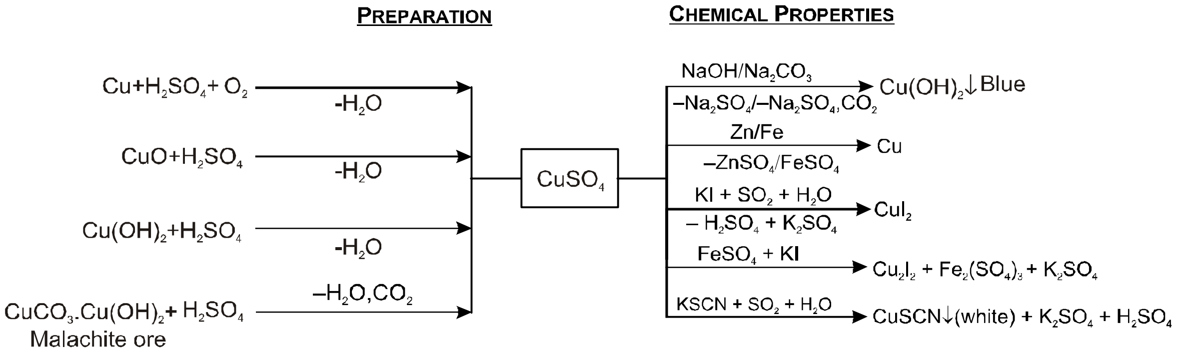
Uses : It is used as

(i) eye lotion.
(ii) for making lithophone-mixture of BaS + $ZnSO_4$ (while paint).
(iii) mordant in dyeing.

3. Copper sulphate, $CuSO_4.5H_2O$ (blue vitriol)

Also called as 'Nilathotha'

Physical Properties **:** Blue crystalline compound soluble in water.



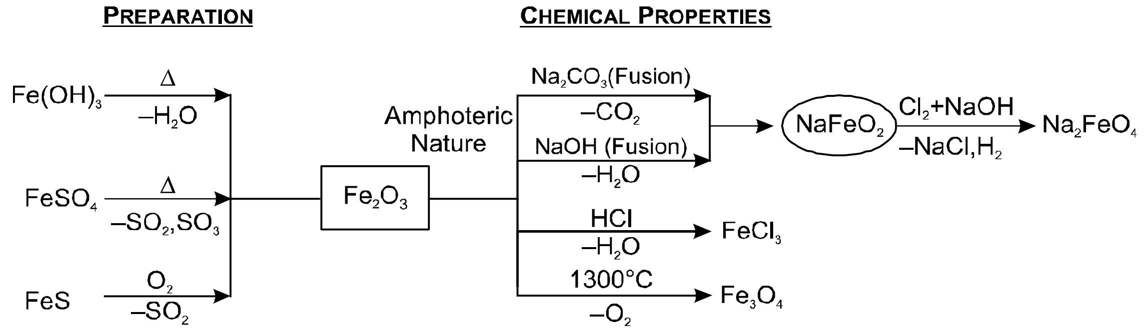
$$CuSO_4.5H_2O \xrightarrow[\text{effloresces}]{\text{air}} CuSO_4.4H_2O \xrightarrow{100°C} CuSO_4.H_2O \xrightarrow{250°C} CuSO_4 \xrightarrow{750°C} CuO+SO_2+O_2$$

Uses : It is used
(i) for making other copper compounds.
(ii) for electroplating, electrotyping, as mordant in dyeing.
(iii) in making Bordeaux mixture which is used in agriculture as fungicide and germicide.
(iv) in making Fehlings solution.
(v) in medicine as antiseptic.
(vi) in electric batteries.

Oxides of Fe^{2+}, Cu^{2+}, Zn^{2+} & Ag^{+}

4. Ferric Oxide, Fe_2O_3

Physical Properties :
Deep red coloured powder and insoluble in water.



Uses : It is used
(i) as red pigment.
(ii) an abrasive polishing powder.
(iii) as a catalyst.

5. **ZnO, Zinc oxide (Chinese white or Philosopher's wool)**

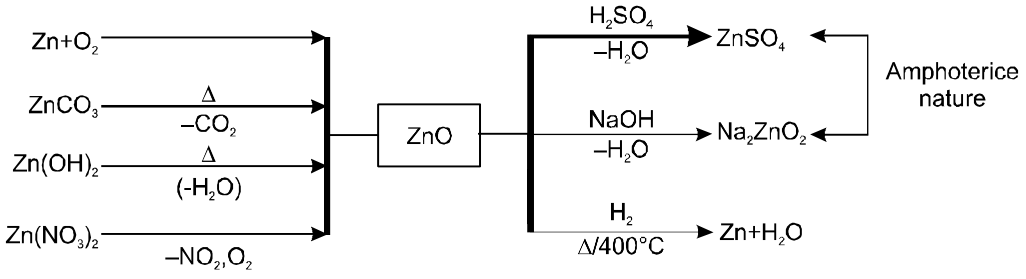
It is found in nature as zincite or red zinc ore.

Physical Properties :

(i) White powder which becomes yellow on heating due to change in the structure of latlice again turns white on cooling.

(ii) Insoluble in water and sublimes at 400°C.

PREPARATION **CHEMICAL PROPERTIES**



Uses : It is used

(i) as a white paint. It does not get tarnished even in presence of H_2S because ZnS is also white.

(ii) for preparing Rinmann's green (green paint $ZnCoO_2$).

(iii) as a catalyst for preparation of methyl alchol.

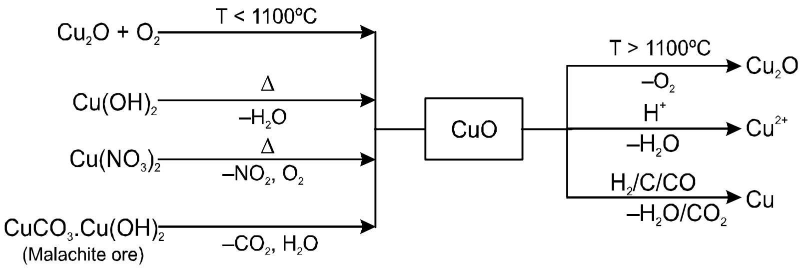
(iv) for making soft rubber.

6. **Cupric oxide, (CuO) :**

It is called black oxide of copper and is found in nature as tenorite.

Physical properties : Black powder, insoluble in water and stable to moderate heating.

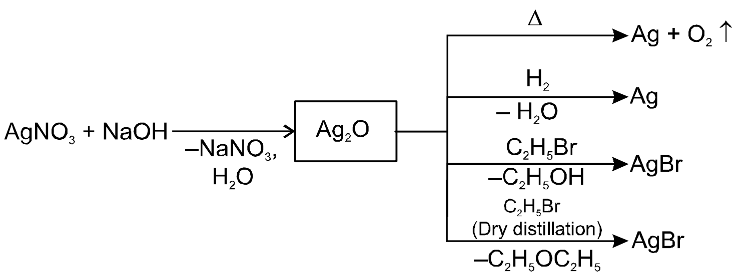
PREPARATION **CHEMICAL PROPERTIES**



7. **Silver oxide (Ag_2O) :**

Physical properties : Brown solid sparingly soluble in water properties.

PREPARATION **CHEMICAL PROPERTIES**



Uses : It is used

(i) as Tollen's reagent for detection of aldehydes, formic acid, and terminal alkynes.

(ii) in the manufacturing of mirrors.

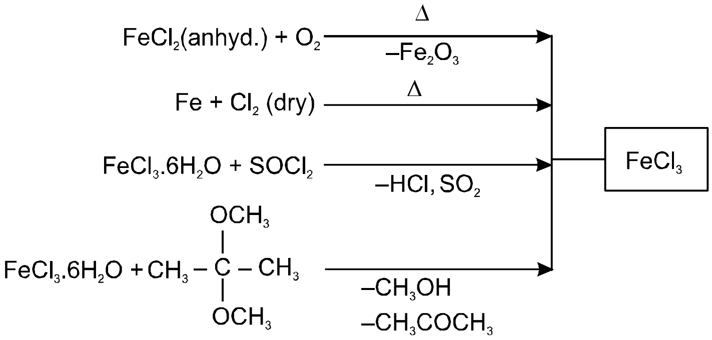
Chlorides (Cl^-) of Fe^{2+} , Zn^{2+} and Cu^{2+}

8. Ferric Chloride, $FeCl_3$

Prepration

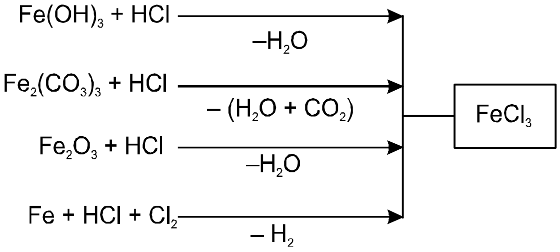
(a) Anhydrous $FeCl_3$.

PREPARATION



(b) Hydrated $FeCl_3$.

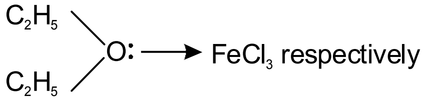
PREPARATION



Properties :

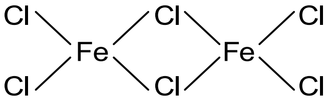
- Anhydrous $FeCl_3$ is dark black solid, while hydrated salt. $FeCl_3.6H_2O$ is yellowish-brown deliquescent crystalline liquid.
- Both hydrous $FeCl_3$ and hydrated $FeCl_3$, are soluble in water as well as ether forming solvated species.

$[Fe(H_2O)_4Cl_2]Cl.2H_2O$ and



$(C_2H_5)_2O: \longrightarrow FeCl_3$ respectively

- It sublimes at 300ºC giving a dimeric gas.



Chemical Properties :

(i) Action of heat :

(a) $FeCl_3\text{(anhydrous)} \xrightarrow{\Delta} 2FeCl_2 + Cl_2$

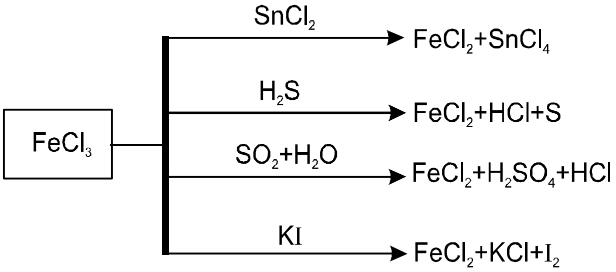
$2FeCl_3.6H_2O \xrightarrow{\Delta} Fe_2O_3+6HCl+9H_2O$

(ii) Aqueous solution is acidic due to hydrolysis.

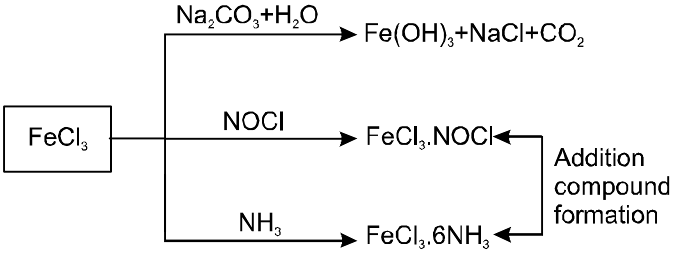
$$\underset{\text{Acid}}{[Fe(H_2O)_6]^{3+}} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Base}}{[Fe(H_2O)_5(OH)]^{2+}} + \underset{\text{Acid}}{H_3O^{\oplus}}$$

(iii) As an oxidising agent.

$$Fe^{3+} \xrightarrow{\text{reducing agent}} Fe^{2+}$$



(iv)



Uses : It is used

(i) as a medicine.

(ii) for detection of phenols.

(iii) for making Prussian blue dyes.

(iv) as an oxidising agent.

9. **<u>Zinc Chloride</u>**

Prepration of Hydrated $ZnCl_2$ ($ZnCl_2.2H_2O$)

$$ZnO+HCl \longrightarrow ZnCl_2.2H_2O \xrightarrow[-HCl,\ H_2O]{\Delta} Zn(OH)Cl \xrightarrow{\Delta} ZnO+HCl$$

Anhydrous $ZnCl_2$

$$Zn+Cl_2 \xrightarrow{\Delta} ZnCl_2 \xleftarrow[-Hg]{\text{distilling}} Zn+HgCl_2$$

Properties

White crystalline solid, deliquescent and soluble in water.

Its concentrated solution sets to a hard mass when mixed with ZnO and product is used as a dental filling.

10. Cupric chloride, $CuCl_2.2H_2O$

Physical Properties

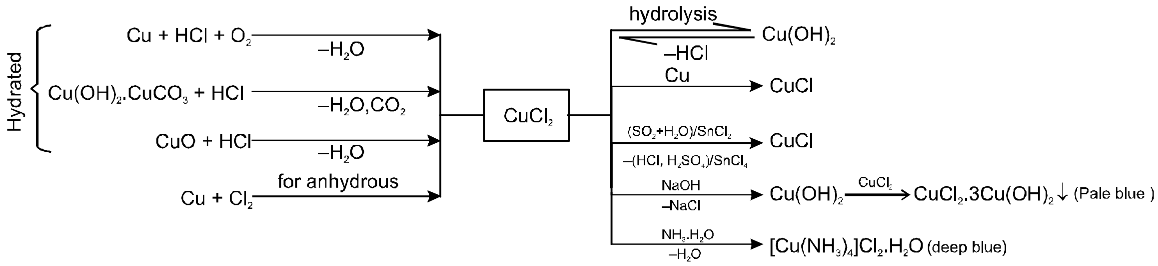
It is deliquescent compound. readily soluble in water.

Dilute & solution is blue but concentrated solutions is green.

It changes to yellow when concentrated HCl is added.

Blue colour is due to complex cation $[Cu(H_2O)_4]^{2+}$ and yellow colour due to complex axion $[CuCl_4]^{2-}$ and green when both are present.

PREPARATION **CHEMICAL PROPERTIES**



*Anhydrous $CuCl_2$ on heating

$2\,CuCl_2 \xrightarrow{\Delta} 2CuCl+Cl_2$

Heating effect : $CuCl_2.2H_2O \xrightarrow[\text{HCl gas}]{150^\circ C} CuCl_2 + 2H_2O$

11. Silver nitrate, $AgNO_3$ (Lunar Caustic)

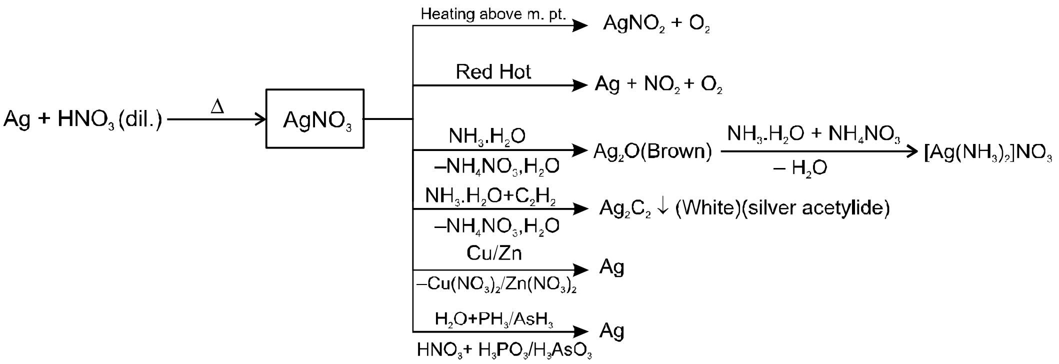
Physical Properties

(i) It is a colourless crystalline compound.
(ii) Soluble in water and alcohol.
(iii) It melts at 212°C.

Chemical Properties

(i) It possesses powerful corrosive action on organic tissues, which at turns black especially in presence of light. The blackening is due to finely divided metalic silver, reduced by organic tissure It is therefore, stored in colored Bottles.
(ii) Solutions of halides phosphates, sulfides chromates thiocyanates, sulphates and thiosulphates salt with silver nitrate solution.
(iii) Ammonical silver nitrate is called as Tollen's reagent and used to identify reducing sugars and aldehydes.

PREPARATION **CHEMICAL PROPERTIES**



It is known as silver mirror test of aldehydes and reducing sugars.

$$Ag_2O + HCHO \longrightarrow 2Ag + HCOOH.$$

$$Ag_2O + C_6H_{12}O_6 \longrightarrow 2Ag + C_6H_{12}O_7.$$

(iv) Reactions with Iodine :

$6\ AgNO_3\ (excess) + 3I_2 + 3H_2O \longrightarrow AgIO_3 + 5AgI + 6HNO_3$

$5\ AgNO_3 + 3I_2\ (excess) + 3H_2O \longrightarrow HIO_3 + 5AgI + 5HNO_3$

Uses : It is used

(i) as a laboratory reagent for the identification of various acidic especially for Cl, Br and I.

(ii) Tollen's reagent is used in organic chemistry for testing aldehydes reducing sugars etc.

(iii) for making AgBr, used in photography.

(iv) in the preparation of inks and hair dyes.

(v) in preparation of silver mirror.

12. Photography :

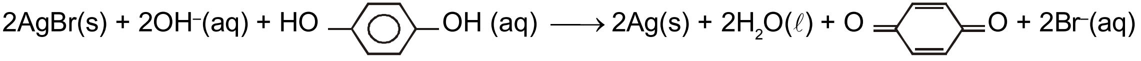
(i) A photographic film consists of a light sensitive emulsion of fine particles (grains) of silver salts in gelatine spread on a clear celluloid strip or a glass plate. AgBr is mainly used as the light sensitive material.

(ii) The film is placed in a camera. When the photograph is exposed, light from the subject enters the camera and is focussed by the lens to give a sharp image on the film. The light starts a photochemical reaction by exciting a halide ion, which loses an electron. The electron moves in a conduction band to the surface of the grain, where it reduces a Ag^+ ion to metallic silver.

$2AgBr(s) \xrightarrow{light} 2Ag + Br_2$

(iii) In modern photography only a short exposure of perhaps 1/100th of a second is used. In this short time, only a few atoms of silver (perhaps 10–50) are produced in each grain exposed to light. Parts of the film which have been exposed to the bright parts of the subject contain a lot of grains with some silver.

(iv) Next the film is placed a developer solution. This is a mild reducing agent, usually containing quinol. Its purpose is to reduce more silver halide to Ag metal. Ag is deposited mainly where there are already some Ag atoms. Thus the developing process intensifies the latent image on the film so it becomes visible.



hydroquinol hydroquinone

(v) If the film was brought out into daylight at this stage, the unexposed parts of the emulsion would turn black and thus destroy the picture. To prevent this happening any unchanged silver halides are removed by placing the film in a fixer solution. A solution of sodium thiosulphate is used as fixer. It forms a soluble complex with silver halides.

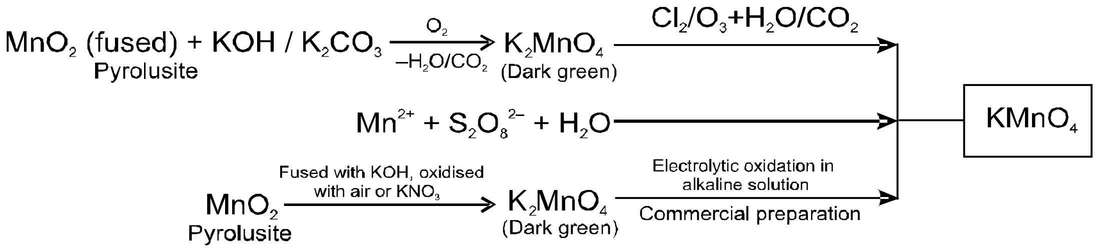
$AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

After fixing, the film can safely be brought out into daylight. This is called "negative".

Light is passed through the negative onto a piece of paper coated with AgBr emulsion. This is then developed and fixed in the same way as before.

13. Potassium Permanganatic ($KMnO_4$)

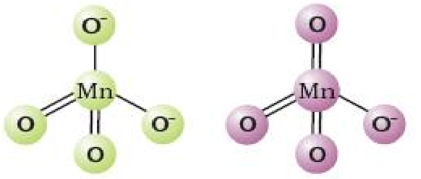
PREPARATION



Physical Properties *:*

Purple coloured crystalline compound.

Moderately soluble in water at room temperature.



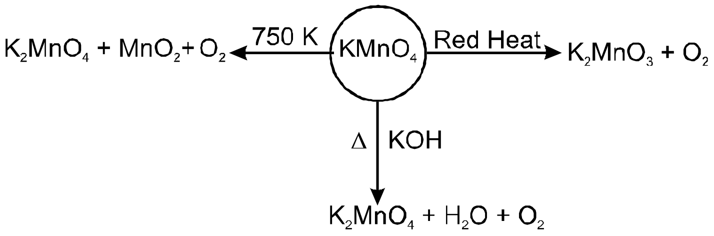
Tetrahedral manganate (green) ion

Tetrahedral permanganate (purple) ion

Structure of manganate and permanganate ion.

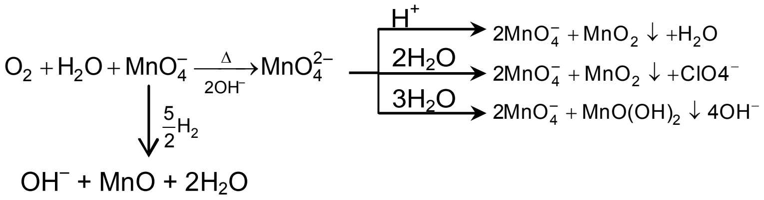
Chemical Properties

(i) Heating effect



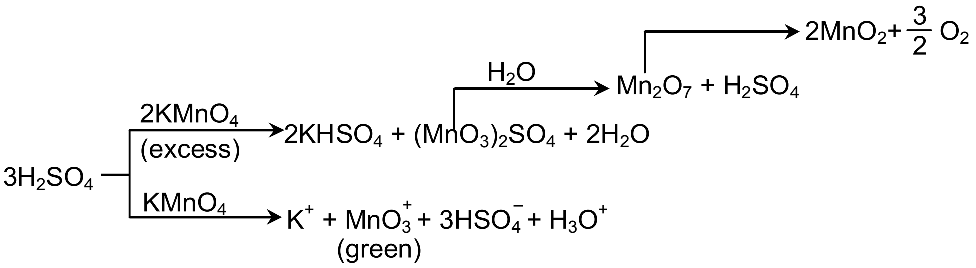
$$\begin{tikzcd}
K_2MnO_4 + MnO_2 + O_2 & \boxed{KMnO_4} \arrow[l, "750\text{ K}"'] \arrow[r, "\text{Red Heat}"] \arrow[d, "\Delta"', "KOH"] & K_2MnO_3 + O_2 \\
 & K_2MnO_4 + H_2O + O_2 &
\end{tikzcd}$$

(ii) Reactions with MnO_4^{2-} in dil. alkaline, water and acidic solutions



$$\begin{tikzcd}
 & & 2MnO_4^- + MnO_2 \downarrow + H_2O \\
O_2 + H_2O + MnO_4^- \arrow[r, "\Delta", "2OH^-"'] \arrow[d, "\frac{5}{2}H_2"] & MnO_4^{2-} \arrow[ur, "H^+"] \arrow[r, "2H_2O"] \arrow[dr, "3H_2O"] & 2MnO_4^- + MnO_2 \downarrow + ClO4^- \\
OH^- + MnO + 2H_2O & & 2MnO_4^- + MnO(OH)_2 \downarrow 4OH^-
\end{tikzcd}$$

(iii) with conc. H_2SO_4,



$$\begin{tikzcd}
 & & & 2MnO_2 + \frac{3}{2}O_2 \\
 & & Mn_2O_7 + H_2SO_4 \arrow[ur] & \\
 & 2KHSO_4 + (MnO_3)_2SO_4 + 2H_2O \arrow[ur, "H_2O"] & & \\
3H_2SO_4 \arrow[ur, "2KMnO_4", "(\text{excess})"'] \arrow[dr, "KMnO_4"] & & & \\
 & K^+ + \overset{+}{MnO_3} + 3\overset{-}{HSO_4} + H_3O^+ \ (\text{green}) & &
\end{tikzcd}$$

(iv) $KMnO_4$ is a powerful O.A.

Potassium permanganate acts as an oxidising agent in alkaline, neutral or acidic solutions.

A mixture of sulphur, charcoal and $KMnO_4$ forms an explosive powder. A mixture of oxalic acid and $KMnO_4$ catches fire spontaneous after a few seconds. The same thing happens when glycerine is poured over powdered $KMnO_4$

In alkaline & neutral medium :

In strongly alkaline medium $KMnO_4$ is reduced to manganate.

$$2KMnO_4 + 2KOH\ (conc.) \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

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

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

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

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

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

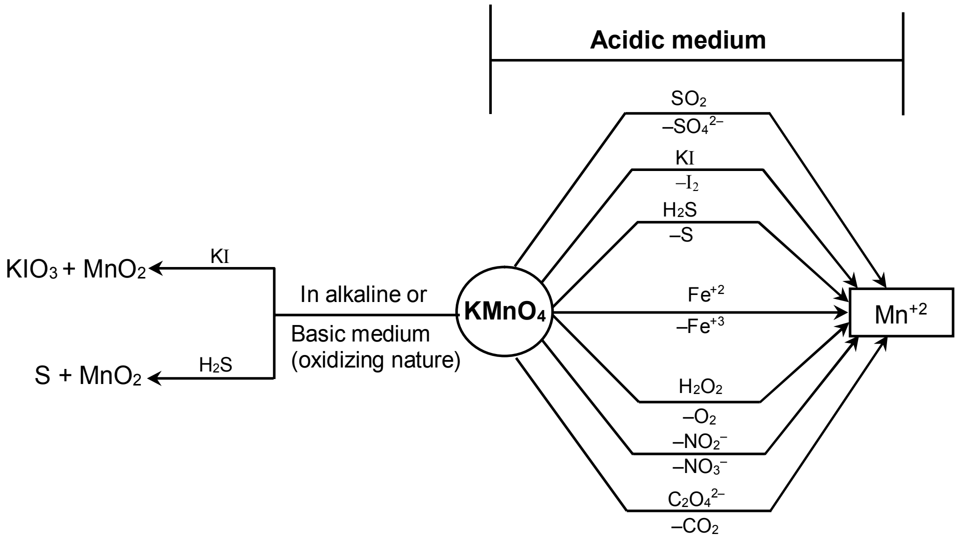
$$3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$$

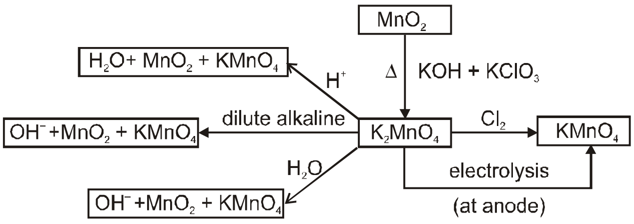
$$\boxed{3e^- + 2H_2O + MnO_4^- \xrightarrow[\text{dilute}]{} \underset{\text{brown ppt}}{MnO_2} \downarrow + H_2O \xleftarrow{-2[O]} 2MnO_4^{2-} + 2H_2O}$$

Note : $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O$

This medium is used in quantitative (Volumetric) Estimations. The eq. mass of $KMnO_4$ in acidic medium is = $\dfrac{\text{Molecular Mass}}{5}$

Reactions of $KMnO_4$:





Uses : It is used

(i) $KMnO_4$ is used as an oxidising agent in laboratory and industry.

(ii) Alkaline potassium permanganate is called Bayer's reagent. This reagent is used in organic chemistry for the test of unsaturation. $KMnO_4$ is used in the manufacture of saccharin, benzoic acid, acetaldehyde etc.

(iii) $KMnO_4$ is used in qualitative analysis for detecting halides, sulphites, oxalates, etc.

14. POTASSIUM DICHROMATE ($K_2Cr_2O_7$) :

Preparation :

The chromite ore is roasted with sodium carbonate in presence of air in a reverberatory furnace.

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

$$\Big\downarrow 4H_2SO_4$$

$$\underset{\text{(orange)}}{4Na_2CrO_7} + \underset{\text{(Crystalise)}}{4Na_2SO_4} + 4H_2O$$

$$\Big\downarrow 8\ KCl$$

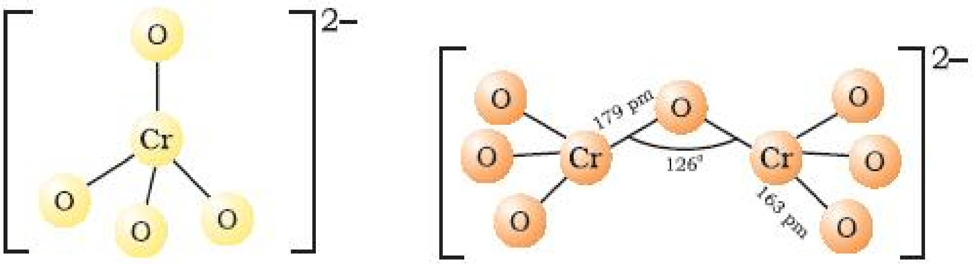
$$\boxed{K_2Cr_2O_7} + 8NaCl$$

Properties

(a) Physical :

It is orange-red coloured crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at 398°C.

Structure of Chromate and Dichromate ion

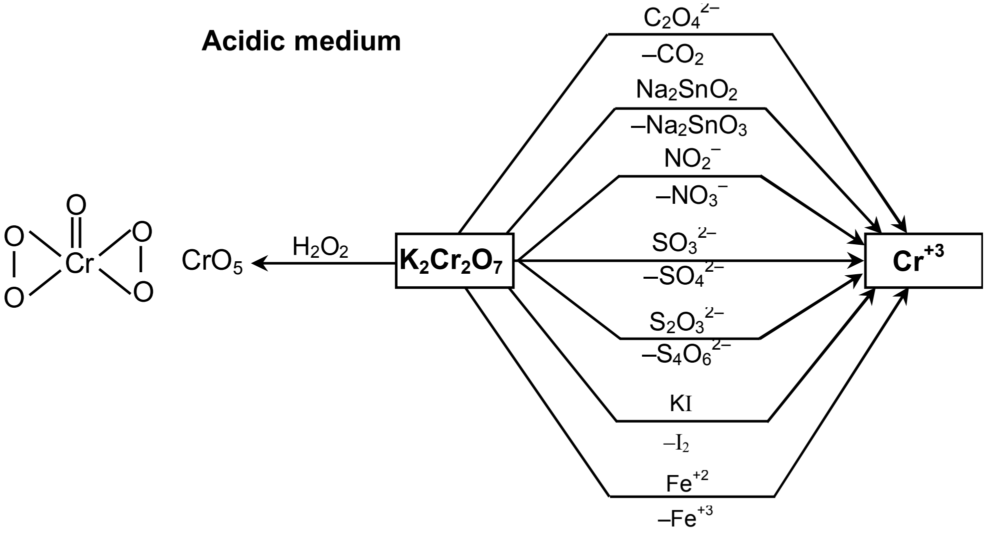


Chromate ion Dichromate ion

(b) Chemical :

Chemical Properties →

Reactions of $K_2Cr_2O_7$:



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

(i) Effect of heating : On heating strongly, it decomposes liberating oxygen.

$$\begin{tikzcd}
\boxed{\underset{\text{(Orange)}}{Cr_2O_7^{-2}}} \arrow[r, "\Delta"] \arrow[dr, "2KOH"'] & 2K_2CrO_4 + Cr_2O_3 + \frac{3}{2}O_2 \\
& \underset{\text{(yellow)}}{2CrO_4^{2-} + H_2O}
\end{tikzcd}$$

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

CrO_4^{2-} and $Cr_2O_7^{2-}$ exist in equilibrium and are interconvertable by altering the pH of solution.
In alkaline solution, chromate ions are present while in acidic solution, dichromate ions are present.

Chrome alum preparation →

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 + 23H_2O \xrightarrow{T<70°C} K_2SO_4.Cr_2(SO_4)_3.24H_2O$$

Oxidizes ethyl alcohol to acetaldehyde to acetic acid

→ $C_2H_5OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH$

→ It also oxidizes nitrites to nitrates, arsenates to arsenates, HBr to Br_2, HI to I_2 etc.

→ $K_2Cr_2O_7 + 2C(\text{Charcoal}) \xrightarrow[\Delta]{} Cr_2O_3 + K_2CO_3 + CO$

Chromyl chloride test :

$$\begin{tikzcd}
2Cl^- + \frac{1}{2}Cr_2O_7^{2-} + 3H^+ \arrow[r] & \boxed{\underset{\text{(deep red)}}{CrO_2Cl_2}} \arrow[d, "4OH^-"] & \\
& \underset{\text{(yellow)}}{CrO_4^{2-}} + 2Cl^- + 2H_2O \arrow[d, "Pb^{+2}"] & \\
& \underset{\text{(yellow)}}{PbCrO_4\downarrow} &
\end{tikzcd}$$

Reaction of potassium dichromate with Ag^+ -

$$\begin{tikzcd}
2BaCrO_4\downarrow + 2H^+ & \boxed{\underset{\text{(conc.)}}{Cr_2O_7^{2-}}} \arrow[l, "Ba^{2+} + H_2O"', "\text{Partial precipitation}"] \arrow[r, "2Ag^+"] & \underset{\text{(reddish brown)}}{Ag_2Cr_2O_7\downarrow} \arrow[d, "H_2O"', "\text{boil}"] \\
& & Ag_2CrO_4\downarrow + CrO_4^{2-} + 2H^+
\end{tikzcd}$$

$$Cr_2O_7^{2-} + Ba^{2+} + H_2O \rightleftharpoons 2BaCrO_4\downarrow + 2H^+$$

As strong acid is produced, the precipitation is only partial. But if NaOH or CH_3COONa is added, precipitate becomes quantitative.

Uses : It is used :

(i) as a volumetric reagent in the estimation of reducing agents such as oxalic acid, ferrous ions, iodide ions, etc. It is used as a primary standard.

(ii) for the preparation of several chromium compounds such as chrome alum, chrome yellow, chrome red, zinc yellow, etc.

(iii) in dyeing, chrome tanning, calico printing, photography etc.

(iv) as a cleansing agent for glass ware in the form of chromic acid.

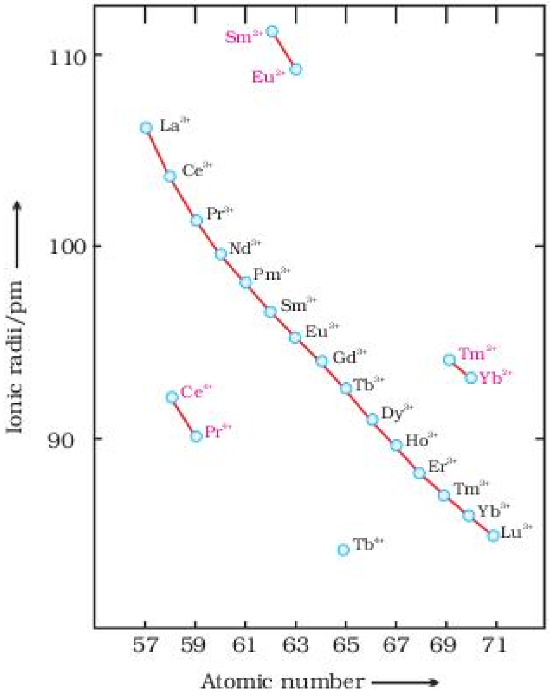
(v) in leather industry and as an oxidant for preparation of azo compounds.

<table>
<tr><th colspan="3">NCERT **f-block elements (JEE-Mains only)**</th></tr>
<tr><td colspan="3">**Differentiating electrons enters in (n – 2)f subshell.**
f-block elements lie on the Bottom portion of periodic table.</td></tr>
<tr><th>S.No.</th><th>Properties</th><th>DISCRIPTION</th></tr>
<tr><td>**1.**</td><td>**General character's**</td><td>All the f-block elements are heavy metals.
It shows high melting and boiling point.
The most common oxidation state of these elements is +3.</td></tr>
<tr><td>**2.**</td><td>**No. of elements**</td><td>Total number of f-block elements – (28)</td></tr>
<tr><td>**3.**</td><td>**Groups**</td><td>IIIB/3rd group is called longest group having 32 elements including 14 Lanthanides and 14 Actinides.
<table>
<tr><td>III B/ 3rd</td><td></td></tr>
<tr><td>Sc</td><td></td></tr>
<tr><td>Y</td><td></td></tr>
<tr><td>La</td><td>Lanthanides (14) Ce_{58} – Lu_{71}</td></tr>
<tr><td>Ac</td><td>Actinides (14) Th_{90} – Lr_{103}</td></tr>
</table></td></tr>
<tr><td>**4.**</td><td>**E.C.**</td><td>Lanthanide series $4f^{1-14}\,5d^{0\text{ or }1}\,6s^{2}$
Actinide series $5f^{1-14}\,6d^{0\text{ or }1}\,7s^{2}$</td></tr>
<tr><td>**5.**</td><td>**Period**</td><td>
<table>
<tr><th>Period</th><th>III B/ 3rd</th><th></th></tr>
<tr><td></td><td>Sc</td><td></td></tr>
<tr><td></td><td>Y</td><td></td></tr>
<tr><td>6th period</td><td>La</td><td>Lanthanides (14) Ce_{58} – Lu_{71}</td></tr>
<tr><td>7th period</td><td>Ac</td><td>Actinides (14) Th_{90} – Lr_{103}</td></tr>
</table></td></tr>
<tr><td>**6.**</td><td>**Inner transition elements**</td><td>The elements in which all the three shells that is ultimate (n) penultimate (n– 1) and pre or antipenultimate (n – 2) shell are incomplete are called inner transition elements.Ce_{58} = [Xe] $6s^2$, $5d^1$, $4f^1$
Inner transition elements are divided into two series.</td></tr>
<tr><td></td><td>**(i) Lanthanide series or Rare earth elements or Lanthenones**</td><td>Ce_{58} – Lu_{71} 14 elements
Lanthanides are found rarely on earth so these are called rare earth metals.
The first element of this series is Cerium and not Lanthanum.
In these elements, last electron enters into 4f subshell.
They are present in IIIB group and 6th period of the periodic table.
Promethium ($_{61}Pm$) is the only lanthanide which is synthetic and radioactive in nature.</td></tr>
<tr><td></td><td>**(ii) Actinide series or Man made elements or Actinones**</td><td>Th_{90} – Lr_{103} 14 elements.
All the actinides are radioactive elements.
The first element of this series is Thorium and not Actinium.
In these elements, last electron enters into 5f subshell.
They are present in IIIB group and 7th period of the periodic table.
All the actinides are radioactive in nature.
First three elements (Th, Pa, U) are found in nature while others are synthetic in nature.
Transuranic actinides are man-made elements (Np_{93} – Lw_{103})
After U_{92} i.e. from Np_{93} onwards elements are called transuranic elements because
(i) They are heavier than uranium.
(ii) They are derived from uranium by nuclear reactions.</td></tr>
</table>

The Lanthanides : The names, symbols, electronic configurations of atomic and some ionic states and atomic and ionic radii of lanthanum and lanthanide (for which the general symbol Ln is used) are given in Table.

Electronic Configurations : It may be noted that atoms of these elements have electronic configuration with $6s^2$ common but with variable occupancy of 4f level (Table). However, the electronic configurations of all the tripositive ions (the most stable oxidation state of all the lanthanides) are of the form $4f^n$ (n = 1 to 14 with increasing atomic number).

Atomic and Ionic Sizes : The overall decrease in atomic and ionic radii from lanthanum to lutetium (the lanthanide contraction). The shielding of one 4 f electron by another is less than one d electron by another with the increase in nuclear charge along the series. There is fairly regular decrease in the sizes with increasing atomic number. The cumulative effect of the contraction of the lanthanide series, known as lanthanide contraction, causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanide contraction.



Oxidation States : In the lanthanides, La(III) and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained.

This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or filled f subshell. Thus, the formation of Ce^{IV} is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The $E^{\ominus}$ value for Ce^{4+}/Ce^{3+} is + 1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent.

Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO_2. Eu^{2+} is formed by losing the two s electrons and its f^7 configuration accounts for the formation of this ion.

However, Eu^{2+} is a strong reducing agent changing to the common +3 state. Similarly Yb^{2+} which has f 14 configuration is a reductant.

Tb^{IV} has half-filled f-orbitals and is an oxidant. The behaviour of samarium is very much like europium, exhibiting both +2 and +3 oxidation states.

Table :- Electronic Configurations and Radii of Lanthanum and Lanthanides

Atomic Number	Name	symbol	Electronic configurations*				Radii/pm	
			Ln	Ln^{2+}	Ln^{3+}	Ln^{4+}	Ln	Ln^{3+}
57	Lanthanum	La	$5d^16s^2$	$5d^1$	$4f^0$		187	106
58	Cerium	Ce	$4f^15d^16s^2$	$4f^2$	$4f^1$	$4f^0$	183	103
59	Praseodymium	Pr	$4f^36s^2$	$4f^3$	$4f^2$	$4f^1$	182	101
60	Neodymium	Nd	$4f^46s^2$	$4f^4$	$4f^3$	$4f^2$	181	99
61	Promethium	Pm	$4f^56s^2$	$4f^5$	$4f^4$		181	98
62	Samarium	Sm	$4f^66s^2$	$4f^6$	$4f^5$		180	96
63	Europium	Eu	$4f^76f^2$	$4f^7$	$4f^6$		199	95
64	Gadolinium	Gd	$4f^75d^16s^2$	$4f^75d^1$	$4f^7$		180	94
65	Terbium	Tb	$4f^96s^2$	$4f^9$	$4f^8$	$4f^7$	178	92
66	Dysprosium	Dy	$4f^{10}6s^2$	$4f^{10}$	$4f^9$	$4f^8$	177	91
67	Holmium	Ho	$4f^{11}6s^2$	$4f^{11}$	$4f^{10}$		176	89
68	Erbium	Er	$4f^{12}6s^2$	$4f^{12}$	$4f^{11}$		175	88
69	Thulium	Tm	$4f^{13}6s^2$	$4f^{13}$	$4f^{12}$		174	87
70	Ytterbium	Yb	$4f^{14}6s^2$	$4f^{14}$	$4f^{13}$		173	86
71	Lutetium	Lu	$4f^{14}5d^16s^2$	$4f^{14}5d^1$	$4f^{14}$	-	-	-

General Characteristics :

All the lanthanides are silvery white soft metals and tarnish rapidly in air.

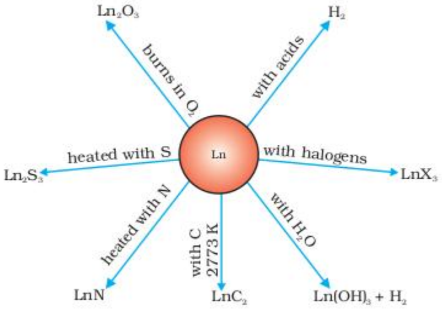
The hardness increases with increasing atomic number, samarium being steel hard.

Their melting points range between 1000 to 1200 K but samarium melts at 1623 K.

They have typical metallic structure and are good conductors of heat and electricity. Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm.

Many trivalent lanthanide ions are coloured both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the presence of f electrons. Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so. However, absorption bands are narrow, probably because of the excitation within f level.

The lanthanide ions other than the f° type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism rises to maximum in neodymium.



The first ionisation enthalpies of the lanthanides are around 600 kJ mol^{-1}, the second about 1200 kJ mol^{-1} comparable with those of calcium.

A detailed discussion of the variation of the third ionisation enthalpies indicates that the exchange enthalpy consideration (as in 3d orbitals of the first transition series), appear to impart a certain degree of stability to empty, half-filled and completely filled orbitals f level. This is indicated from the abnormally low value of the third ionization enthalpy of lanthanum, gadolinium and lutetium.

In their chemical behaviour, in general, the earlier members of the series are quite reactive similar to calcium but, with increasing atomic number, they behave more like aluminium.

Values for E^{-} for the half-reaction:

Ln^{3+} (aq) + $3e^{-} \rightarrow$ Ln(s) are in the range of –2.2 to –2.4 V except for Eu for which the value is – 2.0 V. This is, of course, a small variation.

The metals combine with hydrogen when gently heated in the gas.

The carbides, Ln_3C, Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon.

They liberate hydrogen from dilute acids and burn in halogens to form halides.

They form oxides M_2O_3 and hydroxides M $(OH)_3$. The hydroxides are definite compounds, not just hydrated oxides.

They are basic like alkaline earth metal oxides and hydroxides.

The best single use of the lanthanides is for the production of alloy steels for plates and pipes. A well known alloy is mischmetall which consists of a lanthanide metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A good deal of mischmetall is used in Mg-based alloy to produce bullets, shell and lighter flint. Mixed oxides of lanthanides are employed as catalysts in petroleum cracking. Some individual Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.

The Actinides :

The actinides include the fourteen elements from Th to Lr. The names, symbols and some properties of these elements are given in Table.

Table : Electronic Configurations and Radii of Actinium and Actinoids

Atomic Number	Name	symbol	Electronic configurations*			Radii/pm	
			M	M^{3+}	M^{4+}	M^{3+}	M^{4+}
89	Actinium	Ac	$6d^17s^2$	$5f^0$		111	
90	Thorium	Th	$6d^27s^2$	$5f^1$	$5f^0$		99
91	Proctactiniium	Pa	$5f^26d^17s^2$	$5f^2$	$5f^1$		96
92	Uranium	U	$5f^36d^17s^2$	$5f^3$	$5f^2$	103	93
93	Neptunium	Np	$5f^46d^17s^2$	$5f^4$	$5f^3$	101	92
94	Plutonium	Pu	$5f^67s^2$	$5f^5$	$5f^4$	100	90
95	Americium	Am	$5f^77s^2$	$5f^6$	$5f^5$	99	89
96	Curium	Cm	$5f^76d^17s^2$	$5f^7$	$5f^7$	99	88

97	Berkelium	Bk	$5f^9 7s^2$	$5f^8$	$5f^7$	98	87
98	Californium	Cf	$5f^{10} 7s^2$	$5f^9$	$5f^8$	98	86
99	Einstenium	Es	$5f^{11} 7s^2$	$5f^{10}$	$5f^9$	-	-
100	Fermium	Fm	$5f^{12} 7s^2$	$5f^{11}$	$5f^{10}$	-	-
101	Mendelevium	Md	$5f^{13} 7s^2$	$5f^{12}$	$5f^{11}$	-	-
102	Nobelium	No	$5f^{14} 7s^2$	$5f^{13}$	$5f^{12}$	-	-
103	Lawrencium	Lr	$5f^{14} 6s^1 7s^2$	$5f^{14}$	$5f^{13}$	-	-

The actinides are radioactive elements and the earlier members have relatively long half-lives, the latter ones have half-life values ranging from a day to 3 minutes for lawrencium (Z =103). The latter members could be prepared only in nanogram quantities. These facts render their study more difficult.

Electronic Configurations :

All the actinides are believed to have the electronic configuration of $7s^2$ and variable occupancy of the 5f and 6d subshells.

The fourteen electrons are formally added to 5f, though not in thorium (Z = 90) but from Pa onwards the 5f orbitals are complete at element 103.

The irregularities in the electronic configurations of the actinides, like those in the lanthanides are related to the stabilities of the f° , f^7 and f^{14} occupancies of the 5f orbitals. Thus, the configurations of Am and Cm are [Rn] $5f^7 7s^2$ and [Rn] $5f^7\ 6d^1\ 7s^2$.

Although the 5f orbitals resemble the 4f orbitals in their angular part of the wave-function, they are not as buried as 4f orbitals and hence 5f electrons can participate in bonding to a far greater extent.

Ionic Sizes :

The general trend in lanthanides is observable in the actinides as well. There is a gradual decrease in the size of atoms or M^{3+} ions across the series. This may be referred to as the actinide contraction (like lanthanide contraction). The contraction is, however, greater from element to element in this series resulting from poor shielding by 5f electrons.

Oxidation States :

There is a greater range of oxidation states, which is in part attributed to the fact that the 5f, 6d and 7s levels are of comparable energies. The known oxidation states of actinides are listed in Table.

Table : Oxidation States of Actinium and Actinides

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

The actinides show in general +3 oxidation state.

The elements, in the first half of the series frequently exhibit higher oxidation states. For example, the maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements.

The actinides resemble the lanthanides in having more compounds in +3 state than in the +4 state. However, +3 and +4 ions tend to hydrolyse.

Because the distribution of oxidation states among the actinides is so uneven and so different for the earlier and latter elements, it is unsatisfactory to review their chemistry in terms of oxidation states.

General Characteristics and Comparison with Lanthanides :

The actinide metals are all silvery in appearance but display a variety of structures. The structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanides.

The actinides are highly reactive metals, especially when finely divided. The action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most non metals takes place at moderate temperatures. Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers; alkalies have no action.

The magnetic properties of the actinides are more complex than those of the lanthanides. Although the variation in the magnetic susceptibility of the actinides with the number of unpaired 5 f electrons is roughly parallel to the corresponding results for the lanthanides, the latter have higher values.

It is evident from the behaviour of the actinides that the ionisation enthalpies of the early actinides, though not accurately known, but are lower than for the early lanthanides. This is quite reasonable since it is to be expected that when 5f orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The 5f electrons, will therefore, be more effectively shielded from the nuclear charge than the 4f electrons of the corresponding lanthanides. Because the outer electrons are less firmly held, they are available for bonding in the actinides.

A comparison of the actinides with the lanthanides, with respect to different characteristics as discussed above, reveals that behaviour similar to that of the lanthanides is not evident until the second half of the actinide series. However, even the early actinides resemble the lanthanides in showing close similarities with each other and in gradual variation in properties which do not entail change in oxidation state. The lanthanide and actinide contractions, have extended effects on the sizes, and therefore, the properties of the elements succeeding them in their respective periods. The lanthanide contraction is more important because the chemistry of elements succeeding the actinides are much less known at the present time.

Some Applications of d- and f-Block Elements :

Iron and steels are the most important construction materials. Their production is based on the reduction of iron oxides, the removal of impurities and the addition of carbon and alloying metals such as Cr, Mn and Ni.

TiO for the pigment industry and MnO_2 for use in dry battery cells. The battery industry also requires Zn and Ni/Cd.

The 'silver' UK coins are a Cu/Ni alloy.

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. **Among the following statements choose the true or false statement(s).**

(a) $K_2Cr_2O_7$ on heating with charcoal gives metallic potassium and Cr_2O_3.

(b) On heating in current of H_2 the crystalline $KMnO_4$ is converted into KOH and Mn_3O_4.

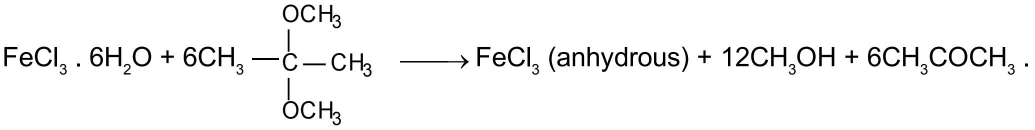
(c) Hydrated ferric chloride on treatment with 2, 2–dimethoxypropane gives anhydrous ferric chloride.

Ans. **(a)** False **(b)** False **(c)** True

Sol. **(a)** $K_2Cr_2O_7 + 2C \text{ (charcoal)} \xrightarrow{\Delta} Cr_2O_3 + K_2CO_3 + CO\uparrow$.

(b) $2KMnO_4 + 5H_2 \xrightarrow{\Delta} 2\,KOH + 2MnO + 4H_2O$.

(c)



$$FeCl_3\,.\,6H_2O + 6CH_3-\overset{OCH_3}{\underset{OCH_3}{C}}-CH_3 \longrightarrow FeCl_3\text{ (anhydrous)} + 12CH_3OH + 6CH_3COCH_3\,.$$

2. A compound (A) is used in paints instead of salts of lead. Compound (A) is obtained when a white compound (B) is strongly heated. Compound (B) is insoluble in water but dissolves in sodium hydroxide forming a solution of compound (C). The compound (A) on heating with coke gives a metal (D) and a gas (E) which burns with blue flame. (B) also dissolves in ammonium sulphate solution mixed with ammonium hydroxide. Solution of compound (A) in dilute HCl gives a bluish white / white precipitate (F) with excess of $K_4[Fe(CN)_6]$. Identify (A) to (F) and explain the reactions.

Ans. (A) ZnO, (B) $\xrightarrow{\Delta}$ $Zn(OH)_2$, (C) Na_2ZnO_2 , (D) Zn, (E) CO, (F) $K_2Zn_3\,[Fe(CN)_6]_2$

Sol. $Zn(OH)_2$ (B) ZnO (A) + H_2O.

$Zn(OH)_2\text{ (B)}\downarrow + 2OH^- \longrightarrow [Zn(OH)_4]^{2-}$ (C) (soluble complex).

ZnO (A) + C $\xrightarrow{\Delta}$ Zn (D) + CO (E).

$Zn(OH)_2\text{ (B)} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$ (soluble complex) + $2OH^-$.

$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$.

$3ZnCl_2 + 2K_4[Fe(CN)_6] \longrightarrow K_2Zn_3[Fe(CN)_6]_2\downarrow$ (bluish white/white) (F) + 6KCl.

3. An unknown inorganic compound (X) gave the following reactions:

(i) The compound (X) on heating gave a residue, oxygen and oxide of nitrogen.

(ii) An aqueous solution of compound (X) on addition to tap water gave a turbidity which did not dissolve in HNO_3.

(iii) The turbidity dissolves in NH_4OH.

Identify the compound (X) and give equations for the reactions (i), (ii) & (iii).

Ans. $X = AgNO_3$

Sol. $2AgNO_3\ (X) \xrightarrow{\Delta} 2\ Ag + 2NO_2 + O_2$.

$AgNO_3\ (aq.) + Cl^- \longrightarrow AgCl \downarrow$ (white) $+ NO_3^-$.

$AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2]^+$ (soluble complex).

4. Amongst $[TiF_6]^{2-}$, $[CoF_6]^{3-}$, $Cu_2\,Cl_2$ and $[NiCl_4]^{2-}$ [Atomic number ; Ti = 22, Co = 27, Cu = 29, Ni = 28] the colourless species are :

(A) $[TiF_6]^{2-}$ and $[Cu_2Cl_2]$ (B) Cu_2Cl_2 and $[NiCl_4]^{2-}$ (C) $[TiF_6]^{2-}$ and $[CoF_6]^{3-}$ (D) $[CoF_6]^{3-}$ and $[NiCl_4]^{2-}$

Ans. (A)

Sol. In $[TiF_6]^{2-}$ the titanium is in +4 oxidation state having the electronic configuration $[Ar]^{18}\,3d^0\,4s^0$. Similarly in Cu_2Cl_2 the copper is in +1 oxidation state having the electronic configuration $[Ar]^{18}\,3d^{10}\,4s^0$. As they do not have any unpaired electrons for d-d transition, they are therefore colourless.

In $[NiCl_4]^{2-}$ the nickel is in +2 oxidation state and electronic configuration is $[Ar]^{18}\,3d^8\,4s^0$. As it has two unpaired electrons, so the complex is coloured.

In $[CoF_6]^{3-}$, the cobalt is in +3 oxidation state having electron configuration [Ar] $3d^6\,4s^0$. As it has four unpaired electrons, so the complex is coloured.

5. On the basis of trends in the properties of the 3d-series elements, suggests possible M^{2+} aqua ions for use as reducing agents, and write a balanced chemical equation for the reaction of one of these ions with O_2 in acidic solution.

Sol. Because oxidation state +2 is most stable for the later elements of 3d-series elements, strong reducing agents include ions of the metals on the left of the series: such ions include V^{2+} (aq) and Cr^{2+} (aq) The Fe^{2+} (aq) ion is only weakly reducing. The Co^{2+} (aq), Ni^{2+} (aq), and Cu^{2+} (aq) ions are not oxidized in water.

$$Fe^{3+} \xrightarrow{+0.77} Fe^{2+} \xrightarrow{-0.44} Fe$$

The chemical equation for the oxidation is then

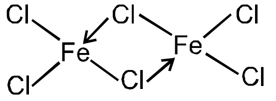
$$4\ Fe^{2+}\ (aq) + O_2(g) + 4H^+\ (aq) \longrightarrow 4Fe^{3+}\ (aq) + 2H_2O\ (\ell).$$

6. **Match the reactions given in column-I with the characteristic(s) of the reaction products given in column-II.**

	Column-I		**Column-II**
(A)	$TiCl_4 \xrightarrow{Zn}$	(p)	One of the products is bright orange coloured but diamagnetic.
(B)	$FeCl_3 \xrightarrow{573K}$	(q)	One of the products is green coloured and paramagnetic.
(C)	$KMnO_4 \xrightarrow{750K}$	(r)	One of the products is violet and paramagnetic.
(D)	$K_2Cr_2O_7 + H_2SO_4$ (cold & conc.)	(s)	One of the products exists as dimer.

Ans. [A – r] ; [B – s ; [C – q] ; [D – p].

Sol. (A) $TiCl_4 \xrightarrow{Zn} TiCl_3$, violet (one unpaired electron so d-d transition is possible).

(B) $2FeCl_3 \xrightarrow{573K}$  gas dimer.

(C) $2KMnO_4$ $K_2MnO_4 \xrightarrow{750K}$ green (one unpaired electron so d-d transition is possible) + $MnO_2 + O_2$.

(D) $K_2Cr_2O_7 + 2H_2SO_4$ $2CrO_3 \longrightarrow$ bright orange (diamagnetic) + $2KHSO_4 + H_2O$.

7. Which of the following is true for the species having $3d^4$ configuration ?

(A) Cr^{2+} is reducing in nature. (B) Mn^{3+} is oxidising in nature.

(C) Both (A) and (B) (D) None of these

Sol. Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a half-filled t^3_{2g} energy level of 3d orbitals in octahedral crystal field spliting. On the other hand, the change from Mn^{3+} to Mn^{2+} results in the half-filled (d^5) configuration which has extra stability.

Therefore, (C) option is correct.

8. Which of the following increasing order of oxidising power is correct for the following species ?

VO_2^+, MnO_4^-, $Cr_2O_7^{2-}$

(A) $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$ (B) $VO_2^+ < MnO_4^- < Cr_2O_7^{2-}$

(C) $Cr_2O_7^{2-} < VO_2^+ < MnO_4^-$ (D) $Cr_2O_7^{2-} < MnO_4^- < VO_2^+$

Sol. This is attributed to the increasing stability of the lower species to which they are reduced.

MnO_4^- is reduced to Mn^{2+} which has stable half filled valence shell electron configuration [$3d^5$].

$Cr_2O_7^{2-}$ is reduced to Cr^{3+} which has half filled t^3_{2g} energy level of 3d orbitals in octahedral crystal field spliting

VO_2^+ is reduced to V^{3+} which has electronic configuration $[Ar]^{18}\ 3d^2\ 4s^0$.

So the order of increasing stability of the reduced species is $Mn^{2+} > Cr^{3+} > V^{3+}$ and, therefore, the increasing order of oxidising power is $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$.

Therefore, (A) option is correct.

9. Which of the following statement(s) is/are correct ?

(A) Transition metals and many of their compounds show paramagnetic behaviour.

(B) The enthalpies of atomisation of the transition metals are high

(C) The transition metals generally form coloured compounds

(D) Transition metals and their many compounds act as good catalyst.

Sol. (A) As metal ions generally contain one or more unpaired electrons in them & hence their complexes are generally paramagnetic.

(B) Because of having larger number of unpaired electrons in their atoms, they have stronger inter atomic interaction and hence stronger bonding between the atoms.

(C) According to CFT, in presence of ligands the colour of the compound is due to the d-d transition of the electrons.

(D) This activity is ascribed to their ability to adopt multiple oxidation state and to form complexes.

Therefore, (A,B,C,D) options are correct.

10. When CO_2 is passed into aqueous :

(A) Na_2CrO_4 solution, its yellow colour changes to orange.

(B) K_2MnO_4 solution, it disproportionates to $KMnO_4$ and MnO_2.

(C) $Na_2Cr_2O_7$ solution, its orange colour changes to green.

(D) $KMnO_4$ solution, its pink colour changes to green.

Sol. (A) $Na_2CrO_4 \xrightarrow{H^+} Na_2Cr_2O_7$ (orange colour)

(B) $MnO_4^{2-} \xrightarrow{H^+} MnO_4^- + MnO_2$, in neutral or acidic medium

(C) False - In acidic medium no colour change takes place.

(D) $MnO_4^- + e^- \xrightarrow{OH^-} MnO_4^{2-}$; in strong alkaline medium pink colour of $KMnO_4$ changes to green.

Therefore, (A,B) options are correct.

11. Which of the following statement(s) is (are) not correct with reference to **ferrous** and **ferric** ions

(A) Fe^{3+} gives brown colour with potassium ferricyanide

(B) Fe^{2+} gives blue precipitate with potassium ferricyanide

(C) Fe^{3+} gives red colour with potassium sulphocyanide

(D) Fe^{2+} gives brown colour with potassium sulphocyanide

Sol. Fe^{3+} produces red colouration with KSCN but Fe^{2+} does not give brown colour with KSCN.

Therefore, (D) option is correct.

12. **Statement-1 :** Ammonical silver nitrate converts glucose to gluconic acid and metallic silver is precipitated.
Statement-2 : Glucose acts as a weak reducing agent.
(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(C) Statement-1 is True, Statement-2 is False
(D) Statement-1 is False, Statement-2 is True

Sol. **(A)** $Ag_2O + C_6H_{12}O_6 \rightarrow 2Ag + C_6H_{12}O_7$.

13. **Statement-1 :** The number of unpaired electrons in the following gaseous ions Mn^{3+}, Cr^{3+}, V^{3+} and Ti^{3+} are 4, 3, 2 and 1 respectively.
Statement-2 : Cr^{3+} is most stable in aqueous solution among these ions.
(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(C) Statement-1 is True, Statement-2 is False
(D) Statement-1 is False, Statement-2 is True

Sol. **(B)** $Mn^{3+} = [Ar]^{18}\ 3d^4$, $Cr^{+3} = [Ar]^{18}\ 3d^3$, $V^{3+} = [Ar]^{18}\ 3d^2$, $Ti^{3+} = [Ar]^{18}\ 3d^1$
Cr^{3+} is most stable in aqueous solution because it has half filled t^3_{2g} energy level of 3d orbitals in octahedral crystal field spliting and according to crystal field theory (CFT) it has highest value of CFSE i.e. $1.2\ \Delta_O$.

14. $\mathbf{S_1}$ **:** Interstitial compounds have high melting points, higher than those of pure metals.
$\mathbf{S_2}$ **:** Permanganate titrations in presence of hydrochloric acid are unsatisfactory.
$\mathbf{S_3}$ **:** $KMnO_4$ does not act as an oxidising agent in strong alkaline medium.
$\mathbf{S_4}$ **:** $KMnO_4$ on heating in a current of H_2 gives MnO.
(A) T T F T (B) T F F T (C) T F T T (D) F F T F

Sol. $\mathbf{S_1}$ **:** Due to strong interatomic forces.
$\mathbf{S_2}$ **:** Some of the hydrochloric acid is oxidised to chlorine and thus we get less volume of $KMnO_4$ than the actual one.
$\mathbf{S_3}$ **:** $MnO_4^- + e^- \xrightarrow{OH^-} MnO_4^{2-}$
$\mathbf{S_4}$ **:** $2KMnO_4 + 5H_2 \longrightarrow 2KOH + 2MnO + H_2O$.
Therefore, (A) option is correct.

15. Match the reactions in **Column I** with nature of the reactions/type of the products in **Column II**.

Column I	**Column II**
(A) $AgNO_3(aq) + I_2$ (excess) $+ H_2O \longrightarrow$	(p) Disproportionation
(B) $K_2MnO_4(aq) + CO_2(g) \longrightarrow$	(q) Comproportionation
(C) $Na_2Cr_2O_7 + C \xrightarrow{\Delta}$	(r) Redox
(D) $CuCl_2(aq) + Cu(s) \longrightarrow$	(s) One of the products is insoluble in water

Ans. (A → p, r, s) ; (B → p, r, s) ; (C → r, s) : (D → q, r, s)

Sol. (A) $5AgNO_3(aq) + 3\overset{0}{I}_2$ (excess) $+ 3H_2O \longrightarrow \overset{+V}{HIO_3} + 5\overset{-1}{AgI} + 5HNO_3$
So it is redox and disproportionation reaction. AgI insoluble in water.

(B) $3K_2\overset{+VI}{MnO_4}$ (aq) $+ 2CO_2(g) \longrightarrow \overset{+VII}{2KMnO_4} + \overset{+IV}{MnO_2} + 2K_2CO_3$
So it is redox and disproportionation reaction. MnO_2 insoluble in water.

(C) $\overset{0}{2C} + Na_2\overset{+VI}{Cr_2}O_7 \xrightarrow{\Delta} \overset{+III}{Cr_2}O_3 + Na_2\overset{+IV}{C}O_3 + \overset{+II}{CO}\uparrow$
So it is redox reaction. Cr_2O_3 (green pigment) is insoluble in water.

(D) $\overset{+II}{CuCl_2}$ (aq) $+ \overset{0}{Cu}$ (s) $\longrightarrow \overset{+I}{Cu_2Cl_2}$ (s)
So it is redox and comproportionation reaction. Cu_2Cl_2 is insoluble in water.

16. What is the composition of mischmetal alloy and what are it's uses ?

Ans. Mischmetal consists of lanthanoid metal (~95%) and iron (~5%) and traces of S,C,Ca and Al. Mischmetal is used in Mg based alloy to produce bullets, shell and lighter flint.

Exercise # 1

✍ **Marked Questions may have for Revision Questions.**

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Periodic trends

A-1._ What are the two most common oxidation states of the first transition series?

A-2.✍ Why are ionization energies of 5d-elements greater then those of 3d-elements ?

Section (B) : Chemical Bonding

B-1._ Draw the structures of $Cr_2O_7^{2-}$,MnO_4^-, MnO_4^{2-}

B-2._ Why Zn has lowest metallic bond strength amongst 3d series elements ?

B-3._ Write the increasing order of acidic nature of V_2O_3,V_2O_4, V_2O_5

B-4._✍ Which is more basic $Fe(OH)_2$ or $Fe(OH)_3$?

Section (C) : Properties of elements

C-1.✍ Which of the following ions would form (i) coloured and (ii) colourless complexes in water ?
Cu^{2+}, Zn^{2+}, Ti^{3+}, Ti^{+4}, Cd^{2+}, Mn^{2+}

C-2. Copper dissolves in dilute nitric acid but not in dilute HCl. Why?

C-3._✍ Which of the following element dissolve in hot concentrated NaOH solution?
Fe, Zn, Cu, Ag

C-4._ Silver jewellery items tarnish slowly in the air due to their reactions with______&______.

Section (D) : Oxides & Hydroxides

D-1._ Give the reaction for the preparation of ferric oxide from hydrated ferrous sulphate.

D-2. How do you prepare Ag_2O from $AgNO_3$? Explain with the help of chemical reaction.

D-3._ The precipiate of $Zn(OH)_2$ dissolves in the following reagents- potassium cyanide, ammonia and sodium hydroxide. Explain with the help of reactions.

D-4. What happens when :
(a) Zinc oxide and cobalt oxide is fused.
(b) Lunar caustic is made to react with sodium hydroxide and then the product is dried.
(c) $Cu(OH)_2 + NH_3{\cdot}H_2O + (NH_4)_2SO_4 \longrightarrow$

Section (E) : Sulphates and Nitrates

E-1. What happens when :
(a) Green vitriol is strongly heated.
(b) $FeSO_4$ reacts with potassium ferricyanide.
(c) Malachite is made to react with dilute H_2SO_4.
(d) Copper sulphate pentahydrate is exposed to air for a longer period.

E-2. Complete and balance the given reaction : $FeSO_4 + H_2O + O_2 \longrightarrow$

E-3.✍ What happens when silver nitrate solution is added to $Na_2S_2O_3$ solution and then content is allowed to keep for a longer period ?

E-4. Why does $AgNO_3$ produce a black stain on the skin ?

E-5. Copper sulphate dissolves in $NH_3.H_2O$ solution but $FeSO_4$ does not why?

Section (F) : Halides

F-1.✍ The aqueous solution of $FeCl_3$ is acidic. Why?

F-2.✍ Cuprous chloride is insoluble in water and dilute HCl but dissolves in concentrated HCl.

F-3._✍ The species $[CuCl_4]^{2-}$ exists but $[CuI_4]^{2-}$ does not. Why?

F-4.✍ Why is AgBr used in photography ?

F-5. What happens when :

(a) Gold is dissolved in aqua regia ? (b) $CuCl_2 . 2H_2O \xrightarrow[\text{strong}]{\Delta}$

F-6._✍ Anhydrous $FeCl_3$ cannot be obtained by heating hydrated ferric chloride. Explain

F-7. Although Cu^+ does not exist in solution state, but $CuCl_{(s)}$ is formed in presence of Cl^- ions in aqueous solution of $Cu_{(s)}$ and Cu^{2+}.

Section (G) : Miscellaneous

G-1. Complete and balance the following reactions :

(a) $KMnO_4 + Na_2S_2O_3 + H_2O \longrightarrow$ (b) $K_2Cr_2O_7 + H_2SO_4 + SO_2 + H_2O \xrightarrow{\text{Tempt} < 70°C}$
(c) $Fe(III) + 3NH_4SCN \longrightarrow$

G-2.✍ Which type of reaction MnO_4^{2-} shows with acid, dilute-alkali or water ?

G-3.✍ Why it is not advisable to dissolve $KMnO_4$ in cold and concentrated H_2SO_4?

G-4. State true or false : Reaction of $K_2Cr_2O_7$ with cold and concentrated H_2SO_4 yields bright orange/red precipitate of CrO_3. Write reactions involved.

Section (H) : f-block elements

H-1. Actinoid contraction is greater from element to element than lanthanide contraction. Why ?

H-2.✍ Why Sm^{2+}, Eu^{2+} and Yb^{2+} ions in solutions are good reducing agents but an aqueous solution of Ce^{4+} is a good oxidizing agent ?

PART - II : OBJECTIVE TYPE QUESTIONS

Section (A) : Periodic trends

A-1.✍ First IE of 5d series elements are generally higher than those of 3d and 4d series elements. This is due to :
(A) bigger size of atoms of 5d-series elements than 3d-series elements.
(B) greater effective nuclear charge is experienced by valence electrons because of the weak shielding of the nucleus by 4f-electrons in 5d series.
(C) (A) and (B) both.
(D) None of these.

Section (B) : Chemical Bonding

B-1._ Which of the following d-block elements has lowest probable interatomic forces ?
(A) Mercury (B) Chromium (C) Iron (D) Zinc

B-2._ Which is the strongest oxidising agent ?
(A) $KMnO_4$ in acidic medium (B) Mn^{+2} in acidic medium
(C) $K_2Cr_2O_7$ in acidic medium (D) Cr^{+3} in acidic medium.

Section (C) : Properties of elements

C-1. Which one of the ionic species will impart colour to an aqueous solution ?
(A) Ti^{4+} (B) Cu^+ (C) Zn^{2+} (D) Cr^{3+}

C-2. When copper is placed in the atmosphere for sufficient time, a green crust is formed on its surface. The composition of the green crust is :
(A) $Cu(OH)_2$ (B) CuO (C) $CuCO_3$ (D) $CuCO_3.Cu(OH)_2$

C-3.✍ When same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide, the ratio of volume of hydrogen evolved is.
(A) 1 : 1 (B) 1 : 2 (C) 2 : 1 (D) 9 : 4

C-4.✍ Dilute H_2SO_4 dissolves Fe to produce :
(A) $FeSO_4$ and H_2 (B) $Fe_2(SO_4)_3$ and H_2O (C) SO_2 (D) H_2

C-5. Why is metallic iron harder than alkali metals ? Choose the best possible reason.
(A) Iron atoms are small. (B) Iron atoms are more closely packed
(C) Metallic bonds are stronger in alkali metals. (D) Metallic bonds are stronger in iron.

Section (D) : Oxides & Hydroxides

D-1._ Hot copper wire reacts with oxygen to produce :
(A) Cu_2O (B) CuO_2 (C) Cu_2O_2 (D) CuO.

D-2.✍ Which of the following oxides will not decompose to release oxygen on heating?
(A) CrO_3 (B) Cr_2O_3 (C) MnO_2 (D) Mn_2O_7

Section (E) : Sulphates and Nitrates

E-1. When $AgNO_3$ (aq) reacts with excess of iodine, we get :
(A) $AgIO_3$ (B) HIO_3 (C) AgO (D) HI

E-2.✍ The colour of light absorbed by an aqueous solution of $CuSO_4$ is :
(A) orange red (B) blue–green (C) yellow (D) violet

Section (F) : Halides

F-1. Anhydrous $FeCl_3$ is prepared by
(A) Heating hydrated ferric chloride at a high temperature in a stream of air.
(B) Heating metallic iron in a stream of dry chlorine gas
(C) Reaction of metallic iron with dilute hydrochloric acid
(D) Reaction of metallic iron with concentrated hydrochloric acid.

F-2.✍ VCl_5 undergoes hydrolysis with water and forms :
(A) $VOCl_2$ (B) $VOCl_3$ (C) $V(OH)_2$ (D) $[V(H_2O)_6]^{3+}$

F-3. FeI_3 is not known whereas $FeCl_3$ and $FeBr_3$ are known. Because -
(A) of larger size of I^- (B) of greater electronegativity of Cl and Br.
(C) Cl and Br are oxidising (D) I^- reduces Fe^{3+} to Fe^{2+}

F-4. $FeCl_3$ dissolves in :
(A) water (B) ether (C) ammonia (D) (A) and (B) both

F-5. The solubility of silver bromide in hypo solution (excess) is due to the formation of :
(A) Ag_2SO_3 (B) $Ag_2S_2O_3$ (C) $[Ag(S_2O_3)]^-$ (D) $[Ag(S_2O_3)_2]^{3-}$

F-6. The developer used in photography is an alkaline solution of :
(A) hydroquinol (B) glycerol (C) phenol (D) picric acid

Section (G) : Miscellaneous

G-1. $KMnO_4$ is the salt of :
(A) MnO_2 (B) Mn_2O_7 (C) MnO_3 (D) Mn_2O_3

G-2. Which of the following compounds is used as the starting material for the preparation of potassium dichromate?
(A) $K_2SO_4.Cr_2(SO_4)_3.24H_2O$ (chrome alum) (B) $PbCrO_4$ (chrome yellow)
(C) $FeCr_2O_4$ (chromite) (D) $PbCrO_4.PbO$ (chrome red)

G-3. When acidified solution of $K_2Cr_2O_7$ is shaken with aqueous solution of $FeSO_4$, then :
(A) $Cr_2O_7^{2-}$ ion is reduced to Cr^{3+} ions (B) $Cr_2O_7^{2-}$ ion is converted to CrO_4^{2-} ions
(C) $Cr_2O_7^{2-}$ ion is reduced to Cr (D) $Cr_2O_7^{2-}$ ion is converted to CrO_3

G-4. CrO_3 dissolves in aqueous NaOH to give :
(A) CrO_4^{2-} (B) $Cr(OH)_3$ (C) $Cr_2O_7^{2-}$ (D) $Cr(OH)_2$

G-5. A compound is yellow when hot and white when cold. The compound is :
(A) Al_2O_3 (B) PbO (C) CaO (D) ZnO

G-6.✍ The product of oxidation of I^- with MnO_4^- in alkaline medium is
(A) IO_3^- (B) I_2 (C) IO^- (D) IO_4^-

G-7._ $Cr_2O_7^{2-} \underset{y}{\overset{x}{\rightleftharpoons}} 2CrO_4^{2-}$, x and y are respectively.
(A) $x = OH^-, y = H^+$ (B) $x = H^+, y = OH^-$ (C) $x = OH^-, y = H_2O_2$ (D) $x = H_2O_2, y = OH^-$

Section (H) : f-block elements

H-1. The f-block of the periodic table contains those elements in which :
(A) only 4f orbitals are progressively filled in 6th period.
(B) only 5f orbitals are progressively filled in 7th period.
(C) 4f and 5f orbitals are progressively filled in 6th and 7th periods respectively.
(D) none

H-2. Among the lanthanide the one obtained by synthetic method is :
(A) Lu (B) Pm (C) Pr (D) Gd

H-3.✍ Across the lanthanide series, the basicity of the lanthanide hydroxides :
(A) increases (B) decreases
(C) first increases and then decreases (D) does not change

H-4. The +3 ion of which one of the following has half filled 4f subshell ?
(A) La (57) (B) Lu (71) (C) Gd (64) (D) Pr (59)

H-5. The lanthonoide contraction is reponsible for the fact that
(A) Zr and Y have about the same radius (B) Zr and Nb have similar oxidation state
(C) Zr and Hf have about the same radius (D) Zr and Ce have the same oxidation state

PART - III : MATCH THE COLUMN

1. Match the salts/mixtures listed in column(I) with their respective name listed in column(II).

Column - I	**Column - II**
(A) $K_2SO_4.Cr_2(SO_4)_3.24H_2O$	(p) Blue vitriol
(B) $FeSO_4\ (NH_4)_2SO_4.\ 6H_2O$	(q) Green vitriol
(C) $CuSO_4.5H_2O$	(r) chrome alum
(D) $FeSO_4.7H_2O$	(s) Mohr's salt

2. Match the pairs of complexes/compounds listed in column(I) with the characteristic(s) of the reaction products listed in column(II).

Column - I	**Column - II**
(A) Cu(I) and Zn(II) complexes	(p) Pair of compounds having similar colour and same but non-zero magnetic moment.
(B) $KMnO_4$ and $K_2Cr_2O_7$	(q) Pair of compounds which are diamagnetic but coloured.
(C) Cu_2O and HgI_2	(r) Pair of compounds having metals in the highest stable oxidation states.
(D) $[Cu(NH_3)_4]^{2+}$ and $[Ni(NH_3)_4]^{2+}$	(s) Pair of compounds which show diamagnetism and are colourless.

Exercise # 2

✍ **Marked Questions may have for Revision Questions.**

PART - I : ONLY ONE OPTION CORRECT TYPE

1.✍ Ionisation energies of Ni and Pt in kJ mol^{-1} are given below.

	$\underbrace{(IE)_1+(IE)_2}$	$\underbrace{(IE)_3+(IE)_4}$
Ni	2.49	8.80
Pt	2.60	6.70

So, (select the correct statement)

(A) nickel (II) compounds tend to be thermodynamically more stable than platinum (II)

(B) platinum (IV) compounds tend to be more stable than nickel (IV)

(C) (A) & (B) both

(D) none is correct

2.✍ Atoms of the transition elements are smaller than those of the s-block elements, because :

(A) there is increase in the nuclear charge along the period.

(B) orbital electrons are added to the penultimate d–subshell rather than to the outer shell of the atom.

(C) the shielding effect of d-electrons is small.

(D) All of these

3.✍ Match the compounds of column X with oxidation state of central atom in column Y.

	Column X	**Column Y**
I	$[Cr(H_2O)_6]Cl_3$	5
II	CrO_5	8
III	HNO_3	6
IV	OsO_4	3

	I	II	III	IV
(A)	3	6	5	8
(B)	3	8	5	6
(C)	8	5	6	3
(D)	6	5	8	3

4. Iron is rendered passive by treatment with concentrated :
(A) HCl (B) H_2SO_4 (C) HNO_3 (D) both (B) & (C)

5. Which one of the following dissolves in hot concentrated NaOH ?
(A) Fe (B) Zn (C) Cu (D) Ag

6. Aqueous solutions of (P) and (Q) are violet. (P) turns green on oxidation while (Q) turns green on reduction. They may respectively be :
(A) VCl_2, CrO_3 (B) VCl_3, $KMnO_4$ (C) VSO_4, $KMnO_4$ (D) $VOSO_4$, K_2MnO_4

7. At 300ºC, $FeCl_3(s)$:
(A) decomposes into $FeCl_2$ and Cl_2. (B) decomposes into Fe and Cl_2.
(C) sublimes to give liquid $FeCl_3$. (D) sublimes to give gaseous dimer $(FeCl_3)_2$.

8.✍ In the reaction, $2CuCl_2 + 2H_2O + SO_2 \rightarrow A + H_2SO_4 + 2HCl$; A is
(A) CuCl (B) Cu (C) $CuSO_4$ (D) CuS

9. German silver is an alloy of copper and :
(A) Zn + Ni (B) Al + Ag (C) Zn + Ag (D) Sn + Zn

10. When H_2O_2 is added to an acidified solution of $K_2Cr_2O_7$:
(A) solution turns green due to formation of Cr_2O_3
(B) solution turns yellow due to formation of K_2CrO_4
(C) a blue coloured compound $CrO(O_2)_2$ is formed
(D) solution gives green ppt of $Cr(OH)_3$

11. Sodium thiosulphate is used in photography because of its :
(A) oxidising behaviour (B) reducing behaviour
(C) complexing behaviour (D) photochemical behaviour

12.✍ Lanthanide contraction is due to increase in :
(A) shielding by 4f electrons (B) atomic number
(C) effective nuclear charge (D) size of 4f orbitals

13. The correct statement(s) from among the following is/are ?
(i) all the d and f-block elements are metals
(ii) all the d and f-block elements form coloured ions
(iii) all the d- and f-block elements form paramagnetic ions
(A) (i) only (B) (i) and (ii) (C) (ii) and (iii) (D) All

14.✍ Which of the following statements is not correct ?
(A) $La(OH)_3$ is less basic than $Lu(OH)_3$.
(B) In lanthanide series ionic radius of Ln^{3+} ions decreases.
(C) La is actually an element of transition series rather than lanthanide series.
(D) Atomic radii of Zr and Hf are same because of lanthanide contraction.

PART - II : NUMERICAL TYPE QUESTIONS

1.✍ Total number of 3d-series transition elements contain either $3d^1$ or $4s^1$ orbital in their ground state electronic configuration.

2.✍ How many of the following show variable oxidation states in their compounds ?
Sc, Cr, Cu, Zn, Fe, Hg, La

3. Magnetic moment value for a d-block ion is 4.90 BM determine value of total spin for it
(consider clock wise spin)

4. Determine total number of unpaired electrons in following ions
Ti^{3+}, V^{3+}, Cr^{3+}, Cr^{2+}, Mn^{3+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}

5. An element of Ist transition series X^{+3} have highest magnetic moment in series and X^{+2} have non magnetic nature as low spin complex. If Atomic number of X is 'a' and number of unpaired e^- in free state X^{+2} and X^{+3} is 'b' and 'c' then calculate a + b + 2c.

6. $FeC_2O_4 \xrightarrow{\Delta}$ products
Number of diamagnetic products= x
Number of unpaired electrons in paramagnetic product = y
Report your answer as (x + y).

7. No. of following reagents in which ppt A is soluble is :
$AgNO_3 + NaCl \longrightarrow A\downarrow$
(i) aq NH_3 (ii) aq. KCN (iii) $Na_2S_2O_3$
(iv) Conc. HCl (v) aq. NaOH (iv) aq. KI

8._✍ The number of water molecule(s) directly bonded to the metal centre in $CuSO_4.5H_2O$ is–

9.✍ Chromite ore is processed through the following sequence :

$$\begin{tikzcd}
FeCr_2O_4 \arrow[r, "Na_2O_2", "Fuse"'] & \{(A)+(B)\} \arrow[r, "Boil", "H_2O"'] & (B)aq. \arrow[rr, "excess\ H^+"] & & (C) \arrow[d, "H_2O_2"] \\
(H) & (G) \arrow[l, "H_2O_2"'] & (F) \arrow[l, "NaOH"', "excess"] & (E) \arrow[l, "NH_3\ little"'] & (D) \arrow[l, "warm\ H^+"', "-O_2"]
\end{tikzcd}$$

In this sequence how many species (from A to H) show green colour ?

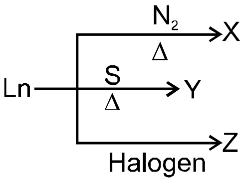
10. $KMnO_4 \xrightarrow[R.A.]{H^+} Mn^x$

$KMnO_4 \xrightarrow[R.A.]{OH^-} Mn^y$

$K_2Cr_2O_7 \xrightarrow{OH^-} Cr^z$

x + y + z is

11. The heavier members of lanthanoid series metal react with following non-metal.



The summation of atomicity of compound X, Y and Z is ?

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Correct statements about transition metals are that they :
(A) form complex (B) show variable oxidation states
(C) show magnetic properties (D) do not form coloured compounds

2. Transition elements have greater tendency to form complexes because they have :
(A) vacant d–orbitals (B) small size
(C) higher nuclear charge (D) variable oxidation states

3.✍ The less stable oxidation states of Cr are :
(A) Cr^{2+} (B) Cr^{3+} (C) Cr^{4+} (D) Cr^{5+}

4. Which of the following statements are correct ?
(A) Transition elements exhibit higher enthalpies of atomization as they have stronger interatomic interaction
(B) IE_2 of $_{23}V < _{24}Cr > _{25}Mn$ and $_{28}Ni < _{29}Cu > _{30}Zn$
(C) Ni(II) compounds are more stable than Pt(II) where as Pt(IV) compounds are more stable than nickel (IV)
(D) The elements which gives the greatest number of oxidation states does not occur in or near the middle of the series.

5._✍ Which of the following is/are soluble is excess of NaOH
(A) $Al(OH)_3$ (B) $Cr(OH)_3$ (C) $Fe(OH)_3$ (D) $Zn(OH)_2$

6. The melting point of Zn is lower as compared to those of the other elements of 3d series because :
(A) the d-orbitals are completely filled.
(B) the d-orbitals are partially filled.
(C) d-electrons do not participate in metallic bonding.
(D) size of Zn atom is smaller

7. The colour of the transition metal ions is/are due to :
(A) d-d transition of electrons in presence of ligands
(B) charge transfer from ligand to metal ion.
(C) change in the geometry
(D) polarisation of anion by cation

8. Which of the following ions give(s) colourled aqueous solution?
(A) Ni^{2+} (B) Fe^{2+} (C) Cu^{2+} (D) Cu^{+}

9. What are the characteristics of products obtained when green vitriol is strongly heated ?
(A) Basic oxide (B) Neutral oxide (C) acidic oxide (D) Reducing agent

10. Which of the following reaction(s) is/are used for the preparation of anhydrous $FeCl_3$?
(A) $FeCl_3\,6H_2O + 6SOCl_2 \longrightarrow FeCl_3 + 12HCl + 6SO_2$
(B) $Fe(OH)_3\downarrow + 3HCl \longrightarrow FeCl_3 + 3H_2O$
(C) $2Fe + 4HCl\ (aq.) + Cl_2 \longrightarrow 2FeCl_3 + 2H_2$
(D) $2Fe + 3Cl_2(dry) \longrightarrow 2FeCl_3$

11.✍ Cuprous chloride can be prepared :
(A) by passing SO_2 through the solution containing $CuSO_4$ and NaCl.
(B) by heating excess of copper with concentrated HCl in presence of a little $KClO_3$.
(C) by boiling copper sulphate solution with excess of copper turnings in presence of hydrochloric acid.
(D) by dissolving cupric oxide or copper carbonate in concentrated HCl.

12. Which of the following chemical reaction(s) is/are involved in developing of photographic plate ?
(A) $C_6H_4(OH)_2 + 2AgBr \longrightarrow 2Ag + C_6H_4O_2 + 2HBr$
(B) $AgBr + 2Na_2S_2O_3 \longrightarrow Na_3\,[Ag(S_2O_3)_2] + NaBr$
(C) $2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$
(D) $AgNO_3 + KCN \longrightarrow AgCN + KNO_3$

13. Which of the following statements are correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4 ?
(A) Deep red vapours are liberated
(B) Deep red vapours dissolve in NaOH (aq.)forming a yellow solution.
(C) Greenish yellow gas is liberated
(D) Deep red vapours dissolve in water forming yellow solution

14. Which of the following statement (s) is/are correct ?
(A) $S_2O_8^{2-}$ oxidises Mn^{2+} to give pink colour.
(B) MnO_4^{2-} disproportionates to yield MnO_4^- and MnO_2 in presence of H^+ ions.
(C) In $Cr_2O_7^{2-}$ each Cr is linked to four oxygen atoms.
(D) Ti^{3+} is purple while Ti^{4+} is colourless.

15. Pyrolusite is MnO_2 used to prepare $KMnO_4$. Steps are :

$$MnO_2 \xrightarrow{I} MnO_4^{2-} \xrightarrow{II} MnO_4^{-}$$

Steps I and II are respectively :
(A) fuse with KOH / air, electrolytic oxidation
(B) fuse with KOH / KNO_3, electrolytic oxidation
(C) fuse with concentrated HNO_3 / air, electrolytic reduction
(D) dissolve in H_2O, oxidation

16. Which of the following statements are correct
(A) Tendency to form complex : $Sc^{+3} > Y^{+3} > La^{+3}$
(B) Most of Ln^{3+} are coloured.
(C) Ln(II) hydroxides are mainly basic in character
(D) Lanthanoids release H_2 on reaction with strong acids

PART - IV : COMPREHENSION

Read the following comprehension carefully and answer the questions :

Comprehension # 1

Transition metals usually form coloured complexes and d–d transitions ($t_{2g} \rightleftharpoons e_g$) are responsible for colour as the energy difference between t_{2g} and e_g lies in visible region. But all the coloured ions are not due to d–d transition but charge transfer bands also play important roles. Charge transfer bands may be of two types.
(i) ligand to metal (CTLM) (ii) metal to ligand (CTML).
Charge transfer transition always produces intense colour as compared to d-d transition.

1. Select the incorrect statement :
(A) d-block metal ions are usually coloured.
(B) Colour of the most of d-block metal ions is generally due to d-d transition.
(C) All the complexes of Cu^+ are colourless on account of diamagnetic nature i.e. d^{10} configuration.
(D) CrO_3 is bright orange due to CTLM.

2. MnO_4^- is dark purple coloured although Mn is in (+ VII) oxidation state with $3d^o$ configuration :
(A) due to d-d transition. (B) due to CTML spectra.
(C) due to CTLM spectra (D) none of these.

Comprehension # 2

Pyrolusite ore on oxidation with $KClO_3/KNO_3$ in basic medium produces dark green coloured compound (A), which on electrolysis produces a purple coloured compound (B). The purple coloured compound can be crystallised to deep purple rhombic prisms. It shows different reactions in different mediums. Excess of compound (B) on heating with concentrated H_2SO_4 gives an explosive oil (C), which on heating decomposes to gives another compound (D) along with oxygen.

3. On passing CO_2 in the solution of (A), a purple coloured solution along with brown precipitate is observed. Select the correct statement.
(A) This is a disproportionation reaction where oxidation number changes from +6 to +7 , +4.
(B) This is a comproportionation reaction where oxidation number changes from +3 to +2.
(C) both (A) and (B)
(D) none

4. The nature of compound (C) is :
(A) basic (B) acidic (C) neutral (D) amphoteric

5. Identify (D).
(A) Mn_2O_7 (B) MnO_2 (C) $MnSO_4$ (D) Mn_2O_3

Exercise # 3

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

*** Marked Questions may have more than one correct option.**

1. Reduction of the metal centre in aqueous permanganate ion involves : **[JEE 2011, 4/180]**
(A) 3 electrons in neutral medium (B) 5 electrons in neutral medium
(C) 3 electrons in alkaline medium (D) 5 electrons in acidic medium

2. The colour of light absorbed by an aqueous solution of $CuSO_4$ is : **[JEE 2012, 3/136]**
(A) organge-red (B) blue-green (C) yellow (D) violet

3.* Which of the following halides react(s) with $AgNO_3$(aq) to give a precipitate that dissolves in $Na_2S_2O_3$(aq) ?
(A) HCl (B) HF (C) HBr (D) HI **[JEE 2012, 4/136]**

4. Consider the following list of reagents : **[JEE(Advanced) 2014, 3/120]**
Acidified $K_2Cr_2O_7$, alkaline $KMnO_4$, $CuSO_4$, H_2O_2, Cl_2, O_3, $FeCl_3$, HNO_3 and $Na_2S_2O_3$. The total number of reagents that can oxidise aqueous iodide to iodine is

Paragraph For question 5 to 6

An aqueous solution of metal ion **M1** reacts separately with reagents **Q** and **R** in excess to give tetrahedral and square planar complexes, respectively. An aqueous solution of another metal ion **M2** always forms tetrahedral complexes with these reagents. Aqueous solution of **M2** on reaction with reagent **S** gives white precipitate which dissolves in excess of **S**. The reactions are summarized in the scheme given below :

SCHEME:

$$\begin{tikzcd}
\text{Tetrahedral} & \mathbf{M1} \arrow[l, "Q"', "\text{excess}"] \arrow[r, "R", "\text{excess}"'] & \text{Square planar} \\
\text{Tetrahedral} & \mathbf{M2} \arrow[l, "Q"', "\text{excess}"] \arrow[r, "R", "\text{excess}"'] \arrow[d, "\mathbf{S}\text{, stoichiometric amount}"] & \text{Tetrahedral} \\
& \text{White precipitate} \arrow[r, "S", "\text{excess}"'] & \text{precipitate dissolves}
\end{tikzcd}$$

5. **M1**, **Q** and **R**, respectively are **[JEE(Advanced) 2014, 3/120]**
(A) Zn^{2+}, KCN and HCl (B) Ni^{2+}, HCl and KCN
(C) Cd^{2+}, KCN and HCl (D) Co^{2+}, HCl and KCN

6. Reagent **S** is **[JEE(Advanced) 2014, 3/120]**
(A) $K_4[Fe(CN)_6]$ (B) Na_2HPO_4 (C) K_2CrO_4 (D) KOH

7.* The correct statement(s) about Cr^{2+} and Mn^{3+} is (are) : **[JEE(Advanced) 2015, 4/168]**
[Atomic numbers of Cr = 24 and Mn = 25]
(A) Cr^{2+} is a reducing agent
(B) Mn^{3+} is an oxidizing agent
(C) Both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration
(D) When Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration.

8.* Fe^{3+} is reduced to Fe^{2+} by using **[JEE(Advanced) 2015, 4/168]**
(A) H_2O_2 in presence of NaOH (B) Na_2O_2 in water
(C) H_2O_2 in presence of H_2SO_4 (D) Na_2O_2 in presence of H_2SO_4

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

1. The correct order of $E^{\circ}_{M^{2+}/M}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is **[AIEEE 2010, 4/144]**

(1) Mn > Cr > Fe > Co (2) Cr > Fe > Mn > Co (3) Fe > Mn > Cr > Co (4) Cr > Mn > Fe > Co

2. In context of the lanthanoids, which of the following statement is not correct ? **[AIEEE 2011, 4/120]**

(1) There is a gradual decrease in the radii of the members with increasing atomic number in the series.
(2) All the member exhibit +3 oxidation state.
(3) Because of similar properties the separation of lanthanoids is not easy.
(4) Availability of 4f electrons results in the formation of compounds in +4 state for all the members of the series.

3. The outer electron configuration of Lu (Atomic No : 71) is : **[AIEEE 2011, 4/120]**

(1) $4f^3\,5d^5\,6s^2$ (2) $4f^8\,5d^0\,6s^2$ (3) $4f^4\,5d^4\,6s^2$ (4) $4f^{14}5d^1\,6s^2$

4. Iron exhibits +2 and + 3 oxidation states. Which of the following statements about iron is incorrect ?

(1) Ferrous oxide is more basic in nature than the ferric oxide. **[AIEEE 2012, 4/120]**
(2) Ferrous compounds are relatively more ionic than the corresponding ferric compounds
(3) Ferrous compounds are less volatile than the corresponding ferric compounds
(4) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.

5. Which of the following arrangements does not represent the correct order of the property stated against it ?

(1) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behaviour **[JEE(Main) 2013, 4/120]**
(2) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size
(3) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution
(4) Sc < Ti < Cr < Mn : number of oxidation states

6. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E^{0}_{M^{3+}/M^{2+}}$ value ? **[JEE(Main) 2013, 4/120]**

(1) Cr(Z = 24) (2) Mn(Z = 25) (3) Fe(Z = 26) (4) Co(Z = 27)

7. Which series of reactions correctly represents chemical relations related to iron and its compound ? **[JEE(Main) 2014, 4/120]**

(1) $Fe \xrightarrow{\text{dil } H_2SO_4} FeSO_4 \xrightarrow{H_2SO_4, O_2} Fe_2(SO_4)_3 \xrightarrow{\text{heat}} Fe$

(2) $Fe \xrightarrow{O_2,\text{heat}} FeO \xrightarrow{\text{dil } H_2SO_4} FeSO_4 \xrightarrow{\text{heat}} Fe$

(3) $Fe \xrightarrow{Cl_2,\text{heat}} FeCl_3 \xrightarrow{\text{heat, air}} FeCl_2 \xrightarrow{Zn} Fe$

(4) $Fe \xrightarrow{O_2,\text{heat}} Fe_3O_4 \xrightarrow{CO,\ 600°C} FeO \xrightarrow{CO,\ 700°C} Fe$

8. The equation which is balanced and represents the correct product(s) is : **[JEE(Main) 2014, 4/120]**

(1) $Li_2O + 2KCl \rightarrow 2LiCl + K_2O$
(2) $[CoCl(NH_3)_5]^+ + 5H^+ \rightarrow Co^{2+} + 5NH_4^+ + Cl^-$
(3) $[Mg(H_2O)_6]^{2+} + (EDTA)^{4-} \xrightarrow{\text{excess NaOH}} [Mg(EDTA)]^{2+} + 6H_2O$
(4) $CuSO_4 + 4KCN \rightarrow K_2[Cu(CN)_4] + K_2SO_4$

9. The colour of $KMnO_4$ is due to : **[JEE(Main) 2015, 4/120]**

(1) M → L charge transfer transition (2) d – d transition
(3) L → M charge transfer transition (4) $\sigma - \sigma^*$ transition

ANSWER KEY

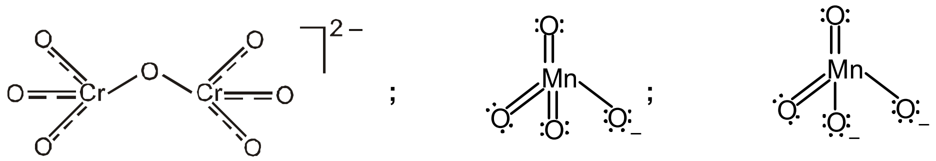
EXERCISE # 1

PART - I

A-1. + 2 & + 3

A-2. In the 5d series, after lanthanum (Z = 57), there is lanthanide contraction. As a result, in each group the atomic size of 5d element is small and its nuclear charge is large. Hence the ionisation energies of 5d elements are large than 3d elements.

B-1.



B-2. Enough unpaired electrons are not available for effective metallic bonding for zinc.

B-3. $V_2O_5 > V_2O_4 > V_2O_3$

B-4. $Fe(OH)_2$ is more basic than $Fe(OH)_3$

C-1. (i) Ti^{3+} ($3d^1$), Cu^{2+} ($3d^9$) and Mn^{2+} ($3d^5$) have unpaired electron(s). Thus they are coloured due to d-d transition of electron according to CFT.

(ii) Zn^{2+}($3d^{10}$), Ti^{+4} ($3d^0$) and Cd^{2+} ($4d^{10}$) do not have unpaired electron(s). Thus they do not under go d-d transition of electron according to CFT and, therefore, are colourless.

C-2. Copper has less standard oxidation potential (E°_{op}) than H_2 and thus cannot liberate H_2 from acids. However, it dissolves in nitric acid because HNO_3 is strong oxidant.

$$3Cu + 8HNO_3\,(\text{dilute}) \longrightarrow 3Cu\,(NO_3)_2 + 4H_2O + 2NO$$

C-3. Zn

C-4. H_2S and O_2.

D-1. $2FeSO_4.H_2O \rightarrow Fe_2O_3 + SO_2\uparrow + SO_3\uparrow + 2H_2O$

D-2. $2AgNO_3 + 2NaOH \rightarrow Ag_2O\downarrow + 2NaNO_3 + H_2O$

D-3. $$Zn(OH)_2\downarrow + 4KCN \longrightarrow \underset{\text{colourless soluble complex}}{K_2[Zn(CN)_4]} + 2KOH$$

$$Zn(OH)_2\downarrow + 4NH_3 \longrightarrow \underset{\text{colourless soluble complex}}{[Zn(NH_3)_4](OH)_2}$$

$$Zn(OH)_2\downarrow + 2NaOH \longrightarrow \underset{\text{colourless soluble complex}}{Na_2[Zn(OH)_4]\,(OH)_2}$$

D-4. (a) $ZnO + CoO \longrightarrow CoZnO_2$ (Rinmann's green)

(b) $2AgNO_3 + 2NaOH \longrightarrow Ag_2O\downarrow$ (black) $+ 2NaNO_3 + H_2O$

(c) $Cu(OH)_2 + 2NH_3{\cdot}H_2O + (NH_4)_2SO_4 \longrightarrow [Cu(NH_3)_4]SO_4$ (Schitzer reagent) $+ 4H_2O$

E-1. (a) $FeSO_4.7H_2O \xrightarrow[-7H_2O]{300^\circ C} FeSO_4 \xrightarrow[\text{tempt}]{\text{high}} Fe_2O_3 + SO_2 + SO_3$

(b) $3FeSO_4 + 2K_3\,[Fe(CN)_6] \longrightarrow \underset{\text{(blue)}}{Fe_3[Fe(CN)_6]_2} + 3K_2SO_4$

(c) $CuCO_3.Cu(OH)_2 + 2H_2SO_4 \longrightarrow 2CuSO_4 + 3H_2O + CO_2\uparrow$

(d) $CuSO_4.5H_2O$ (blue) $\xrightarrow[\text{effloresces}]{\text{air}} CuSO_4.3H_2O$ (pale blue)

E-2. $$4FeSO_4 + 2H_2O + O_2 \longrightarrow \underset{\text{(yellow brown)}}{4Fe\,(OH).SO_4}$$

E-3. White precipitate of $Ag_2S_2O_3$ is obtained which turns yellow, orange, brown and finally black on keeping.

$2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 \downarrow$ (white) $+ 2NaNO_3$

$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S \downarrow$ (black) H_2SO_4

E-4. In presence of organic matter (skin) and light, $AgNO_3$ decomposes to produce a black stain of metallic silver.

$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$

E-5. Copper sulphate dissolves in the ammonium hydroxide due to formation of a copper complex. Ferrous sulphate reacts with NH_4OH to form insoluble $Fe(OH)_2$. It does not form any complex with NH_4OH.

$CuSO_4 + 4NH_3{\cdot}H_2O \longrightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$

Deep blue solution

$FeSO_4 + 2NH_3{\cdot}H_2O \longrightarrow Fe(OH)_2 + (NH_4)_2SO_4$

Insoluble

F-1. In aqueous solution, Fe^{3+} ions undergo hydrolysis as follows :

$Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+$

$Fe(OH)^{2+} + H_2O \rightleftharpoons Fe(OH)_2 + H^+$

$Fe(OH)_2 + H_2O \rightleftharpoons Fe(OH)_3 \downarrow + H^+$

Hence, it forms an acidic solution.

F-2. CuCl dissolves in conc. HCl due to the formation of a chlorido complex.

$CuCl + 2HCl \longrightarrow 2H[CuCl_2]$

F-3. Cu^{+2} is reduced to Cu^+ by I^-, hence cupric iodide is converted into cuprous iodide. Cl^- cannot affect this change, since it is not a reductant.

F-4. AgBr is sensitive to light and undergoes photo decomposition to metallic silver instantaneously on exposure to light.

$2AgBr \longrightarrow 2Ag + Br_2$

Unexposed AgBr can be dissolved in hypo ($Na_2S_2O_3$) solution, obtaining a black image on the original paper where the light rays fall. Thus produces the "negative" photograph.

$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr.$

F-5. (a) $Au + 5HCl + HNO_3 \longrightarrow HAuCl_4 + NOCl \uparrow + 2H_2O$

(b) $3CuCl_2.2H_2O \xrightarrow[\text{strong}]{\Delta} CuO + Cu_2Cl_2 + 2HCl + Cl_2 + H_2O$

F-6. On heating hydrated ferric chloride, anhydrous ferric chloride is not formed, as water of crystallization reacts to from Fe_2O_3 and HCl.

F-7. In presence of Cl^- ion the disproportionation of Cu^+ i.e.

$2Cu^+_{(aq)} \longrightarrow Cu_{(s)} + Cu^{2+}_{(aq)}$

is reversed because precipitation of copper (I) chloride drives the disproportionation reaction to the left.

$Cu_{(s)} + Cu^{2+}_{(aq)} + 2Cl^-_{(aq)} \longrightarrow 2CuCl_{(s)}$

G-1. (a) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

(b) $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 + 23H_2O \xrightarrow[\text{crystallise}]{\text{temp.}<70°C} K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$

(c) $Fe(III) + 3NH_4SCN \longrightarrow [Fe(SCN)_3]$ (blood red colouration) $+ 3NH_4^+$

G-2. It is unstable in acidic medium and disproportionates. It is stable only around pH 14. It disproportionates at lower pHs.

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

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

G-3. Because explosive Mn_2O_7 is formed.

$$2KMnO_4 + 2H_2SO_4 \longrightarrow Mn_2O_7 + 2KHSO_4 + H_2O$$

On warming, this Mn_2O_7 can explode.

$$2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$$

G-4. True

H-1. The 5f electrons are more effectively shielded from nuclear charge. In other words the 5f electrons themselves provide poor shielding from element to element in the series.

H-2. The most stable oxidation state of lanthanides is +3. Hence, ions in +2 state tend to change to +3 state by loss of electron and those in +4 state tend to change to +3 state by gain of electron.

PART - II

A-1.	(B)	**B-1.**	(A)	**B-2.**	(A)	**C-1.**	(D)	**C-2.**	(D)
C-3.	(A)	**C-4.**	(A)	**C-5.**	(D)	**D-1.**	(D)	**D-2.**	(B)
E-1.	(B)	**E-2.**	(A)	**F-1.**	(B)	**F-2.**	(B)	**F-3.**	(D)
F-4.	(D)	**F-5.**	(D)	**F-6.**	(A)	**G-1.**	(B)	**G-2.**	(C)
G-3.	(A)	**G-4.**	(A)	**G-5.**	(D)	**G-6.**	(A)	**G-7.**	(A)
H-1.	(C)	**H-2.**	(B)	**H-3.**	(B)	**H-4.**	(C)	**H-5.**	(C)

PART - III

1. (A) - r ; (B) - s ; (C) - p ; (D) - q.

2. (A) - s ; (B) - q, r ; (C) - q ; (D) - q

EXERCISE # 2

PART - I

1.	(C)	**2.**	(D)	**3.**	(A)	**4.**	(D)	**5.**	(B)
6.	(C)	**7.**	(D)	**8.**	(A)	**9.**	(A)	**10.**	(C)
11.	(C)	**12.**	(C)	**13.**	(A)	**14.**	(A)		

PART - II

1.	3	**2.**	4	**3.**	2	**4.**	34	**5.**	39
6.	6	**7.**	4	**8.**	4	**9.**	3	**10.**	12
11.	11								

PART - III

1.	(ABC)	**2.**	(ABC)	**3.**	(ACD)	**4.**	(ABC)	**5.**	(ABD)
6.	(AC)	**7.**	(ABD)	**8.**	(ABC)	**9.**	(ABCD)	**10.**	(AD)
11.	(ABC)	**12.**	(AB)	**13.**	(ABD)	**14.**	(ABCD)	**15.**	(AB)
16.	(ABCD)								

PART - IV

1.	(C)	**2.**	(C)	**3.**	(A)	**4.**	(B)	**5.**	(B)

EXERCISE # 3

PART - I

1.	(ACD)	**2.**	(A)	**3.**	(ACD)	**4.**	7	**5.**	(B)
6.	(5 & 6)	**7.**	(ABC)	**8.**	(CD)				

PART - II

1.	(1)	**2.**	(4)	**3.**	(4)	**4.**	(4)	**5.**	(1)
6.	(4)	**7.**	(4)	**8.**	(2)	**9.**	(3)		

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Reliable students.

Self Assessment Test

PART- 1 : PAPER JEE (MAIN) PATTERN

SECTION–I : (Maximum Marks : 80)

- This section contains **TWENTY** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :
  Full Marks : +4 If only the bubble corresponding to the correct option is darkened.
  Zero Marks : 0 If none of the bubbles is darkened.
  Negative Marks : –1 In all other cases

1. The maximum oxidation state shown by V(Z = 23), Cr(Z = 24), Co(Z = 27), Sc(Z = 21) are respectively :
(A) + 5 , + 6 , + 3 , + 3 (B) + 3 , + 4 , + 5, + 2
(C) + 5, + 3 , + 2 , + 1 (D) + 4 in each case.

2. Which oxide of manganese is most acidic in nature ?
(A) MnO (B) Mn_2O_7 (C) Mn_2O_3 (D) MnO_2 .

3. The first ionisation energies of the elements of the first transition series :
(A) generally increases as the atomic numbers increase.
(B) decrease as the atomic number increase.
(C) do not show any change as the addition of electrons takes place in the inner (n – 1) d–orbitals.
(D) increase from Ti to Mn and then decrease from Mn to Cu.

4. Which of the followings ions are colourless :
(i) Ti^{4+} , (ii) Cu^{+1} , (iii) Co^{3+} , (iv) Fe^{2+} .
(A) (i) and (ii) only (B) (i), (ii) and (iii) (C) (iii) and (iv) (D) (ii) and (iii).

5. Which of the following transition metal ions has least magnetic moment ?
(A) Co^{3+} (B) Fe^{3+} (C) Cr^{2+} (D) V^{3+}

6. If a non metal is added to the interstitial sites of a metal, then the metal becomes :
(A) softer (B) less tensile (C) less malleable (D) more ductile.

7. The pair of the compounds in which both the metals are in the highest possible oxidation state is,
(A) $[Fe(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$ (B) CrO_2Cl_2 , MnO_4^- .
(C) TiO_2 , MnO_2 (D) $[Co(CN)_6]^{3-}$, Mn_2O_7 .

8. Solution of CuCl in $NH_3.H_2O$ does not absorb :
(A) N_2 (B) SO_2 (C) C_2H_2 (D) CO.

9. A compound of iron exists as a dimer in vapour state. It is hygroscopic in nature and dissolves in water giving brown acidic solution. The compound is :
(A) Fe_3O_4 (B) $FeSO_4$ (C) $FeCl_3$ (D) $FeCl_2$.

10. Select the correct statement(s) regarding oxides of copper:
(A) CuO is black & Cu_2O is white in colour.
(B) Commercially, CuO is obtained by calcination of haematite ore.
(C) Hydrated cupric chloride upon strong heating produces CuO as one of the product.
(D) Upon partial roasting of chalcopyrites ore in metallurgy, Cu_2O is obtained as one of the product.

11. Select the correct statements :
(A) $CuCl_2.2H_2O$ is a green crystalline solid.
(B) Blue vitriol is used for making Fehling's solution & Bordeause mixture.
(C) Anhydrous $CuCl_2$ is dark brown solid.
(D) All of these

12. $2CuSO_4 + 2NaCl + SO_2 + 2H_2O \longrightarrow \underset{X}{\text{Compound}} + Na_2SO_4 + 2H_2SO_4$
Compound X gradually turns green on exposure in air due to oxidation.
Correct statement about compound X is :
(A) Compound X is Cu_2Cl_2 (B) Compound X forms black ppt with H_2S
(C) Compound X is soluble in aq. NH_3 solution (D) All of these

13. Which of the following are correct ?
(A) Anhydrous ferric chloide can not be obtained by heating hydrated ferric chloride.
(B) $FeSO_4$ can be used as primary standard.
(C) $ZnCl_2$ solution on treating with H_2S gives black precipitate.
(D) $CuSO_4$ and $FeSO_4$ both gets dissolved in NH_4OH.

14. Cu^{2+} can be reduced to Cu^+ on addition of :
(A) Hyposolution (B) KCN (aq) (C) KSCN (D) All of these

15. When $FeSO_4$ is strongly heated, the number of acidic gases produced is :
(A) One (B) Two (C) Three (D) Four

16. $Fe(CN)_3 + KCN \longrightarrow X \xrightarrow{\text{FeCl3 SCl}_n} Y$
Y is :
(A) Brown colored complex,Inner orbital complex
(B) White colored complex , Inner orbital complex
(C) Blue colored complex, outer orbital complex
(D) Blue coloured compex, Inner orbital complex

17. On heating $KMnO_4$, one among the following is not formed :
(A) K_2MnO_4 (B) O_2 (C) MnO_2 (D) MnO.

18. Reaction of $KMnO_4$ in neutral or very weakly alkaline solution can be represented as :
(A) $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$. (B) $2MnO_4^- + 2OH^- \rightarrow 2MnO_4^{2-} + 1/2O_2 + H_2O$.
(C) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$. (D) $MnO_4^- + e^- \rightarrow MnO_4^{2-}$.

19. $KMnO_4$ in excess on treatment with concentrated H_2SO_4 forms a compound (X) which decomposes explosively on heating forming (Y) . The (X) and (Y) are respectively :
(A) Mn_2O_7 , MnO_2 (B) Mn_2O_7 , Mn_2O_3 (C) $MnSO_4$, Mn_2O_3 (D) Mn_2O_3 , MnO_2

20. Which of the following statement is wrong ?
(A) An acidified solution of $K_2Cr_2O_7$ liberates iodine from iodides.
(B) In acidic solution dichromate ions are converted to chromate ions.
(C) Ammonium dichromate on heating undergo exothermic decomposition to give Cr_2O_3 .
(D) Potassium dichromate is used as a titrant for Fe^{2+}.

SECTION-II : (Maximum Marks: 20)

- This section contains **FIVE** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:

  Full Marks : +4 If ONLY the correct numerical value is entered as answer.

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21. Pick out the correct statements from the following :
1. Cobalt (III) is more stable in octahedral complexes.
2. Zinc forms coloured ions or complexes
3. Most of the d-block elements and their compounds are ferromagnetic
4. Osmium shows (VIII) oxidation state
5. Cobalt (II) is more stable in octahedral complexes.

22._ Oil of Vitriol (X), after adding water, was reacted with three metals A, B and C separately and produced white vitriol, green vitriol and blue vitriol. The metal A on dissolving in HCl, liberated hydrogen and produced a salt D which gave white precipitate on passing H_2S in alkaline medium. The salt D dissolved in excess NaOH and excess NH_3 forming E and F. The metal B, however did not liberate hydrogen from HCl. It was dissolved in nitric acid to give a salt G. The salt produced black precipitate of H on passing H_2S in acidic medium. The metal C on being heated with chlorine produces a dark black solid 'I', which sublimes at 300ºC to form a dimer. When 'I' reacts with KI, 'J' is produced. How many of the following are correctly matched?

A – Zn	A – Al
B – Mg	B – Cu
C – Cu	C – Al
D – $ZnCl_2$	D – $AlCl_3$
E – Na_2ZnO_2	E – $NaAlO_2$
F – $[Zn(NH_3)_4]Cl_2$	F – $[Al(NH_3)_6]Cl_3$
G – $Cu(NO_3)_2$	G – $Fe(NO_3)_2$
H – CuS	H – FeS
X – HNO_3	X – H_2SO_4
I – $AlCl_3$	I – $ZnCl_2$
J – I_2	J – FeI_2

23._ When equimolar amount of potassium dichromate and boric acid are fused, it gives hydrated chromium oxide ($Cr_2O_3.2H_2O$). This compound is a brilliant green coloured powder, also known as Guigret's green. in this process, the number of elements which undergo oxidation or reduction is :

24._ How many of given statements are true for lanthanides ?

(1) The common oxidation state of all lanthanoids is +3.
(2) All lantanides belongs to group III of modern periodic table.
(3) All lanthanoids belongs to seventh period of periodic table.
(4) The radius for all lanthanoids cations(M^{+3}) decrease from Ce^{+3} to Lu^{+3}.
(5) The basic character of hydroxide increases on moving from $Ce(OH)_3$ to $Lu(OH)_3$.
(6) All lanthanides are metals.
(7) The reducing power of lanthanides decreases from Ce to Lu.
(8) Lanthanides reacts with cold water to liberate H_2.

25._ The no. of electrons satisfying n+l = 7 for Lu (Atomic number : 71)

PART 2 : PAPER JEE (ADVANCED) PATTERN

SECTION-I : (Maximum Marks : 12)

- This section contains **FOUR** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :

Full Marks : +3 If only the bubble corresponding to the correct option is darkened.
Zero Marks : 0 If none of the bubbles is darkened.
Negative Marks : –1 In all other cases

1. Among the following series of transition metal ions, the one where all metal ions have $3d^2$ electronic configuration is ;
(A) Ti^{3+}, V^{2+}, Cr^{3+}, Mn^{4+} (B) Ti^{+} , V^{4+} , Cr^{6+} , Mn^{7+} (C) Ti^{2+}, V^{3+}, Cr^{2+}, Mn^{3+} (D) Ti^{2+} , V^{3+} , Cr^{4+} , Mn^{5+} .

2. The pair of the compounds in which both the metals are in the highest possible oxidation state is,
(A) $[Fe(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$ (B) CrO_2Cl_2 , MnO_4^- (C) TiO_2 , MnO_2 (D) $[Co(CN)_6]^{3-}$, Mn_2O_7 .

3. VO_2 is an amphoteric oxide and in acidic medium it forms :
(A) VO^{2+} (B) VO^+_2 (C) V^{3+} (D) VO_2^{2+}

4. **S_1 :** Mn^{2+} compounds are more stable than Fe^{2+} towards oxidation to their +3 state.
S_2 : Titanium and copper both in the first series of transition metals exhibits +1 oxidation state most frequently.
S_3 : Cu^+ ion is stable in aqueous solutions.
S_4 : The E^θ value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}.
(A) T T F T (B) T F F T (C) T F T T (D) F F T F

SECTION-II : (Maximum Marks: 32)

- This section contains **EIGHT** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +4 If only (all) the correct option(s) is (are) chosen.
Partial Marks : +3 If all the four options are correct but ONLY three options are chosen.
Partial Marks : +2 If three or more options are correct but ONLY two options are chosen, both of which are correct options.
Partial Marks : +1 If two or more options are correct but ONLY one option is chosen and it is a correct option.
Zero Marks : 0 If none of the options is chosen (i.e. the question is unanswered).
Negative Marks : –1 In all other cases.

- **For Example :** If first, third and fourth are the **ONLY** three correct options for a question with second option being an incorrect option; selecting only all the three correct options will result in +4 marks. Selecting only two of the three correct options (e.g. the first and fourth options), without selecting any incorrect option (second option in this case), will result in +2 marks. Selecting only one of the three correct options (either first or third or fourth option), without selecting any incorrect option (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), with or without selection of any correct option(s) will result in –1 marks.

5. Select the correct statement(s) with respect to oxides and oxoanions of transition metals.
(A) Among oxides of chromium, CrO is basic, Cr_2O_3 is amphoteric and CrO_3 is acidic.
(B) No higher oxides of iron above Fe_2O_3 are found.
(C)Ti,V,Cr and Mn form oxides MO and their correct increasing order of acidic character is MnO<CrO<VO<TiO.
(D) Vandium(V) oxide does not react with acids but reacts with alkalies only.

6. Fenton's reagent is X + H_2O_2. X combines readily with Y and H_2O to form crystals of Mohr salt. X can be made in laboratory from Kipp's waste. When Kipp's waste is heated in the presence of O_2 and water, Z is also produced along with X. The reaction of X with $KMnO_4$ in the presence of H_2SO_4 also gives Z.
Identify the correct match.
(A) X = $FeSO_4$ (B) X = $Fe_2(SO_4)_3$ (C) Y = $(NH_4)_2SO_4$ (D) Z = $FeSO_4$

7. Cuprous chloride can be prepared :
(A) by passing SO_2 through the solution containing $CuSO_4$ and NaCl.
(B) by heating excess of copper with concentrated HCl in presence of a little $KClO_3$.
(C) by boiling copper sulphate solution with excess of copper turnings in presence of hydrochloric acid.
(D) by dissolving cupric oxide or copper carbonate in concentrated HCl.

8. Potassium manganate (K_2MnO_4) is formed when :
(A) potassium permanganate reacts with formaldehyde in acidic medium.
(B) manganese dioxide is fused with potassium hydroxide in air.
(C) manganese hydroxide reacts with K_2O_2 in alkaline medium.
(D) potassium permanganate is heated at 750K.

9. Select the incorrect statement(s) :
(A) In K_2MnO_4 and CrO_2Cl_2, the central transition metals/ions have same oxidation state.
(B) Both sodium and potassium dichromate can be used as primary standard in volumetric estimations.
(C) Potassium dichromate on strong heating evolves oxygen gas and forms green powder.
(D) Potassium permanganate on heating with solid KOH evolves oxygen gas and forms a black powder.

10. Why silver chloride is used in photochromic spectacles ?
(A) Silver halides darken in light owing to photochemical decomposition
(B) Silver halides produced elemental silver in light.
(C) If the halogen produced is kept in close proximity to finely divided silver chloride, the silver metal is formed.
(D) silver chloride is not affected by light

11. In which of the following reactions, reaction of silver with the given acids lead to the formation of compound & silver, along with liberation of gas ?
(A) Ag + dilute HNO_3. (B) Ag + Conc. HNO_3
(C) Ag + conc. H_2SO_4 (D) Ag + Conc. HCl

12. Which of the following can be used for the conversion of potassium manganate to potassium permanganate?
(A) O_3 (B) Cl_2 (C) CO_2 (D) H_2S

SECTION-III : (Maximum Marks: 18)

- This section contains **SIX** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the **second decimal place**; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.
  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:
  Full Marks : +3 If ONLY the correct numerical value is entered as answer.
  Zero Marks : 0 In all other cases.

13. How many of the following are coloured or paramagnetic or coloured and paramagnetic both.
NO_2, $Cu^{+1,}$ O_2, O_3, Hg_2^{+2}, Cd^{+2}, Al, C(graphite), Sc^{+3}

14. How many of the following ions have spin maganetic moment more than four B.M.
Ti^{3+}, Cu^{+}, Ni^{2+}, Fe^{3+}, Mn^{2+}, Co^{2+}

15. In how many of the following reactions, colored precipitate is obtained ?

(a) $CuSO_4 + NaOH(excess) \longrightarrow$

(b) $CuCl_2 + NH_3 (excess) \longrightarrow$

(c) $ZnSO_4 + NaOH(excess) \longrightarrow$

(d) $ZnSO_4 + NH_3 (excess) \longrightarrow$

(e) $FeSO_4 + NaOH(excess) \xrightarrow[\text{air}]{\text{in}}$

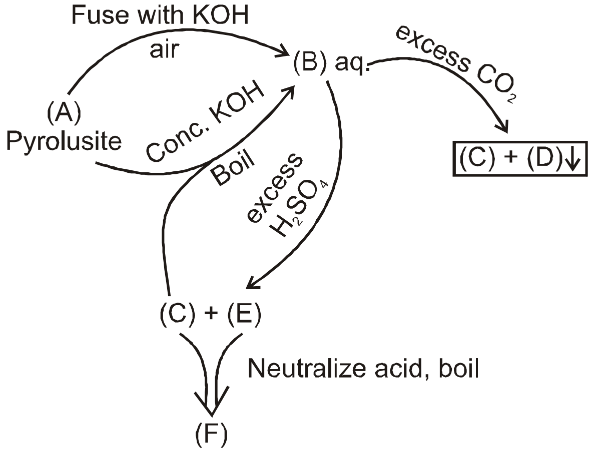
(f) $FeCl_3 + NaOH(excess) \longrightarrow$

(g) $CuSO_4 + KI (excess) \longrightarrow$

(h) $ZnSO_4 + NaHCO_3 \longrightarrow$

(i) $CuCl_2 + NaNO_3 \longrightarrow$

16.



In the above reaction scheme, MnO_2 appears more than once. From (A) – (F), How many of them contain MnO_2 ?

17. How many of the following compounds are diamagnetic and colored ?

K_2MnO_4, Cu_2Cl_2, Hg_2I_2, Ag_2S, HgI_2, K_2CrO_4, Cr_2O_3, AgCl, Ag_2O, $CuSO_4$, HgS, AgF, CrO_5, Mn_2O_7, MnO_2,

18. How many of given statements are true for lanthanums ?

(1) The common oxidation state of all lanthanides is +3.
(2) All lantanides belongs to group III of modern periodic table.
(3) All lanthanides belongs to seventh period of periodic table.
(4) The radius for all lanthanides cations(M^{+3}) decrease from Ce^{+3} to Lu^{+3}.
(5) The basic character of hydroxide increases on moving from $Ce(OH)_3$ to $Lu(OH)_3$.
(6) All lanthanides are metals.
(7) The reducing power of lanthanides decreases from Ce to Lu.
(8) Lanthanides reacts with cold water to liberate H_2.

PART - 3 : OLYMPIAD (PREVIOUS YEARS)

1. When a piece of copper wire is immersed in a silver nitrate solution, the colour of the solution turns blue due to **[NSEC-2000]**
(A) oxidation of silver (B) reduction of copper
(C) oxidation of copper (D) formation of soluble complex

2. The oxidation state of Cr in $K_2Cr_2O_7$ is : **[NSEC-2000]**
(A) + 3 (B) + 6 (C) + 4 (D) – 4

3. Oxidation Number of Mn in $[MnO_4]$ is : **[NSEC-2001]**
(A) –7 (B) + 7 (C) + 2 (D) – 2

4. The reduction potentials of Zn, Cu, Fe and Ag are in the order : **[NSEC-2001]**
(A) Zn > Cu > Fe > Ag (B) Cu > Ag > Fe > Zn (C) Ag >Cu > Fe > Zn (D) Fe > Zn > Cu > Ag

5. The outermost electron configuration of one of the element is $5f^2$, $6d^1$, $7s^2$. This element belongs to **[NSEC-2002]**
(A) s-block (B) transition series (C) lanthanide series (D) actinide series.

6. If H_2S gas is passed in a acidified $ZnSO_4$, the precipitation of ZnS does not take place because
(A) K_{sp} of ZnS is not exceeded (B) K_{sp} of ZnS is decreases **[NSEC-2002]**
(C) K_{sp} of ZnS is increases (D) none of these

7. Platinum metal (Pt) dissolves in aqua- regia but not in concentrated HCl or HNO_3 because **[NSEC-2003]**
(A) HCl oxidises Pt in the presence of HNO_3
(B) HNO_3 reacts with HCl to form chlorine which attacks Pt
(C) HNO_3 oxidises Pt which is followed by formation of a chloro complex
(D) HCl and HNO_3 together give O_2 that oxidises Pt.

8. The aqueous solution of a salt of a transition metal ion changes colour from pink to blue, when concentrated hydrochloric acid is added to it. The change in colour is due to **[NSEC-2003]**
(A) evolution of hydrogen that changes the oxidation state of the metal ion
(B) change in the coordination number of the metal ion from 6 to 4 and formation of new species in solution
(C) formation of a coordination complex of the metal ion with hydrochloric acid
(D) protonation of the metal ion.

9. A solution containing Co^{2+} , Zn^{2+} and Al^{3+} is mixed with an excess of KSCN solution. The resulting solution besides the unreacted ions, should contain **[NSEC-2003]**
(A) $[Co(SCN)_6]^{4-}$ (B) $[Zn(NCS)_6]^{2-}$ (C) $Al(SCN)_3$ (D) $Zn(SCN)_2$.

10. The blue pigment prussian blue is an iron complex with formula **[NSEC-2003]**
(A) $K_4[Fe(CN)_6]$ (B) $K_2[Fe(CN)_4(NH_3)_2]$ (C) $Fe_4[Fe(CN)_6]_3$ (D) $Na_2[Fe(CN)_5NO]$.

11. When H_2S is passed through a solution containing Cu^{2+}, Cd^{2+} and an excess of cyanide ions, cadmium sulphide precipitates while copper ions remain in solution. This is because **[NSEC-2003]**
(A) Cu^{2+} forms a stable complex with cyanide while Cd^{2+} does not
(B) Cu^{2+} forms a more stable complex with cyanide than Cd^{2+}
(C) Cu^{2+} does not form a sulphide
(D) both CdS and CuS are formed, but CuS is soluble.

12. Iron articles get rusted on weathering due to the formation of **[NSEC-2003]**
(A) FeO (B) Fe_2O_3 (C) Fe_3O_4 (D) $Fe(OH)_3$

13. Generation of a blue colour which is not due to metal ammonia complex formation is seen when
(A) sodium is dissolved in liquid ammonia **[NSEC-2003]**
(B) copper (II) sulphate is reacted with ammonium hydroxide
(C) cobalt (II) chloride is reacted with ammonium hydroxide
(D) formaldehyde is reacted with ammonuim hydroxide.

14. Chromium has the lowest oxidation state in **[NSEC-2003]**
(A) chromium sulphate (B) chromium trioxide
(C) potassium chromate (D) potassium dichromate.

15. Paramagnetism is not exhibited by **[NSEC-2004]**
(A) $CuSO_45H_2O$ (B) $CuCl_25H_2O$ (C) CuI (D) $NiSO_4.6H_2O$.

16. Silver iodide is used to produce artificial rain because. **[NSEC-2005]**
(A) it is stable at high temperature (B) it is insoluble in rain water
(C) it can be easily spread (D) it has a seeding effect.

17. Articles made of copper or bronze slowly tarnish in air and turn green. The green colour is due to the formation of **[NSEC-2005]**
(A) copper sulphide (B) copper oxide
(C) basic copper carbonate (D) copper oxalate.

18. The cation containing maximum number of unpaired electrons is **[NSEC-2005]**
(A) Fe (II) (B) Fe (III) (C) Co (II) (D) Ni (II)

19. 1000 mL of a gas weighs 1.5 g at NTP. Its gram molecular weight is **[NSEC-2005]**
(A) 22.4 g (B) 33.6 g (C) 11.2 g (D) 15 g.

20. Rusting of iron is due to the formation of **[NSEC-2006]**
(A) hydrated ferrous oxide (B) hydrated ferric oxide
(C) only ferric oxide (D) a mixture of ferric oxide and $Fe(OH)_3$.

21. The brown ring test for NO_2^- and NO_3^- is due to formation of complex ion with formula **[NSEC-2006]**
(A) $[Fe(H_2O)_6]^{2+}$ (B) $[Fe(CN)_5(NO)]^{2-}$ (C) $[Fe(H_2O)_5(NO)]^{2+}$ (D) $[Fe(H_2O)(NO)_5]^{2+}$

22. In which of the following compounds is the oxidation number of the transition metal zero? **[NSEC-2007]**
(A) $[Ni(CO)_4]$ (B) $[Pt(C_2H_4)Cl_3$ (C) $[Co(NH_3)_6]Cl_2$ (D) $[Fe(H_2O)_3](OH)_2$

23. As the number of electrons in d-orbitals of transition elements increases, the screening effect on the valence electrons- **[NSEC-2007]**
(A) increases (B) decreases greatly (C) is not observed (D) decreases slightly

24. The magnetic moment of $MnSO_4.4H_2O$ is: **[NSEC-2007]**
(A) 1.73 BM (B) 3.87 BM (C) 4.09 BM (D) 5.92 BM

25. Metal carbonyls have the metal ions in zero or unusually lower oxidation states. This is because **[NSEC-2007]**
(A) carbonyl ligand is reducing in nature. (B) carbonyl is a highly electron rich ligand.
(C) carbonyl is a strongly o –bonding ligand. (D) carbonyl is a strongly p -acidic ligand.

26. For the reaction shown below, which statement is true ? **[NSEC-2007]**
$2Fe + 3CdCl_2 \rightleftharpoons 2FeCl_3 + 3Cd$
(A) Fe is the oxidizing agent (B) Cd undergoes oxidation
(C) Cd is the reducing agent (D) Fe undergoes oxidation

27. Which of these ion is expected to be colored in aqueous solution ? **[NSEC-2008]**
[I] Fe^{3+} [II] Zn^{2+} [III] Al^{3+} [IV] Sc^{3+}
(A) [I] only (B) [III] only (C) [I] and [II] only (D) [I], [II] and [III]

28. How many unpaired electrons are in a Fe^{2+} ion in the ground state ? **[NSEC-2008]**
(A) 0 (B) 2 (C) 4 (D) 6

29. 1 mL of concentrated aqueous ammonia is added dropwise to 1 mL of a dilute aqueous solution of Cu(II). What observations can be made during this process ? **[NSEC-2008]**
(A) The colorless Cu(II) nitrate solution turns blue and yields a dark blue precipitate
(B) The colorless copper (II) nitrate solution yields a white precipitate which turns dark blue upon standing.
(C) The light blue copper (II) nitrate solution yields a white precipitate which redissolves to form a dark blue solution.
(D) The light blue copper (II) nitrate solution turns dark

30. Two white solids, lead (II) chloride and silver chloride can be distinguished from each other by -
(A) adding cold water to each : the silver chloride will dissolve. **[NSEC-2008]**
(B) adding hot water to each : the lead (II) chloride will dissolve.
(C) adding sodium chloride solution to each : the lead (II) chloride will become warm and release chlorine gas.
(D) adding zinc chloride solution to each : the silver chloride will change to metallic silver.

31. $CuSO_4$ reacts with KCN to form water insoluble CuCN. This insoluble precipitate dissolves in excess of KCN, due to formation of the following complex **[NSEC-2008]**
(A) $K_2[Cu(CN)_4]$ (B) $K_3[Cu(CN)_4]$ (C) $Cu(CN)_2$ (D) $Cu[KCu(CN)_4]$

32. The ion which has 18 electrons in the outermost shell is – **[NSEC-2009]**
(A) Cu^+ (Z = 29) (B) Al^{3+} (Z = 13) (C) K^+ (Z = 19) (D) Th^{4+} (Z = 90)

33. The compound with the lowest oxidation state of iron is – **[NSEC-2009]**
(A) Fe_2O (B) Fe_3O_4 (C) $K_3Fe(CN)_6$ (D) $K_4Fe(CN)_6$

34. The aqua ion which will be almost colorless is – **[NSEC-2009]**
(A) Cu^{2+} (B) Cr^{2+} (C) Ti^{4+} (D) Mn^{2+}

35. MnO_4^{1-} is of intense pink colour, though Mn is in +VII oxidation state. This is due – **[NSEC-2009]**
(A) d-d transition
(B) charge transfer when Mn gives electron to oxygen
(C) charge transfer when oxygen gives its electrons to Mn making it +VI
(D) absorption of IR frequencies

36. The product formed when chlorine gas is passed over hot iron is **[NSEC-2010]**
(A) Iron(II) chloride is formed.
(B) Iron(III) chloride is formed.
(C) A mixture of iron(II)chloride and iron(III) chloride is formed.
(D) No reactions will take place.

37. The group that has the species correctly listed in the order of decreasing radius is **[NSEC-2011]**
(A) Cu^{2+}, Cu^+, Cu (B) V, V^{2+}, V^{3+} (C) F^-, Br^-, I (D) B, Be, Li

38. The compound in which Mn has oxidation state of +3 is **[NSEC-2011]**
(A) $KMnO_4$ (B) $K_2[Mn(CN)_6]$ (C) $MnSO_4$ (D) $CsMn(SO_4)_2.12H_2O$

39. Lanthanide contraction is caused due to **[NSEC-2012]**
(A) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge
(B) the appreciable shielding on outer electrons by 5d electrons from the nuclear charge
(C) the same effective nuclear charge from Ce to Lu.
(D) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge

40. Which of the following ion is colourless ? **[NSEC-2012]**
(A) Mn^{2+} (B) Cu^{+} (C) Cr^{3} (D) Fe^{2+}

41. The lanthanide compound which is used as a most powerful liquid laser after dissolving in selenium oxychloride is : **[NSEC-2012]**
(A) Cerium oxide (B) Neodynium oxide
(C) Promethium sulphate (D) Cerium sulphate

42. Which of the following weighs less when weighed in magnetic field ? **[NSEC-2012]**
(A) $ScCl_3$ (B) $FeCl_3$ (C) $TiCl_3$ (D) VCl_3

43. In which of the following compounds is the oxidation number of the transition metal, zero ? **[NSEC-2013]**
(A) $[Fe(H_2O)_3](OH_2)$ (B) $[Co(NH_3)_6]Cl_2$ (C) $[Ni(CO_4)]$ (D) $[Pt(C_2H_4)Cl_3]$

44. One of the constituents of German silver is **[NSEC-2013]**
(A) Ag (B) Mg (C) Cu (D) Al

45. A catalyst is a substance that **[NSEC-2013]**
(A) undergoes chemical change to accelerate the rate of the reaction
(B) decreases the energy of activation of the reaction
(C) increases the kinetic energy of the reaction
(D) lowers the potential energy of the products with respect to that of the reactants.

46. The number of unpaired electrons in Ni^{2+} is **[NSEC-2013]**
(A) 0 (B) 2 (C) 3 (D) 4

47. The colourless ion from among the following is **[NSEC-2013]**
(A) Mn^{2+} (B) Cu^{+} (C) Cr^{3+} (D) Fe^{2+}

48. The metal carbonyl which is paramagnetic is **[NSEC-2013]**
(A) $Ni(CO)_4$ (B) $V(CO)_6$ (C) $Cr(CO)_6$ (D) $Fe(CO)_5$

49. Bell metal is an alloy of copper and **[NSEC-2013]**
(A) Tin (B) Aluminium (C) Zinc (D) Nickel

50. Europium (Eu) and Terbium (Tb) attain stable $4f^7$ configuration by exhibiting oxidation states of **[NSEC-2013]**
(A) +2 and +4 (B) +3 and +4 (C) +2 and +3 (D) +1 and +3

51. The number of unpaired electrons in Ni^{2+} ion is 2,therefore its spin multiplicity is **[NSEC-2013]**
(A) 2 (B) 1 (C) 3 (D) 4

52. When zinc rod is directly placed in copper sulphate solution **[NSEC-2013]**
(A) the blue colour of the solution starts intensifying
(B) the solution remains electrically neutral
(C) the temperature of the solution falls
(D) the weight of zinc rod starts increasing

53. The ions which give black precipitates on passing H_2S gas in acidic medium are **[NSEC-2013]**
(A) Al^{3+} and Ni^{2+} (B) Ni^{2+} and Co^{2+} (C) Cu^{2+} and Bi^{3+} (D) Zn^{2+} and Mn^{2+}

RRP ANSWER KEY

PART- 1

1.	(A)	**2.**	(B)	**3.**	(A)	**4.**	(A)	**5.**	(D)
6.	(C)	**7.**	(B)	**8.**	(A)	**9.**	(C)	**10.**	(C)
11.	(D)	**12.**	(D)	**13.**	(A)	**14.**	(D)	**15.**	(B)
16.	(A)	**17.**	(D)	**18.**	(A)	**19.**	(A)	**20.**	(B)
21.	2 (1 & 4)	**22._**	10	**23._**	2	**24._**	6	**25._**	15

PART- 2

1.	(D)	**2.**	(B)	**3.**	(A)	**4.**	(B)	**5.**	(AB)
6.	(AC)	**7.**	(ABC)	**8.**	(BCD)	**9.**	(BD)	**10.**	(ABC)
11.	(ABC)	**12.**	(ABC)	**13.**	4	**14.**	2	**15.**	3
16.	3	**17.**	9	**18.**	6				

PART- 3

1.	(C)	**2.**	(B)	**3.**	(B)	**4.**	(C)	**5.**	(D)
6.	(A)	**7.**	(B)	**8.**	(C)	**9.**	(A)	**10.**	(C)
11.	(B)	**12.**	(C)	**13.**	(B)	**14.**	(A)	**15.**	(C)
16.	(D)	**17.**	(B)	**18.**	(B)	**19.**	(B)	**20.**	(D)
21.	(C)	**22.**	(A)	**23.**	(A)	**24.**	(D)	**25.**	(D)
26.	(D)	**27.**	(A)	**28.**	(C)	**29.**	(C)	**30.**	(B)
31.	(B)	**32.**	(A)	**33.**	(A)	**34.**	(C)	**35.**	(C)
36.	(B)	**37.**	(B)	**38.**	(D)	**39.**	(D)	**40.**	(B)
41.	(B)	**42.**	(A)	**43.**	(C)	**44.**	(C)	**45.**	(B)
46.	(B)	**47.**	(B)	**48.**	(B)	**49.**	(A)	**50.**	(A)
51.	(C)	**52.**	(B)	**53.**	(C)				

RRP SOLUTIONS

PART - 1

1. (A) Electron configuration of V is [Ar] $3d^3\ 4s^2$ and thus maximum 5 electrons participate in bonding.
(B) Electron configuration of Cr is [Ar] $3d^5\ 4s^1$ and thus maximum 6 electrons participate in bonding.
(C) Electron configuration of Co is [Ar] $3d^7\ 4s^2$. In octahedral splitting in presence of ligands, half filled t_{2g}^6 has higher CFSE and thus +3 oxidation state is most stable.
(D) Electron configuration of Sc is [Ar] $3d^1\ 4s^2$ and thus maximum 3 electrons participate in bonding.

2. Transition metal oxide with highest oxidation states is most acidic in character because of the very less difference in the values of electronegativity between Mn^{7+} and O^{2-}, and the decreasing order of acidic character is $\overset{+7}{Mn}_2O_7 > \overset{+4}{Mn}O_2 > \overset{+3}{Mn}_2O_3 >> \overset{+2}{Mn}O$.

3. First ionisation energies of 3d-series (first transition series) increase with increase in atomic number due to (A) increase in nuclear charge (B) decrease in atomic size.

4. (i) Valence shell electron configuration of Ti^{4+} is $3d^{10}\ 4s^0$. As there is no unpaired electrons for d–d transition, the solution of ions will be colourless.
(ii) Valence shell electron configuration of Cu^+ is $3d^{10}\ 4s^0$. As all electrons are paired, there is no d–d transition, so the solution of ions will be colourless.
(iii) Valence shell electron configuration of Co^{3+} is $3d^6\ 4s^0$. As there are 4 unpaired electrons, there is d–d transition of electron, so the solution of ions will be coloured.
(iv) Valence shell electron configuration of Fe^{2+} is $3d^6\ 4s^0$. As there are 4 unpaired electrons, there is d–d transition of electron, so the solution of ions will be coloured.

5. (A) Valence shell electron configuration of Co^{3+} is $3d^6 4s^0$. So has 4 unpaired electrons.
(B) Valence shell electron configuration of Fe^{3+} is $3d^5 4s^0$. So has 5 unpaired electrons.
(C) Valence shell electron configuration of Cr^{2+} is $3d^4 4s^0$. So has 4 unpaired electrons.
(D) Valence shell electron configuration of V^{3+} is $3d^2 4s^0$. So has 2 unpaired electrons.
It has least number of unpaired electrons, so it has least magnetic moment.

6. If a non-metal occupies interstitial sites of a metal, the metal becomes less malleable. This is because the non-metal atom forms covalent bonds with metal atoms and covalent bond is rigid and directional.

7. (A) Oxidation state of iron is +3 but it can exceed to a maximum of +6. Oxidation state of cobalt is +3 but it can exceed to a maximum of +4.
(B) Highest oxidation state of Cr in CrO_2Cl_2 is + 6 and highest oxidation state of Mn in MnO_4^- is + 7.
(C) Oxidation state of titanium is +2 but it can exceed to a maximum of +4. Oxidation state of Mn is +4 but it can exceed to a maximum of +7.
(D) Oxidation state of cobalt is +3 but it can exceed to a maximum of +4. Oxidation state of Mn is +7 which is its highest oxidation state.

8. CuCl absorbs CO, SO_2, C_2H_2 ; $CuCl + 2CO \longrightarrow 2CuCl.CO$.

9. (C) $FeCl_3$ exists as Fe_2Cl_6 (a dimer) in vapour state.The solution is acidic due to the formation of HCl and brown due to the formation of $Fe(OH)_3$.
$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3$ (Brown) + 3HCl

10. (A) Cu_2O is red white CuO is black.
(B) Obtained on heating malchite ore not heamatite

$$CuCO_3.Cu(OH)_2 \xrightarrow{\Delta} 2\,CuO + CO_2 + H_2O$$

(C) $3\,CuCl_2.2H_2O \xrightarrow{\Delta} CuO + 2CuCl + 2HCl + Cl_2 + 5H_2O$
(D) $2CuFeS_2 + 4O_2 \longrightarrow Cu_2S + 2FeO + 3SO_2$

11. All are facts.

12. $2CuSO_4 + 2NaCl + SO_2 + 2H_2O \longrightarrow Cu_2Cl_2 + Na_2SO_4 + 2H_2SO_4$
$Cu_2Cl_2 + H_2S \longrightarrow \underset{\text{(Black ppt.)}}{Cu_2S} + 2HCl$
$Cu_2Cl_2 + aq.\ NH_3 \longrightarrow \underset{\text{Soluble complex}}{[Cu(NH_3)_2]Cl}$
$Cu_2Cl_2 + 4\,HCl \longrightarrow 2\,H_2CuCl_3$

13. (A) True, $2FeCl_3.6H_2O \xrightarrow{\text{Heat}} Fe_2O_3 + 6HCl + 9H_2O$
(B) False, $FeSO_4$ is oxidised to Fe^{3+} early, so it is not used as primary standard. But Mohr's salt $[FeSO_4.(NH_4)_2SO_4.6H_2O]$ can be used.
(C) False, $ZnCl_2 + H_2S \longrightarrow \underset{\text{white precipitate}}{ZnS} + 2HCl$
(D) False, $CuSO_4 + 4NH_4OH \longrightarrow \underset{\text{Deep blue solution}}{[Cu(NH_3)_4]SO_4} + 4H_2O$
$FeSO_4 + 2NH_4OH \longrightarrow \underset{\text{Insoluble}}{Fe(OH)_2} + (NH_4)_2SO_4$

14. $S_2O_3^{2-}$, CN^-, SCN^- and I^- act as reducing agent ; $Cu^{2+} + S_2O_3^{2-} \longrightarrow Cu^+ + S_4O_6^{2-}$
$Cu^{2+} + CN^- \longrightarrow Cu^+ + (CN)_2$; $Cu^{2+} + SCN^- \longrightarrow Cu^+ + (SCN)_2$

15. SO_2 and SO_3
$FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2\uparrow + SO_3\uparrow + O_2\uparrow$
The acidic gases produced are SO_2 and SO_3

16. X : $[K_3\,Fe(CN)_6)$ Y : $Fe\,[Fe(CN)_6]$

17. $2KMnO_4 \xrightarrow{750K} K_2MnO_4 + MnO_2 + O_2$.

18. $MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$ (neutral / weak alkaline medium)

19. $2KMnO_4 + 3H_2SO_4 \rightarrow 2KHSO_4 + (MnO_3)_2SO_4 + 2H_2O$
$(MnO_3)_2SO_4 + H_2O \rightarrow Mn_2O_7 + H_2SO_4$

$Mn_2O_7 \xrightarrow{\Delta} 2MnO_2 + \frac{3}{2}O_2$

20. (A) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$.

(B) In acidic solution, actually chromate is converted to dichromate.
$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$.

(C) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$.

(D) $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$.

21. In Co^{+3} ion, electronic configuration $|Ar|_{18}\, 3d^6 4s^0$. For octahedral complex 4 unpaired electron get paired and in configuration become $t_{2g}^{\,6}\, eg^0$ and hybridization d^2sp^3.
Os has maximam VIII oxidation state.

22. Oil of vitriol = H_2SO_4, white vitriol - $ZnSO_4.7H_2O$, Blue vitriol = $CuSO_4.\ 5H_2O$, green vitriol - $FeSO_4.7H_2O$ A is Zn
$Zn + HCl \rightarrow \underset{(D)}{ZnCl_2} + H_2$; $ZnCl_2 + NaOH \text{ (excess)} \rightarrow NaCl + \underset{(E)}{Na_2ZnO_2}$
$ZnCl_2 + NH_3 \text{ (excess)} \rightarrow \underset{(F)}{(Zn(NH_3)_4\, Cl_2}$
metal B is Cu
$Cu + HCl \rightarrow$ no hydrogen liberated
$Cu + HNO_3 \rightarrow \underset{(G)}{Cu(NO_3)_2} + NO_2 + H_2O$
$Cu\,(NO_3)_2 + H_2S \xrightarrow{H^+} \underset{(H)}{CuS} \downarrow$ (black)
metal C = Fe
$Fe + Cl_2 \rightarrow FeCl_3 \xrightarrow{\Delta} Fe_2Cl_6$
$FeCl_3 + KI \longrightarrow FeCl_2 + KCl + I_2$

23. Chromium undergoes reduction while oxygen undergoes oxidation.

24. (1) All lanthanoids exhibits +3 O.N. but few also exhibit +2 and +4 O.N.
(2) Correct (3) Incorrect as all belongs to 6th period.
(4) True due to lanthanoid contraction.
(5) Incorrect as basicing decreases from $Ce(OH)_3$ to $Lu(OH)_3$ becomes of fazans rule.
(6) Correct (7) Correct
(8) All lanthanoids have –ve S.R.P. hence all releases hydrogen.

25. Outer electronic configuration of Lu is $4f^{14}5d^16s^2$
$\therefore$ No. of electrons = 15

PART - 2

1. ${}_{22}Ti = 3d^2 4s^2$, $Ti^{2+} = 3d^2$; ${}_{23}V = 3d^3 4s^2$, $V^{3+} = 3d^2$.
${}_{24}Cr = 3d^5 4s^1$, $Cr^{4+} = 3d^2$; ${}_{25}Mn = 3d^5 4s^2$, $Mn^{5+} = 3d^2$.

2. (A) Oxidation state of iron is +3 but it can exceed to a maximum of +6. Oxidation state of cobalt is +3 but it can exceed to a maximum of +4.
(B) Highest oxidation state of Cr in CrO_2Cl_2 is + 6 and highest oxidation state of Mn in MnO_4^- is + 7.
(C) Oxidation state of titanium is +2 but it can exceed to a maximum of +4. Oxidation state of Mn is +4 but it can exceed to a maximum of +7.
(D) Oxidation state of cobalt is +3 but it can exceed to a maximum of +4. Oxidation state of Mn is +7 which is its highest oxidation state.

3. It is an amphoteric in nature and it reacts with alkalies as well as with acids to give $V_4O_9^{2-}$ and VO^{2+} respectively.

4. **S_1 :** It is because Mn^{2+} has $3d^5$ configuration which has extra stability.
S_2 : Not titanium but Copper, because with +1 oxidation state an extra stable configuration, $3d^{10}$ results.
S_3 : It is not stable as it undergoes disproportionation ; $2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$. The E° value for this is favourable.
S_4 : Much larger third ionisation energy of Mn (where the required change is d^5 to d^4) is mainly responsible for this.

5. (A) and (B) statements are correct. These statements are factual.
(C) Along the period, the electronegativity of metals decreases and therefore the difference of electronegativities between metal and oxygen decreases. Hence, the acidic character increases, so the correct order is TiO < VO < CrO < MnO.
(D) V_2O_5 reacts with alkalies as well as acids to give VO_4^{3-} and VO_2^+ respectively.

6. Fenton's reagent is $FeSO_4 + H_2O$

$$FeSO_4 + \underset{(Y)}{(NH_4)_2 SO_4} + 6\,H_2O \longrightarrow FeSO_4\,.\,(NH_4)_2SO_4\,.\,6\,H_2O$$

$$FeS_2 + O_2 + H_2O \longrightarrow FeSO_4 + \underset{(Z)}{Fe_2\,(SO_4)_3} + H_2SO_4$$

$$\underset{(X)}{FeSO_4} + KMnO_4 + H_2SO_4 \longrightarrow \underset{(Z).}{Fe_2(SO_4)_3} + MnSO_4 + K_2SO_4 + H_2O$$

7. (A) $2CuSO_4 + 2NaCl + 2H_2O + SO_2 \rightarrow Cu_2Cl_2 + Na_2SO_4 + 2H_2SO_4$
(B) $Cu + HCl + [O] \rightarrow CuCl_2 + H_2O$; $CuCl_2 + Cu \rightarrow Cu_2\,Cl_2$
(C) $CuSO_4 + 2HCl \rightarrow CuCl_2 + H_2SO_4$; $CuCl_2 + Cu \rightarrow Cu_2Cl_2$
(D) $CuO + 2HCl \rightarrow CuCl_2 + H_2O$; Cu_2Cl_2 is not formed.

8. (A) $5HCHO + MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5HCOOH + 3H_2O$.
(B) $4KOH + 2MnO_2$ (manganese dioxide) $+ O_2 \rightarrow 2K_2MnO_4$ (potassium mangnate) $+ 2H_2O$.
(C) $Mn(OH)_2 + O_2^{2-} \rightarrow MnO_4^{2-}$(mangnate) $+ 2OH^-$.
(D) $2KMnO_4 \xrightarrow{750\,K} K_2MnO_4$ (potassium mangnate) $+ MnO_2 + O_2$.

9. (A) In both compounds central metals have + 6 oxidation states.
MnO_4^{2-} ; $x + 4(-2) = -2$, So, $x = 6$. ; CrO_2Cl_2 ; $x + 2(-2) + 2(-1) = 0$, So, $x = 6$.
(B) Sodium dichromate is $Na_2Cr_2O_7.2H_2O$, so it can not be weighed correctly for the preparation of standard solution.
(C) $2K_2Cr_2O_7 \xrightarrow{\Delta} 2K_2CrO_4 + Cr_2O_3$ (green) $+ 3/2\,O_2$.
(D) $4KMnO_4 + 4KOH \xrightarrow{\Delta} 4K_2MnO_4$ (green) $+ 2H_2O + O_2$

10. $AgCl \xrightarrow{h\nu} \underset{(black)}{Ag\downarrow} + 1/2\,Cl_2$

If souce of light is removed, we get back Agce and blacknem due to Ag removed.

11. Ag +dilute $HNO_3 \rightarrow AgNO_3 + NO\,(g)$; Ag + conc. $HNO_3 \rightarrow AgNO_3 + NO_2\,(g)$
Ag + conc. $H_2SO_4 \rightarrow Ag_2SO_4 + SO_2\,(g)$

12. $2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$; $2K_2MnO_4 + H_2O + O_3 \rightarrow 2KMnO_4 + 2KOH + O_2$.
$3K_2MnO_4 + 2CO_2 \rightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3$.

13.

*NO_2	Coloured & Paramagnetic
Cu^{+1}	Colourless
*O_2	Paramagnetic
O_3	Diagmagnetic
Hg_2^{+2}	Colourless
Cd^{+2}	Coloureless
*Al	Paramagnetic
*C(graphite)	Paramagnetic
Sc^{+3}	Colourless or diamagnetic

14.

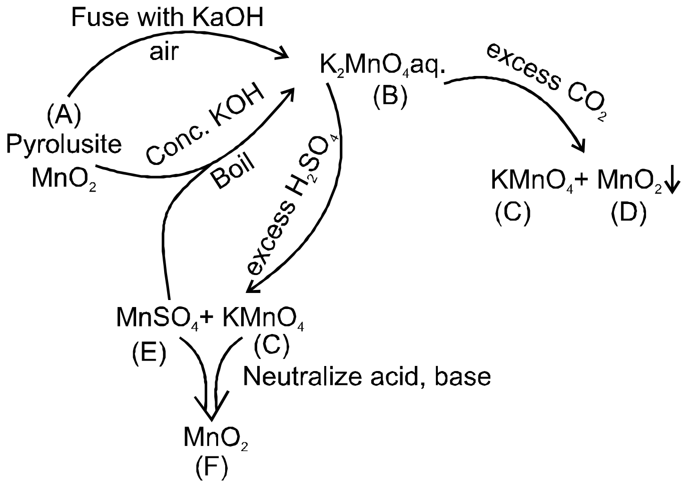
Ions	Outer configuration	Number of unpaired electron (s)	$m_s = \sqrt{n(n+2)}$
Ti^{3+}	$3d^1$	1	$\sqrt{2}$
Cu^+	$3d^{10}$	0	0
Ni^{2+}	$3d^8$	2	$\sqrt{8}$
Fe^{3+}	$3d^5$	5	$\sqrt{35}$
Mn^{2+}	$3d^5$	5	$\sqrt{35}$
Co^{2+}	$3d^7$	3	$\sqrt{15}$

15. (a) $Cu(OH)_2 \downarrow$ (blue) (b) $[Cu(NH_3)_4]^{2+}$ (aq.) (c) $Na_2[Zn(OH)_4]$ (aq.)

(d) $[Zn(NH_3)_4]^{2+}$ (aq.) (e) $Fe(OH)_2 \downarrow$ (greenish) (f) $Fe(OH)_3 \downarrow$ (reddish brown)

(g) $CuI \downarrow$ (white) (h) $ZnCO_3 \downarrow$ (white) (i) $Cu(NO_3)_2$ (aq.)

16.



17. Paramagetic – K_2MnO_4 , Cr_2O_3 , AgO , $CuSO_4$, MnO_2
Diamagnetic and Colored –Hg_2I_2 , Ag_2S , HgI_2 , K_2CrO_4 ,
(black) (Red) (yellow)
Ag_2O (brown), H_gS (black) , A_gF (yellow)
CrO_5 (deep blue) , Mn_2O_7 (dark red oil)

18. (1) All lanthanides exhibits +3 O.N. but few also exhibit +2 and +4 O.N.
(2) Correct
(3) Incorrect as all belongs to 6th period.
(4) True due to lanthanide contraction.
(5) Incorrect as basicing decreases from $Ce(OH)_3$ to $Lu(OH)_3$ becomes of fazans rule.
(6) Correct
(7) Correct
(8) All lanthanides have –ve S.R.P. hence all releases hydrogen.

PART - 3

18. (A) Fe^{+2} : [Ar], $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ $\Rightarrow$ 4 unpair e^- (B) Fe^{+3} : [Ar], $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ $\Rightarrow$ 5 unpair e^-

(C) Co^{+2} : [Ar], $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ $\Rightarrow$ 3 unpair e^- (D) Ni^{+2} : [Ar], $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$ $\Rightarrow$ 2 unpair e^-

33.

Fe_2O	Fe_3O_4	$K_3[Fe(CN)_6]$	$K_4[Fe(CN)_6]$
Fe(+1)	Fe(+8/3)	Fe (+3)	Fe (+2)

${}_{29}Cu$: [Ar] $4s^1 3d^{10}$; ${}_{29}Cu^{1+}$: [Ne] $3s^2\ 3p^6\ 3d^{10}$

34. Ti^{4+} has no unpaired electron.

35. Ligand to metal charge transfer when oxygen gives its electron to Mn making it +VI.

37. $V > V^{+2} > V^{+3}$ Radius of same atom $\propto \dfrac{1}{\text{amount of the charge}}$

38. $Cs[Mn(SO_4)_2.12H_2O]$; $x - 4 = -1$; $x = +3$

39. 4f electrons does imperfect shielding on outer electrons there fore effective nuclear charge increase.

40. $Cu^+ = [Ar]3d^{10}$
All electrons are paired therefore diamagnetic and colourless.

41. It is neodymium oxide.

42. It is for diamagnetic substance (Sc^{+3}). It has all e^- s paired.

43. $[Ni(CO)_4]$, oxidation number of Ni is zero.

44. It is an alloy of copper, zinc & nickel

45. Catalyst lowers the activation energy of reaction.

46. Ni^{2+} : $3d^8$

$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

No. of unpaired electron = 2

47. Cu^+ (No unpaired electron)

48. $[V(CO)_6]$ has one unpaired electron
V : $3d^3\ 4s^2$ or $3d^5$ $t_{2g}^{2,2,1}$, $e_g^{0,0}$

49. Bell metal : An alloy of tin & copper.

50. Tb : [Xe] $4f^9 6s^2$; Eu : [Xe] $4f^7 6s^2$

51. $M = 2 \times |S| + 1$ $S = 2 \times \pm\frac{1}{2}$

$= 2 \times 1 + 1$ $= 1$
$= 3$

53. $$\underbrace{Cu^{2+} \text{ or } Bi^{3+}}_{2^{nd}\text{Group cation}} \xrightarrow{H_2S/H^+} \underset{\text{Black}}{CuS\downarrow} + \underset{\text{Black}}{Bi_2S_3}$$