

d & f-BLOCK ELEMENTS & THEIR IMPORTANT COMPOUNDS

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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 $\text{K}_2\text{Cr}_2\text{O}_7$ 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

Section (A) : Electronic configuration, atomic size and ionic size, density, melting and boiling points, ionization enthalpy and oxidation state.

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 ¹ 4s ²	3d ² 4s ²	3d ³ 4s ²	3d ⁵ 4s ¹	3d ⁵ 4s ²	3d ⁶ 4s ²	3d ⁷ 4s ²	3d ⁸ 4s ²	3d ¹⁰ 4s ¹	3d ¹⁰ 4s ²
	M ⁺	3d ² 4s ⁰	3d ³ 4s ⁰	3d ⁴ 4s ⁰	3d ⁵	3d ⁶ 4s ⁰	3d ⁷ 4s ⁰	3d ⁸ 4s ⁰	3d ⁹ 4s 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, $\Delta_a H^\ominus$ / kJ mol ⁻¹											
		326	473	515	397	281	416	425	430	339	126
Ionisation enthalpy / $\Delta_i H^\ominus$ / kJ mol ⁻¹											
$\Delta_i H^\ominus$	I	631	656	650	653	717	762	758	736	745	906
$\Delta_i H^\ominus$	II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
$\Delta_i H^\ominus$	III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829
Metallic/ionic radii/pm	M	164	147	135	129	137	126	125	125	128	137
	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 [⊕] / 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

General introduction										
1.	Occurrence	Three of transition metals are very abundant in the earth's crust.								
		Fe → 4 th most abundant elements in earth's crust by weight. Ti → 5 th most abundant elements in earth's crust by weight. Mn → 12 th 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 12 th most abundant element by weight.								
	2nd and 3rd row	Less abundant than 1 st d- series elements. Tc → does not occur in nature. Last six members of 2 nd and 3 rd 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, etc.								
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	4 th to 7 th <table><tr><td>4th period</td><td>3d- series (Sc - Zn)</td></tr><tr><td>5th period</td><td>4d- series (Y - Cd)</td></tr><tr><td>6th period</td><td>5d- series (La - Hg)</td></tr><tr><td>7th period</td><td>6d- series (Ac - Uub)</td></tr></table>	4 th period	3d- series (Sc - Zn)	5 th period	4d- series (Y - Cd)	6 th period	5d- series (La - Hg)	7 th period	6d- series (Ac - Uub)
4 th period	3d- series (Sc - Zn)									
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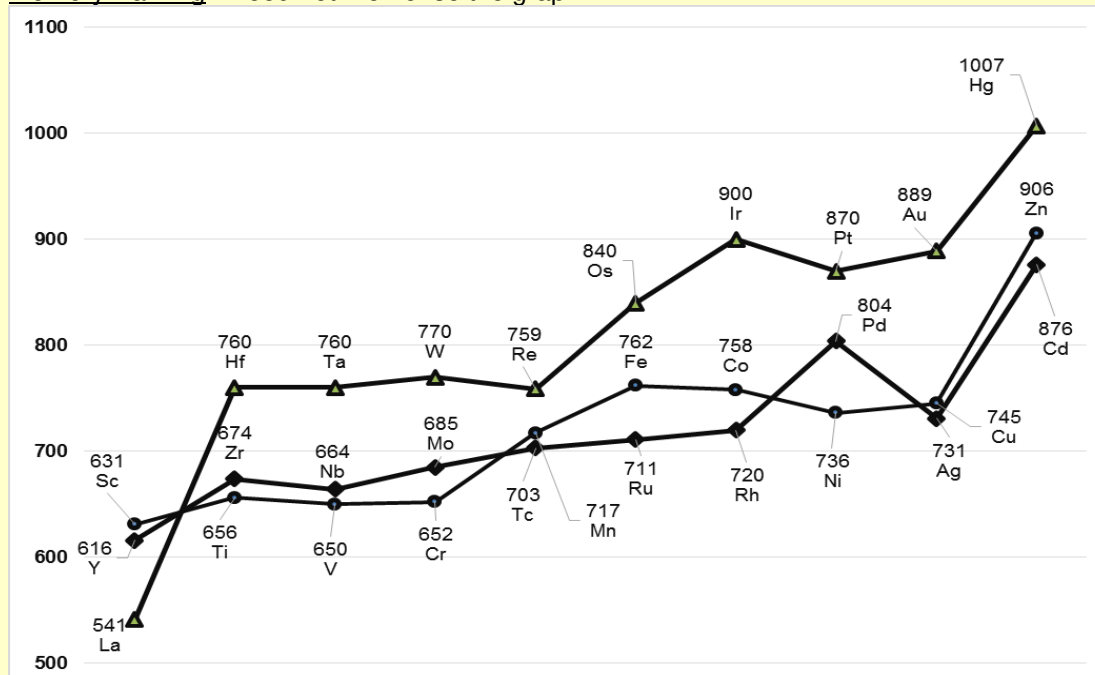
Periodic trends and chemical properties																		
S.N.	Properties		DISCRIPTION															
1	Metallic character		All the transition elements are metals, therefore they are showing all the metallic properties. Good conductor of heat and electricity. Metallic lustre, strong and ductile. With 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 VIII	9 VIII	10 VIII	11 IB	12 IIB						
	3d Series	21 Sc $3d^1 4s^2$	22 Ti $3d^2 4s^2$	23 V $3d^3 4s^2$	24 Cr $3d^5 4s^1$	25 Mn $3d^5 4s^2$	26 Fe $3d^6 4s^2$	27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$							
	4d Series	39 Y $4d^1 5s^2$	40 Zr $4d^2 5s^2$	41 Nb $4d^4 5s^1$	42 Mo $4d^5 5s^1$	43 Tc $4d^5 5s^2$	44 Ru $4d^7 5s^1$	45 Rh $4d^8 5s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10} 4s^1$	48 Cd $4d^{10} 4s^2$							
	5d Series	57 La* $5d^1 6s^2$	72 Hf $4f^{14} 5d^2 6s^2$	73 Ta $5d^3 6s^2$	74 W $5d^4 6s^2$	75 Re $5d^5 6s^2$	76 Os $5d^6 6s^2$	77 Ir $5d^7 6s^2$	78 Pt $5d^9 6s^1$	79 Au $5d^{10} 6s^1$	80 Hg $5d^{10} 6s^2$							
	6d Series	89 Ac** $6d^1 7s^1$	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn							
			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 2 nd and 3 rd rows do not always follow the pattern of the first row, e.g. Group 10 <table><tr><td>Ni</td><td>$3d^8 4s^2$</td></tr><tr><td>Pd</td><td>$4d^{10} 5s^0$</td></tr><tr><td>Pt</td><td>$5d^9 6s^1$</td></tr></table>										Ni	$3d^8 4s^2$	Pd	$4d^{10} 5s^0$	Pt	$5d^9 6s^1$
Ni	$3d^8 4s^2$																	
Pd	$4d^{10} 5s^0$																	
Pt	$5d^9 6s^1$																	
			d-orbitals are complete at Cu, Pd, Ag, Au. <table><tr><td>Ni ($3d^8 4s^2$)</td><td>Cu($3d^{10} 4s^1$)</td><td>Zn($3d^{10} 4s^2$)</td></tr><tr><td>Pd($4d^{10} 5s^0$)</td><td>Ag($4d^{10} 5s^1$)</td><td>Cd($4d^{10} 5s^2$)</td></tr></table> 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.										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($4d^{10} 5s^2$)
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($4d^{10} 5s^2$)																
	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)															



3	Size of atoms and ions	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.																						
	d-orbital contraction	<p>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.</p> <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>	Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Atomic radius (pm)	144	132	122	117	117	117	116	115	117	125
Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn														
Atomic radius (pm)	144	132	122	117	117	117	116	115	117	125														
	Lanthanide Contraction	<p>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 is 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.</p>																						
	<p style="text-align: center;">Ti < Zr ≈ Hf (Lanthanide Contraction) Sc < Y < La</p> <p>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.</p>																							
4	Ionization energies of transition metals	<p>Ionization energy normally increases from left to right in the period. Ionization energy values of third transition series is greater than ionization energy values of first and second transition series.</p>																						



Memory warning : Need not memorise the graph.



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

- The first ionisation potential for the first four 3d-block elements (Sc, Ti, V & Cr) differ only slightly from one another.
- Similarly the value first ionisation energy of Fe, Co, Ni & Cu also are fairly close to one another.
- The value of first ionisation energy for Zn is considerably higher due to the extra stability of 3d¹⁰4s² level which is completely filled in Zn atom.
- The first ionization energy of Mn is slightly higher than adjacent elements in 3d series due to half-filled stable configuration.
- Second ionisation energy value for Cr & Cu are higher as the Cr⁺ & Cu⁺ ion are extra stable due to 3d⁵ and 3d¹⁰ Configuration.
- In vertical columns, the ionisation energy decrease from first member to the second member.
- However the third member (5d series) has higher value than second member (4d-series) due to lanthanide contraction. I.E.(3rdT.S.) > I.E.(2ndT.S.) > I.E.(1stT.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.

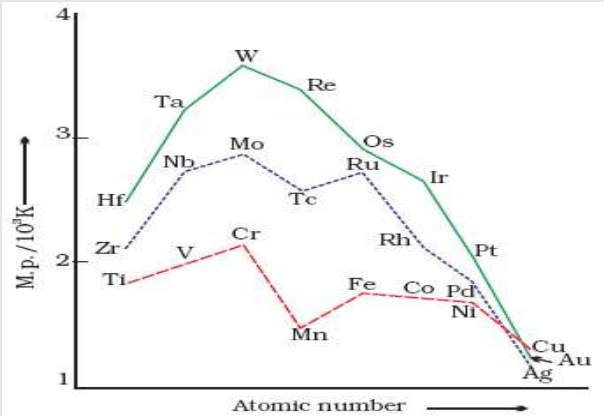
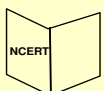
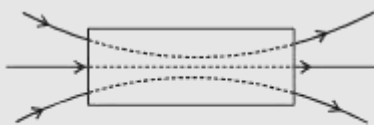


		<p>Trends of Oxidation state</p> <p>Highest oxidation state of 3d-series elements can be calculated by $n + 2$ (where n = number of unpaired electrons) It is not applied for Cr and Cu.</p> <p>The transition metal ions having stable configuration like d^0, d^5 or d^{10} are more stable. Ex. Sc^{+3}, Ti^{+4}, V^{+5}, Fe^{+3}, Mn^{+2}, Zn^{+2} etc.</p> <p>Most common oxidation state among the transition elements is +2.</p> <p>Highest oxidation state shown by transition elements of '4d' and '5d' series is +8 by Ru (44) and Os (76).</p> <p>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.</p> <p>Ex. MnO_4^{+7}, $Cr_2O_7^{+6}$, CrO_4^{+6}, MnO_2^{+4}, MnO_4^{+6}, $CrO_2F_2^{+6}$</p> <p>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.</p> <p>They form ionic compounds in low oxidation states and covalent compounds in Higher oxidation state.</p>																																																																																																																						
	<table><tr><th colspan="11">Formulas of Oxides of 3d Metals (* mixed oxides)</th></tr><tr><th>OXIDATION NUMBER</th><th>Sc</th><th>Ti</th><th>V</th><th>Cr</th><th>Mn</th><th>Fe</th><th>Co</th><th>Ni</th><th>Cu</th><th>Zn</th></tr><tr><td>+7</td><td></td><td></td><td></td><td></td><td>Mn_2O_7</td><td></td><td></td><td></td><td></td><td></td></tr><tr><td>+6</td><td></td><td></td><td></td><td>CrO_3</td><td></td><td></td><td></td><td></td><td></td><td></td></tr><tr><td>+5</td><td></td><td></td><td>V_2O_5</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr><tr><td>+4</td><td></td><td>TiO_2</td><td>V_2O_4</td><td>CrO_2</td><td>MnO_2</td><td></td><td></td><td></td><td></td><td></td></tr><tr><td>+3</td><td>Sc_2O_3</td><td>Ti_2O_3</td><td>V_2O_3</td><td>Cr_2O_3</td><td>Mn_2O_3</td><td>Fe_2O_3</td><td></td><td></td><td></td><td></td></tr><tr><td></td><td></td><td></td><td></td><td></td><td>$Mn_3O_4^*$</td><td>$Fe_3O_4^*$</td><td>$Co_3O_4^*$</td><td></td><td></td><td></td></tr><tr><td>+2</td><td></td><td>TiO</td><td>VO</td><td>(CrO)</td><td>MnO</td><td>FeO</td><td>CoO</td><td>NiO</td><td>CuO</td><td>ZnO</td></tr><tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>Cu_2O</td><td></td></tr></table>										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	
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6	Colour	<p>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 excited to a higher energy d-orbital, if the energy of excitation lies in visible range, complimentary colour is observed.</p> <p>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.</p>																																																																																																																						
	Memory warning : Memorize the table completely.																																																																																																																							
	<table><tr><th>Oxidation State</th><th>Sc</th><th>Ti</th><th>V</th><th>Cr</th><th>Mn</th><th>Fe</th><th>Co</th><th>Ni</th><th>Cu</th><th>Zn</th></tr><tr><td>(I)</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td colspan="2">Colourless</td><td></td></tr><tr><td>(II)</td><td></td><td></td><td></td><td>Blue</td><td>Pink</td><td>Green</td><td>Pink</td><td>Green</td><td>Blue</td><td>Colourless</td></tr><tr><td>(III)</td><td>Colourless</td><td>Purple</td><td>Green</td><td>Green</td><td>Violet</td><td>Yellow</td><td>Blue</td><td></td><td></td><td></td></tr><tr><td>(IV)</td><td></td><td>Colourless</td><td>Blue</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr></table>	Oxidation State	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	(I)								Colourless			(II)				Blue	Pink	Green	Pink	Green	Blue	Colourless	(III)	Colourless	Purple	Green	Green	Violet	Yellow	Blue				(IV)		Colourless	Blue																																																																							
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Section (B) : Electrode potential and chemical reactivity, Magnetic properties, formation of coloured ions, Catalytic properties, formation of interstitial compounds, alloy formation.																																																																																																																								
7	Electrode potential																																																																																																																							
	$E_{M^{2+} / M}^0$	<p>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.</p>																																																																																																																						




		Memory warning : Need not memorize the table but remember the comments.																																								
		<table><tr><th>Element (M)</th><th>$E_{M^{3+}/M^{2+}}^0$</th><th>$E_{M^{2+}/M}^0$</th><th>Comments</th></tr><tr><td>Ti</td><td>-0.37</td><td>-1.63</td><td>+3 Oxidation states is more stable</td></tr><tr><td>V</td><td>-0.26</td><td>-1.18</td><td>+3 Oxidation states is more stable</td></tr><tr><td>Cr</td><td>-0.41</td><td>-0.9</td><td>+3 Oxidation states is more stable</td></tr><tr><td>Mn</td><td>1.57</td><td>-1.18</td><td>+2 Oxidation states is more stable</td></tr><tr><td>Fe</td><td>0.77</td><td>-0.44</td><td>+2 Oxidation states is more stable</td></tr><tr><td>Co</td><td>1.97</td><td>-0.28</td><td>+2 Oxidation states is more stable</td></tr><tr><td>Ni</td><td>-</td><td>-0.25</td><td>+3 Oxidation states does not exist for Ni</td></tr><tr><td>Cu</td><td>-</td><td>0.34</td><td>+3 Oxidation states does not exist for Cu. 0 Oxidation states is more stable</td></tr><tr><td>Zn</td><td>-</td><td>0.76</td><td>+3 Oxidation states does not exist for Zn</td></tr></table>	Element (M)	$E_{M^{3+}/M^{2+}}^0$	$E_{M^{2+}/M}^0$	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
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Zn	-	0.76	+3 Oxidation states does not exist for Zn																																							



9	Melting and Boiling point	<p>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 d⁵, except for anomalous value for Mn, and Tc fall regularly. m.p. and b.p. are generally very high exceptions</p>  <p>→ Zn (420°C) → Cd (321°C) → Hg liquid at room temperature.</p> <p>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.</p> <p>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.</p>
10	 Magnetic character	<p>Metals, which have unpaired electrons show paramagnetism.</p> <p>Spin only magnetic moment $\mu = \sqrt{n(n+2)}$ here n = no. of unpaired electron.</p> <p>Diamagnetic substance is one which is slightly repelled by a magnetic field.</p> <p>A paramagnetic substance is one which is attracted into a magnetic field.</p> <p>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.</p>  <p style="text-align: center;">Paramagnetic material</p>
	Ferromagnetism	<p>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.</p>



11	<div></div> <div>Catalytic Properties</div>	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 NH₃.</td></tr><tr><td>V₂O₅</td><td>Contact process for H₂SO₄ 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>FeSO₄ & H₂O₂</td><td>Fenton's reagent for oxidising alcohol to aldehyde.</td></tr><tr><td>Cu</td><td>Dehydrogenation of alcohols</td></tr><tr><td>Al₂(C₂H₅)₆ + TiCl₄</td><td>Ziegler-Natta catalyst in the production of Polyethene.</td></tr><tr><td>FeCl₃</td><td>For making CCl₄ from CS₂ and Cl₂.</td></tr><tr><td>Pt/PtO</td><td>Adams catalyst, used for reduction.</td></tr></table>	Catalyst	Used	Fe	Haber's process for manufacture of NH ₃ .	V ₂ O ₅	Contact process for H ₂ SO ₄ manufacture.	Pt	Ostwald's process of nitric acid.	Ni	Hydrogenation of oils.	FeSO ₄ & H ₂ O ₂	Fenton's reagent for oxidising alcohol to aldehyde.	Cu	Dehydrogenation of alcohols	Al ₂ (C ₂ H ₅) ₆ + TiCl ₄	Ziegler-Natta catalyst in the production of Polyethene.	FeCl ₃	For making CCl ₄ from CS ₂ and Cl ₂ .	Pt/PtO	Adams catalyst, used for reduction.
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		FeCl ₃	For making CCl ₄ from CS ₂ and Cl ₂ .																			
Pt/PtO	Adams catalyst, used for reduction.																					
12	FORMATION OF INTERSTITIAL COMPOUNDS	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 ₄ N, Fe ₃ H, 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.																				
		13	FORMATION OF ALLOYS	(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.																		



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 %)
		• Tungston 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



Section (C) : Important d-block metal compounds.

Preparations and properties of some important d-Block metal compounds

Sulphates (SO_4^{2-})

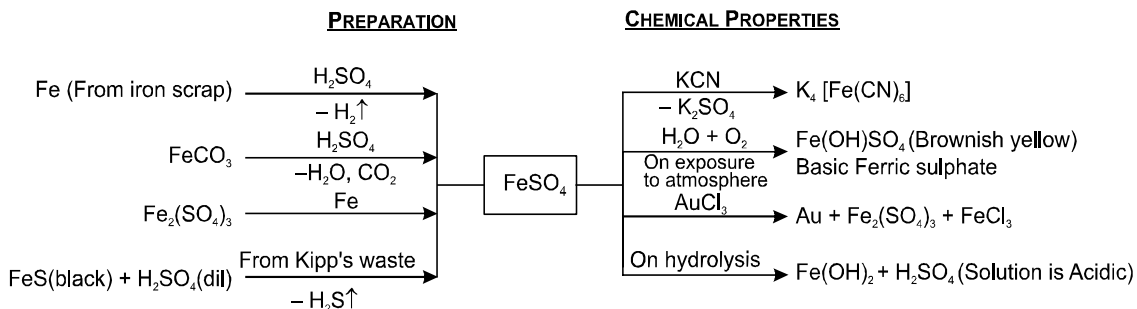
1. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Green Vitriol)

Ferrous sulphate.

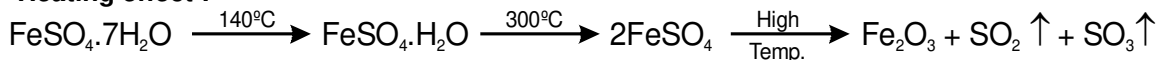
Commonly known as harkasis.

Physical properties

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



Heating effect :



Uses :

- for making Blue - Black ink.
- as mordant in dyeing.
- as insecticide in agriculture.
- for making laboratory reagents like Mohr's salt etc.

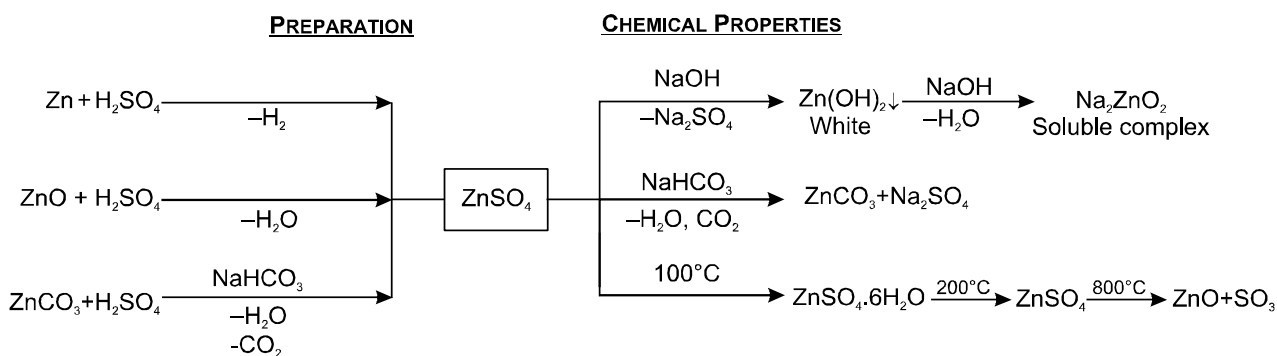


- $\text{FeSO}_4 + \text{H}_2\text{O}_2$ known as Fenton's reagent is used as catalyst.

2. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (white Vitriol)

Physical Properties

- Colourless, crystalline solid, soluble in water.
- It slowly effloresces when exposed to air.
- It is isomorphous with Epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$).



Uses :

- eye lotion.
- for making lithophone-mixture of $\text{BaS} + \text{ZnSO}_4$ (white paint).
- mordant in dyeing.

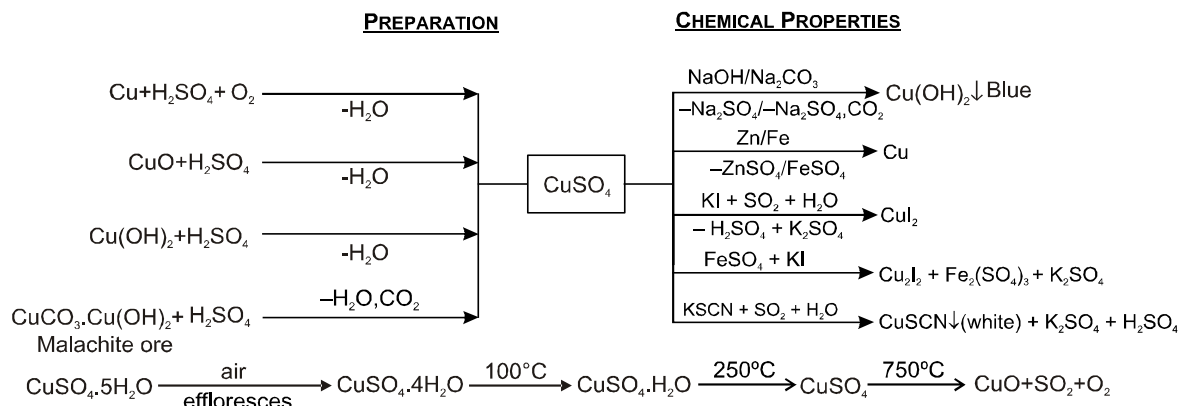




3. Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (blue vitriol)

Also called as 'Nilathotha'

Physical Properties : Blue crystalline compound soluble in water.



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.

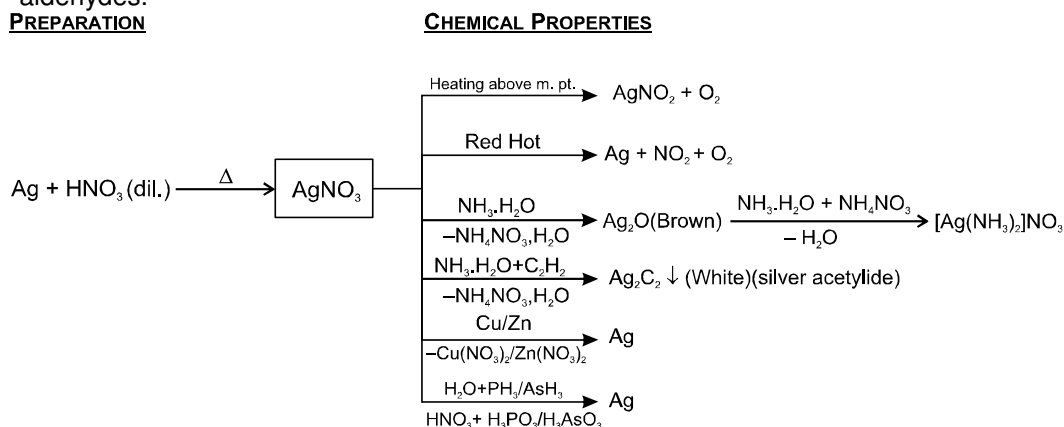
4. Silver nitrate, AgNO_3 (Lunar Caustic)

Physical Properties

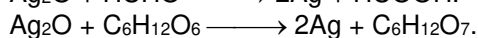
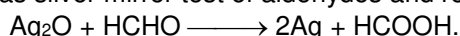
- (i) It is a colourless crystalline compound.
- (ii) Soluble in water and alcohol.
- (iii) It melts at 212°C .

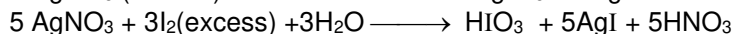
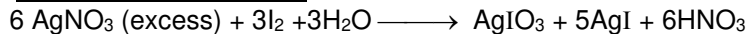
Chemical Properties

- (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 metallic silver, reduced by organic tissue. 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.



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



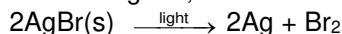
**(iv) Reactions with Iodine :****Uses :** It is used

- (i) as a laboratory reagent for the identification of various acids 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.

5. Photography :

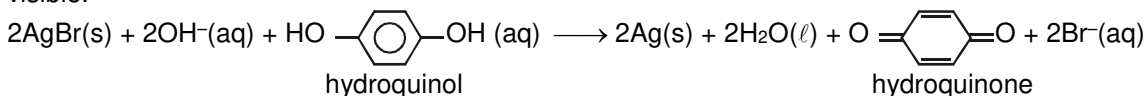
(i) A photographic film consists of a light sensitive emulsion of fine particles (grains) of silver salts in gelatine spread on a clear celluloid strip or a glass plate. AgBr is mainly used as the light sensitive material.

(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.



(iii) In modern photography only a short exposure of perhaps $1/100^{\text{th}}$ 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 in 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.

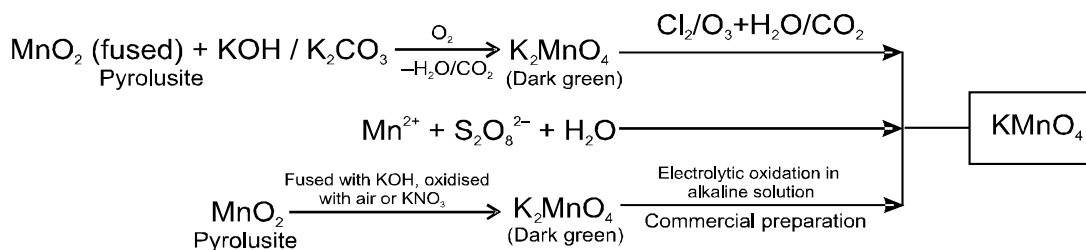


(v) If the film was brought out into daylight at this stage, the unexposed parts of the emulsion would turn black and thus destroy the picture. To prevent this happening any unchanged silver halides are removed by placing the film in a fixer solution. A solution of sodium thiosulphate is used as fixer.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



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

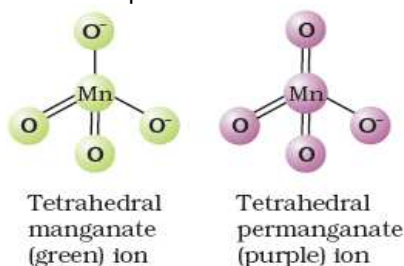
Light is passed through the negative onto a piece of paper coated with AgBr emulsion. This is then developed and fixed in the same way as before.

6. Potassium Permanganate (KMnO_4)**PREPARATION**

**Physical Properties :**

Purple coloured crystalline compound.

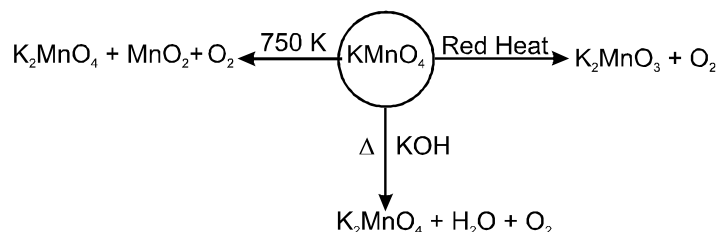
Moderately soluble in water at room temperature.



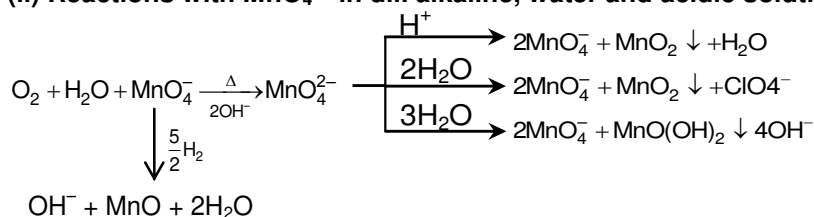
Structure of manganate and permanganate ion.

Chemical Properties

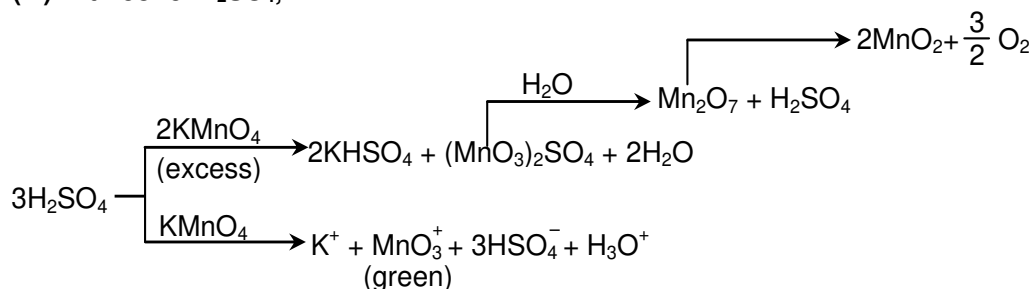
(i) Heating effect



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



(iii) with conc. H_2SO_4 ,



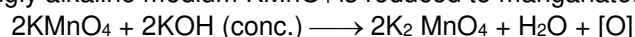
(iv) KMnO_4 is a powerful oxidising agent

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

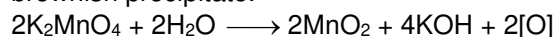
In alkaline & neutral medium :

In strongly alkaline medium KMnO_4 is reduced to manganate.



or $\text{e}^- + \text{MnO}_4^- \longrightarrow \text{MnO}_4^{2-}$

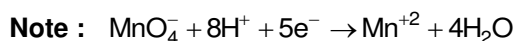
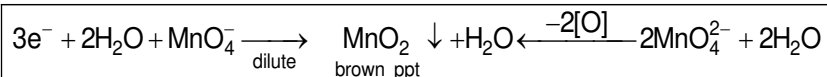
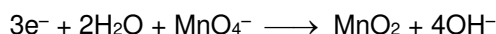
However if solution is dilute then K_2MnO_4 is converted in to MnO_2 which appears as a brownish precipitate.



or $2\text{e}^- + 2\text{H}_2\text{O} + \text{MnO}_4^{2-} \longrightarrow \text{MnO}_2 + 4\text{OH}^-$



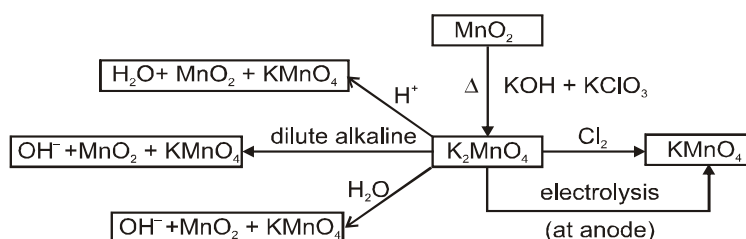
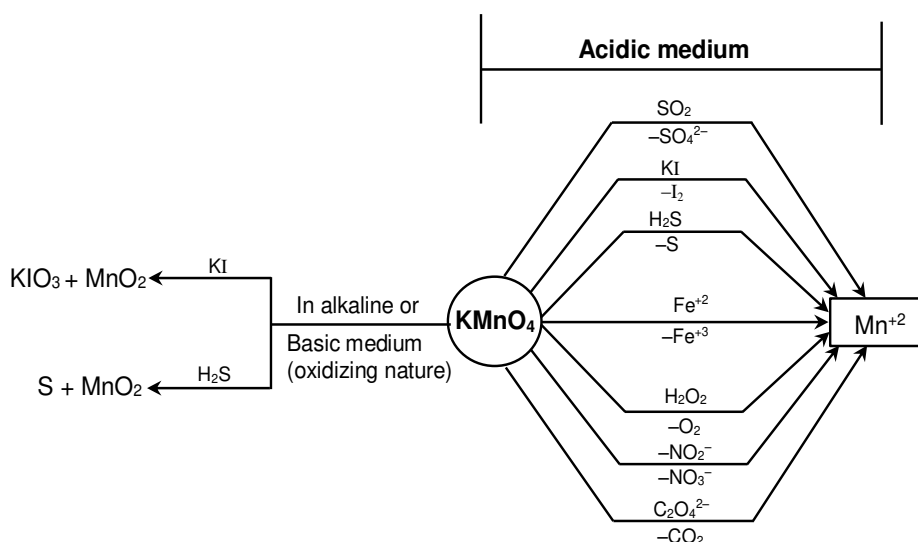
This type of behaviour is shown by KMnO_4 itself in neutral medium.



This medium is used in quantitative (Volumetric) Estimations. The eq. mass of KMnO_4 in acidic

$$\text{medium is} = \frac{\text{Molecular Mass}}{5}$$

Reactions of KMnO_4 :



Uses : It is used

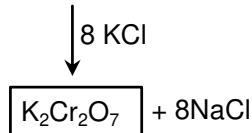
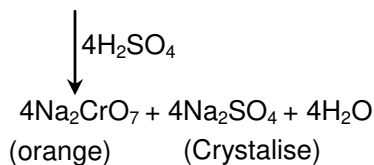
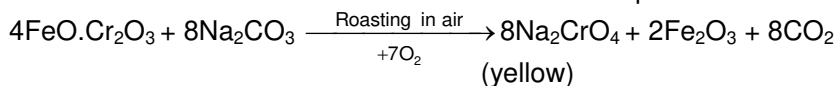
- KMnO_4 is used as an oxidising agent in laboratory and industry.
- Alkaline potassium permanganate is called Bayer's reagent. This reagent is used in organic chemistry for the test of unsaturation. KMnO_4 is used in the manufacture of saccharin, benzoic acid, acetaldehyde etc.
- KMnO_4 is used in qualitative analysis for detecting halides, sulphites, oxalates, etc.



7. POTASSIUM DICHROMATE ($K_2Cr_2O_7$) :

Preparation :

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

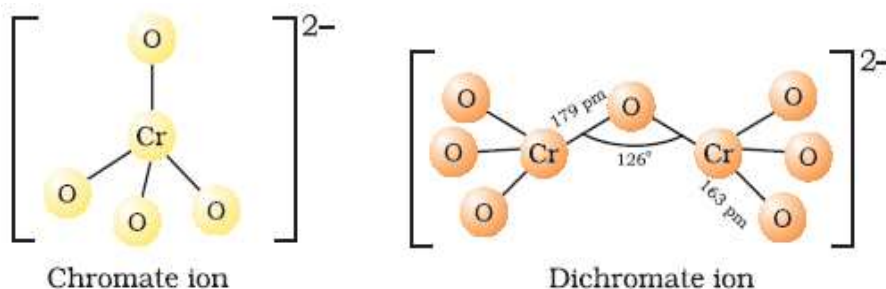


Properties

(a) Physical :

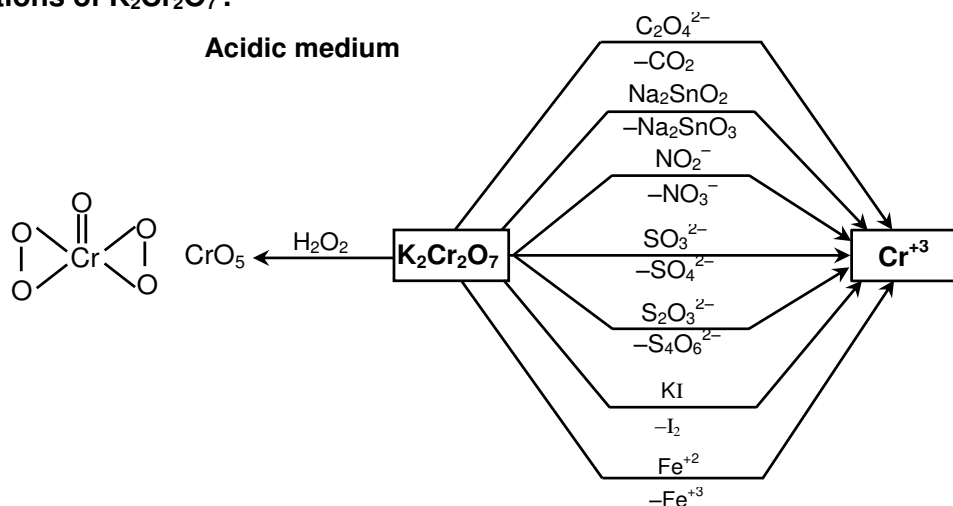
It is orange-red coloured crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at $398^\circ C$.

Structure of Chromate and Dichromate ion



(b) Chemical Properties :

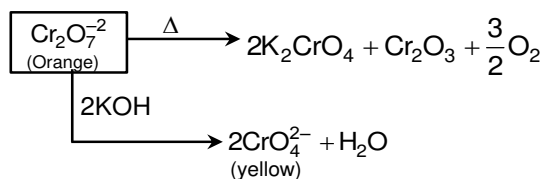
Reactions of $K_2Cr_2O_7$:



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.

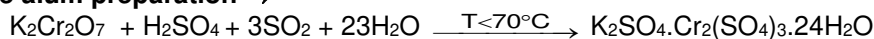


(i) **Effect of heating** : On heating strongly, it decomposes liberating oxygen.

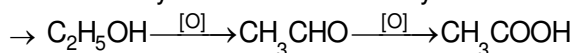


CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ exist in equilibrium and are interconvertable by altering the pH of solution. In alkaline solution, chromate ions are present while in acidic solution, dichromate ions are present.

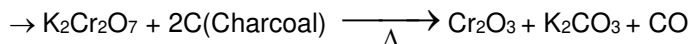
Chrome alum preparation →



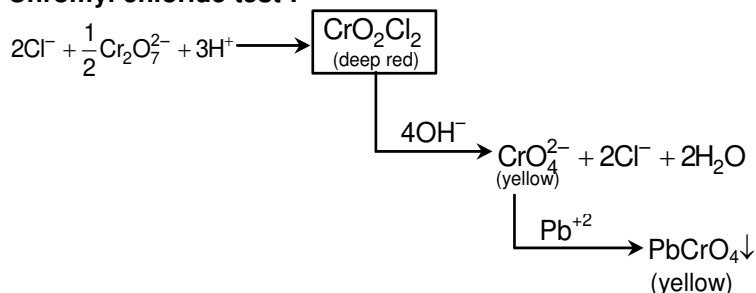
Oxidizes ethyl alcohol to acetaldehyde to acetic acid



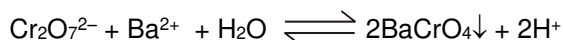
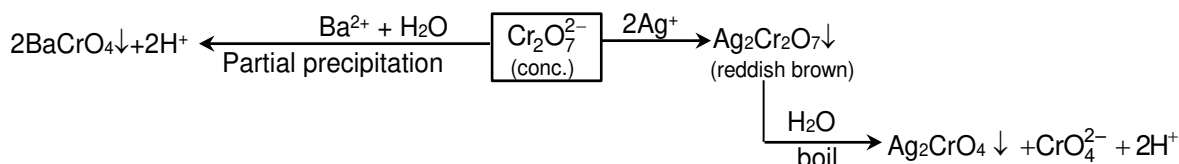
→ It also oxidizes nitrites to nitrates, arsenites to arsenates, HBr to Br_2 , HI to I_2 etc.



Chromyl chloride test :



Reaction of potassium dichromate with Ag^+ -



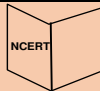
As strong acid is produced, the precipitation is only partial. But if NaOH or CH_3COONa is added, precipitate becomes quantitative.

Uses : It is used :

- 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.
- for the preparation of several chromium compounds such as chrome alum, chrome yellow, chrome red, zinc yellow, etc.
- in dyeing, chrome tanning, calico printing, photography etc.
- as a cleansing agent for glass ware in the form of chromic acid.
- in leather industry and as an oxidant for preparation of azo compounds.



Section (D) : Lanthanoids and actinoids



f-block elements (JEE-Mains only)

Differentiating electrons enters in (n – 2)f subshell.
f-block elements lie on the Bottom portion of periodic table.

S.No.	Properties	DISCRIPTION															
1.	General character's	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.															
2.	No. of elements	Total number of f-block elements – (28)															
3.	Groups	<div> <div> IIIB/ 3rd Sc Y La Ac </div> <div> Lanthanides (14) Ce₅₈ – Lu₇₁ Actinides (14) Th₉₀ – Lr₁₀₃ </div> </div>															
4.	E.C.	Lanthanide series 4f ^{1 – 14} 5d ^{0 or 1} 6s ² Actinide series 5f ^{1 – 14} 6d ^{0 or 1} 7s ²															
5.	Period	<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) Ce₅₈ – Lu₇₁</td> </tr> <tr> <td>7th period</td> <td>Ac</td> <td>Actinides (14) Th₉₀ – Lr₁₀₃</td> </tr> </table>	Period	III B/ 3rd			Sc			Y		6 th period	La	Lanthanides (14) Ce ₅₈ – Lu ₇₁	7 th period	Ac	Actinides (14) Th ₉₀ – Lr ₁₀₃
Period	III B/ 3rd																
	Sc																
	Y																
6 th period	La	Lanthanides (14) Ce ₅₈ – Lu ₇₁															
7 th period	Ac	Actinides (14) Th ₉₀ – Lr ₁₀₃															
6.	Inner transition elements	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.															
	(i) Lanthanide series or Rare earth elements or Lanthanones	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 6 th period of the periodic table. Promethium (₆₁ Pm) is the only lanthanide which is synthetic and radioactive in nature.															
	(ii) Actinide series or Man made elements or Actinones	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 7 th 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.															



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 4f 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° 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.

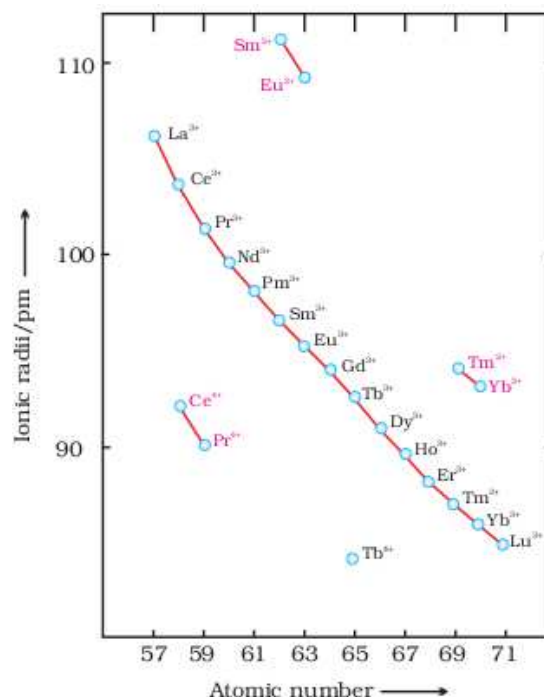


Table :- Electronic Configurations and Radii of Lanthanum and Lanthanides

Atomic Number	Name	symbol	Electronic configurations*				Radii/pm	
			Ln	Ln ²⁺	Ln ³⁺	Ln ⁴⁺	Ln	Ln ³⁺
57	Lanthanum	La	5d ¹ 6s ²	5d ¹	4f ⁰		187	106
58	Cerium	Ce	4f ¹ 5d ¹ 6s ²	4f ²	4f ¹	4f ⁰	183	103
59	Praseodymium	Pr	4f ³ 6s ²	4f ³	4f ²	4f ¹	182	101
60	Neodymium	Nd	4f ⁴ 6s ²	4f ⁴	4f ³	4f ²	181	99
61	Promethium	Pm	4f ⁵ 6s ²	4f ⁵	4f ⁴		181	98
62	Samarium	Sm	4f ⁶ 6s ²	4f ⁶	4f ⁵		180	96
63	Europium	Eu	4f ⁷ 6f ²	4f ⁷	4f ⁶		199	95
64	Gadolinium	Gd	4f ⁷ 5d ¹ 6s ²	4f ⁷ 5d ¹	4f ⁷		180	94
65	Terbium	Tb	4f ⁹ 6s 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 ¹ 6s 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.

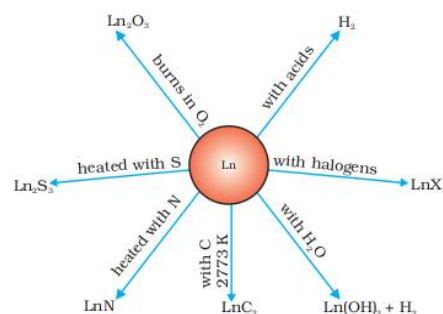
They have typical metallic structure and are good conductors of heat and electricity. Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm.

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^0 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:

$\text{Ln}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Ln}(\text{s})$ 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 $\text{M}(\text{OH})_3$. 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 mischmetal which consists of a lanthanide metal ($\sim 95\%$) and iron ($\sim 5\%$) and traces of S, C, Ca and Al. A good deal of mischmetal 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 ¹ 7s ²	5f ⁰		111	
90	Thorium	Th	6d ² 7s ²	5f ¹	5f ⁰		99
91	Protactinium	Pa	5f ² 6d ¹ 7s ²	5f ²	5f ¹		96
92	Uranium	U	5f ³ 6d ¹ 7s ²	5f ³	5f ²	103	93
93	Neptunium	Np	5f ⁴ 6d ¹ 7s ²	5f ⁴	5f ³	101	92
94	Plutonium	Pu	5f ⁶ 7s ²	5f ⁵	5f ⁴	100	90
95	Americium	Am	5f ⁷ 7s ²	5f ⁶	5f ⁵	99	89
96	Curium	Cm	5f ⁷ 6d ¹ 7s 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	Einsteinium	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 7s² 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 f⁰, f⁷ and f¹⁴ occupancies of the 5f orbitals. Thus, the configurations of Am and Cm are [Rn] 5f⁷7s² and [Rn] 5f⁷ 6d¹ 7s².

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 M³⁺ 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; alkalis 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 MnO₂ 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) $\text{K}_2\text{Cr}_2\text{O}_7$ 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) $\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{C (charcoal)} \xrightarrow{\Delta} \text{Cr}_2\text{O}_3 + \text{K}_2\text{CO}_3 + \text{CO} \uparrow$.

(b) $2\text{KMnO}_4 + 5\text{H}_2 \xrightarrow{\Delta} 2\text{KOH} + 2\text{MnO} + 4\text{H}_2\text{O}$.

(c) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + 6\text{CH}_3\text{—}\overset{\text{OCH}_3}{\underset{\text{OCH}_3}{\text{C}}}\text{—CH}_3 \longrightarrow \text{FeCl}_3 \text{ (anhydrous)} + 12\text{CH}_3\text{OH} + 6\text{CH}_3\text{COCH}_3$.

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 $\text{K}_4[\text{Fe}(\text{CN})_6]$. Identify (A) to (F) and explain the reactions.

Ans. (A) ZnO , (B) $\text{Zn}(\text{OH})_2$, (C) Na_2ZnO_2 , (D) Zn , (E) CO , (F) $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$

Sol. $\text{Zn}(\text{OH})_2$ (B) $\xrightarrow{\Delta} \text{ZnO}$ (A) + H_2O .

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

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

$\text{Zn}(\text{OH})_2$ (B) + $4\text{NH}_3 \longrightarrow [\text{Zn}(\text{NH}_3)_4]^{2+}$ (soluble complex) + 2OH^- .

$\text{ZnO} + 2\text{HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2\text{O}$.

$3\text{ZnCl}_2 + 2\text{K}_4[\text{Fe}(\text{CN})_6] \longrightarrow \text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 \downarrow$ (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. $\text{X} = \text{AgNO}_3$

Sol. 2AgNO_3 (X) $\xrightarrow{\Delta} 2\text{Ag} + 2\text{NO}_2 + \text{O}_2$.

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

$\text{AgCl} + 2\text{NH}_3 \longrightarrow [\text{Ag}(\text{NH}_3)_2]^+$ (soluble complex).

4. Amongst $[\text{TiF}_6]^{2-}$, $[\text{CoF}_6]^{3-}$, Cu_2Cl_2 and $[\text{NiCl}_4]^{2-}$ [Atomic number; $\text{Ti} = 22$, $\text{Co} = 27$, $\text{Cu} = 29$, $\text{Ni} = 28$] the colourless species are :

(A) $[\text{TiF}_6]^{2-}$ and $[\text{Cu}_2\text{Cl}_2]$ (B) Cu_2Cl_2 and $[\text{NiCl}_4]^{2-}$ (C) $[\text{TiF}_6]^{2-}$ and $[\text{CoF}_6]^{3-}$ (D) $[\text{CoF}_6]^{3-}$ and $[\text{NiCl}_4]^{2-}$

Sol. (A) In $[\text{TiF}_6]^{2-}$ the titanium is in +4 oxidation state having the electronic configuration $[\text{Ar}]^{18} 3d^0 4s^0$. Similarly in Cu_2Cl_2 the copper is in +1 oxidation state having the electronic configuration $[\text{Ar}]^{18} 3d^{10} 4s^0$. As they do not have any unpaired electrons for d-d transition, they are therefore colourless.





In $[\text{NiCl}_4]^{2-}$ the nickel is in +2 oxidation state and electronic configuration is $[\text{Ar}]^{18} 3d^8 4s^0$. As it has two unpaired electrons, so the complex is coloured.

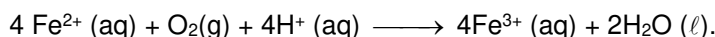
In $[\text{CoF}_6]^{3-}$, the cobalt is in +3 oxidation state having electron configuration $[\text{Ar}] 3d^6 4s^0$. As it has four unpaired electrons, so the complex is coloured.

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 $\text{V}^{2+}(\text{aq})$ and $\text{Cr}^{2+}(\text{aq})$. The $\text{Fe}^{2+}(\text{aq})$ ion is only weakly reducing. The $\text{Co}^{2+}(\text{aq})$, $\text{Ni}^{2+}(\text{aq})$, and $\text{Cu}^{2+}(\text{aq})$ ions are not oxidized in water.



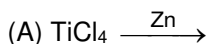
The chemical equation for the oxidation is then



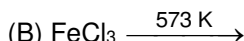
6. Match the reactions given in column-I with the characteristic(s) of the reaction products given in column-II.

Column-I

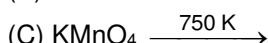
Column-II



(p) One of the products is bright orange coloured but diamagnetic.



(q) One of the products is green coloured and paramagnetic.



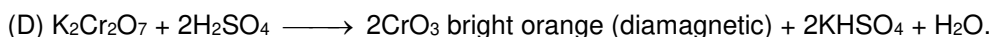
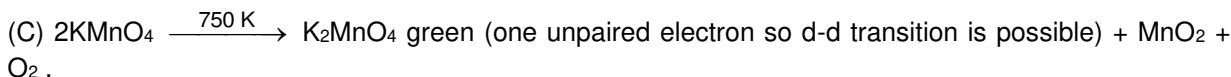
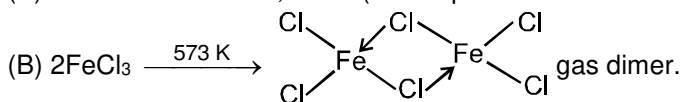
(r) One of the products is violet and paramagnetic.



(s) One of the products exists as dimer.

Ans. $[\text{A} - \text{r}] ; [\text{B} - \text{s}] ; [\text{C} - \text{q}] ; [\text{D} - \text{p}]$.

Sol. (A) $\text{TiCl}_4 \xrightarrow{\text{Zn}} \text{TiCl}_3$, violet (one unpaired electron so d-d transition is possible).



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.

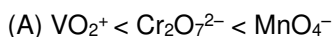
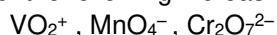
(C) Both (A) and (B)

(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_{2g}^3 energy level of 3d orbitals in octahedral crystal field splitting. 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 ?



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 $[\text{3d}^5]$.

$\text{Cr}_2\text{O}_7^{2-}$ is reduced to Cr^{3+} which has half filled t_{2g}^3 energy level of 3d orbitals in octahedral crystal field splitting



VO_2^+ is reduced to V^{3+} which has electronic configuration $[\text{Ar}]^{18}3d^24s^0$.

So the order of increasing stability of the reduced species is $\text{Mn}^{2+} > \text{Cr}^{3+} > \text{V}^{3+}$ and, therefore, the increasing order of oxidising power is $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$.

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) $\text{Na}_2\text{Cr}_2\text{O}_7$ solution, its orange colour changes to green.
- (D) KMnO_4 solution, its pink colour changes to green.

Sol. (A) $\text{Na}_2\text{CrO}_4 \xrightarrow{\text{H}^+} \text{Na}_2\text{Cr}_2\text{O}_7$ (orange colour)

(B) $\text{MnO}_4^{2-} \xrightarrow{\text{H}^+} \text{MnO}_4^- + \text{MnO}_2$, in neutral or acidic medium

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

(D) $\text{MnO}_4^- + \text{e}^- \xrightarrow{\text{OH}^-} \text{MnO}_4^{2-}$; 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) $\text{Ag}_2\text{O} + \text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 2\text{Ag} + \text{C}_6\text{H}_{12}\text{O}_7$.



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) $\text{Mn}^{3+} = [\text{Ar}]^{18} 3d^4$, $\text{Cr}^{3+} = [\text{Ar}]^{18} 3d^3$, $\text{V}^{3+} = [\text{Ar}]^{18} 3d^2$, $\text{Ti}^{3+} = [\text{Ar}]^{18} 3d^1$

Cr^{3+} is most stable in aqueous solution because it has half filled t_{2g} energy level of 3d orbitals in octahedral crystal field splitting and according to crystal field theory (CFT) it has highest value of CFSE i.e. $1.2 \Delta_o$.

14. **S₁** : Interstitial compounds have high melting points, higher than those of pure metals.

S₂ : Permanganate titrations in presence of hydrochloric acid are unsatisfactory.

S₃ : KMnO_4 does not act as an oxidising agent in strong alkaline medium.

S₄ : KMnO_4 on heating in a current of H_2 gives MnO .

(A) T T F T

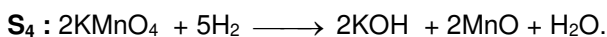
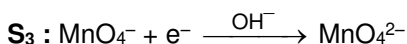
(B) T F F T

(C) T F T T

(D) F F T F

Sol. **S₁** : Due to strong interatomic forces.

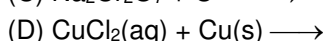
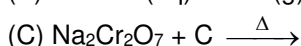
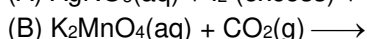
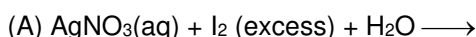
S₂ : Some of the hydrochloric acid is oxidised to chlorine and thus we get less volume of KMnO_4 than the actual one.



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

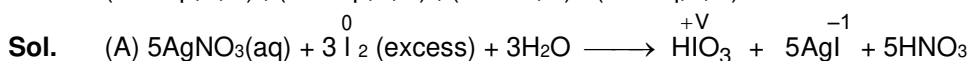
(p) Disproportionation

(q) Comproportionation

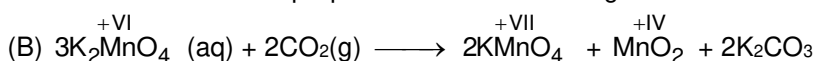
(r) Redox

(s) One of the products is insoluble in water

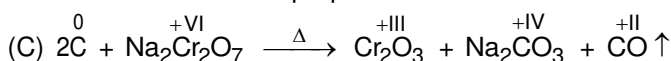
Ans. (A \rightarrow p, r, s) ; (B \rightarrow p, r, s) ; (C \rightarrow r, s) ; (D \rightarrow q, r, s)



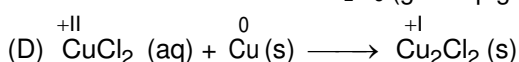
So it is redox and disproportionation reaction. AgI insoluble in water.



So it is redox and disproportionation reaction. MnO_2 insoluble in water.



So it is redox reaction. Cr_2O_3 (green pigment) is insoluble in water.



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 its 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 are recommended for Revision.

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Electronic configuration, atomic size and ionic size, density, melting and boiling points, Ionization enthalpy and oxidation state.

- A-1.** What is the general electronic configuration of transition elements.
- A-2.** Write the electronic configurations of the following ions.
(i) Mn^{2+} (ii) Fe^{3+} (iii) Ni^{2+} (iv) Cr^{3+}
- A-3.** Name the d-block elements which do not have partially filled d-orbitals in their atoms or in their simple ions.
- A-4.** What is meant by the 'lanthanide contraction'? Mention one important fact that can be considered as a consequence of the lanthanide contraction.
- A-5.** Name the (i) lightest and the (ii) heaviest elements (in terms of density) among the transition elements.
- A-6.** Which element among d-block elements has (i) the lowest melting point and (ii) the highest melting point
- A-7.** Why zinc has lowest melting point in 3d series ?
- A-8.** Why are ionization energies of 5d-elements greater than those of 3d-elements ?
- A-9.** Why do transition elements show variable oxidation state ?
- A-10.** What is the most common oxidation state of first transition series?

Section (B) : Electrode potential and chemical reactivity, Magnetic properties, formation of coloured ions, Catalytic properties, formation of interstitial compounds, alloy formation.

- B-1.** Name the three factors which determine the stability of a particular oxidation state in solution.
- B-2.** Explain as to why the E^\ominus value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is much more positive than that for $\text{Cr}^{3+}/\text{Cr}^{2+}$ or $\text{Fe}^{3+}/\text{Fe}^{2+}$.
- B-3.**
- | Element | Cr | Mn | Fe |
|--|----------|----------|---------|
| $E^\ominus(\text{M}^{2+}/\text{M})$ | - 0.90 V | - 1.18 V | - 0.4 V |
| $E^\ominus(\text{M}^{3+}/\text{M}^{2+})$ | - 0.41 V | + 1.57 V | + 0.8 V |
- Use this data to comment upon
(i) The stability of Fe^{3+} and Mn^{2+} in acid solutions.
(ii) The ease with which iron can be oxidised as compared to the similar process for either Cr or Mn metals.
- B-4.** 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+}
- B-5.** Why Ti^{4+} complexes are diamagnetic ?
- B-6.** A substance is found to have a magnetic moment of 3.9 BM. How many unpaired electrons does it contain?
- B-7.** Explain giving reason.
(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.
- B-8.** Describe the general characteristics of transition elements with special reference to the following :
(i) catalytic behaviour. (ii) complex formation. (iii) interstitial compounds.





Section (C) : Important d-block metal compounds.

- C-1. Which type of reaction MnO_4^{2-} shows with acid, dilute-alkali or water.
- C-2. Why KMnO_4 is stored in dark bottle and what happens to its acidic solution ?
- C-3. Why does AgNO_3 produce a black stain on the skin ?
- C-4. Why is AgBr used in photography ?
- C-5. Why it is not advisable to dissolve KMnO_4 in cold and concentrated H_2SO_4 ?
- C-6. What happens when :
 (a) Green vitriol is strongly heated.
 (b) Malachite is made to react with dilute H_2SO_4 .
 (c) Copper sulphate is exposed to air for longer period.
 (d) Lunar caustic is made to react with sodium hydroxide and then product is dried.
 (e) Silver nitrate reacts with excess iodine.
 (f) Potassium dichromate reacts with cold and concentrated H_2SO_4 .
- C-7. State true or false : Reaction of $\text{K}_2\text{Cr}_2\text{O}_7$ with cold and concentrated H_2SO_4 yields bright orange/red precipitate of CrO_3 . Write reactions involved.
- C-8. Write balanced chemical equations for :
 (i) Mixture of $\text{K}_2\text{Cr}_2\text{O}_7$ and NaCl is heated with concentrated H_2SO_4 .
 (ii) Potassium permanganate is added to a hot solution of manganous sulphate.
 (iii) Potassium dichromate and concentrated HCl are heated together.

Section (D) : Lanthanoids and actinoids

- D-1. What are inner-transition elements ? Decide which of the following atomic numbers are the numbers of the inner transition elements : 29, 59, 74, 95, 102, 104.
- D-2. Actinoid contraction is greater from element to element than lanthanoid contraction. Why ?
- D-3. The chemistry of the actinoid elements is not so smooth as that of the lanthanoid. Justify this statement by giving some examples from the oxidation state of these elements.
- D-4. 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 : ONLY ONE OPTION CORRECT TYPE

Section (A) : Electronic configuration, atomic size and ionic size, density, melting and boiling points, ionization enthalpy and oxidation state.

- A-1. The transition elements have a general electronic configuration :
 (A) $ns^2np^6nd^{1-10}$ (B) $(n-1)d^{1-10}ns^0-2np^0-6$
 (C) $(n-1)d^{1-10}ns^{1-2}$ (D) none
- A-2. The atomic volumes of the transition elements are low compared with elements in neighboring group 1 and 2 because :
 (A) the nuclear charge is poorly screened and so attracts all the electrons more strongly.
 (B) the extra electrons added occupy inner orbitals.
 (C) (A) and (B) both.
 (D) none.
- A-3. The wrong statement regarding transition metals among the following is :
 (A) 4s electrons penetrate towards the nucleus more than 3d electrons
 (B) atomic radii of transition metals increase rapidly with increase in atomic number because of poor shielding of nuclear attraction by $(n-1)d$ electrons
 (C) second and third transition series elements have nearly the same size
 (D) their densities are higher and densities of the 5d series elements are higher than those of 4d series elements.



- A-4.** First IE of 5d series elements are 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.

- A-5.** Ionisation energies of Ni and Pt in kJ mol^{-1} are given below.

	$(\text{IE})_1 + (\text{IE})_2$	$(\text{IE})_3 + (\text{IE})_4$
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
- A-6.** Maximum oxidation state is shown by :
 (A) Os (B) Mn (C) Cr (D) Co

Section (B) : Electrode potential and chemical reactivity, Magnetic properties, formation of coloured ions, Catalytic properties, formation of interstitial compounds, alloy formation.

- B-1.** Which of the following statement is false ?
 (A) Of the d^4 species, manganese (III) is strongly reducing while Cr^{2+} is strongly oxidising.
 (B) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.
 (C) The d^1 configuration is very unstable in ions.
 (D) None of these
- B-2.** Which of the following has the maximum number of unpaired d-electron?
 (A) Zn^{2+} (B) Fe^{2+} (C) Ni^{2+} (D) Cu^{2+}
- B-3.** The highest magnetic moment is shown by the transition metal ion with the outermost electronic configuration is :
 (A) $3d^5$ (B) $3d^2$ (C) $3d^7$ (D) $3d^9$
- B-4.** Magnetic moment of Cr^{+2} ($Z = 24$), Mn^{+2} ($Z = 25$) and Fe^{2+} ($Z = 26$) are x, y, z. They are in order :
 (A) $x < y < z$ (B) $x > y > z$ (C) $z < x = y$ (D) $x = z < y$
- B-5.** The magnetic moment of ^{25}Mn in ionic state is $\sqrt{15}$ B.M, then Mn is in :
 (A) +2 state (B) +3 state (C) +4 state (D) +5 state
- B-6.** The colour of transition metal ions is attributed to :
 (A) exceptionally small size of cations (B) absorption of ultraviolet rays
 (C) incomplete $(n - 1)$ d-subshell (D) absorption of infrared radiations
- B-7.** MnO_4^- is of intense pink colour, though Mn is in (+7) oxidation state. It is due to :
 (A) oxygen gives colour to it
 (B) charge transfer when Mn gives its electron to oxygen
 (C) charge transfer when oxygen gives its electron to Mn making it $\text{Mn}(+VI)$ hence coloured
 (D) none is correct
- B-8.** The yellow colour of chromates changes to orange on acidification due to formation of :
 (A) Cr^{3+} (B) Cr_2O_3 (C) $\text{Cr}_2\text{O}_7^{2-}$ (D) CrO_4^{2-}
- B-9.** The catalytic activity of the transition metals and their compounds is ascribed to :
 (A) their chemical reactivity.
 (B) their magnetic behaviour.
 (C) their filled d-orbitals.
 (D) their ability to adopt multiple oxidation state and their complexing ability.



Section (C) : Important d-block metal compounds.

- C-1.** KMnO_4 is the oxo salt of :
 (A) MnO_2 (B) Mn_2O_7 (C) MnO_3 (D) Mn_2O_3
- C-2.** The solubility of silver bromide in hypo solution (excess) is due to the formation of :
 (A) Ag_2SO_3 (B) $\text{Ag}_2\text{S}_2\text{O}_3$ (C) $[\text{Ag}(\text{S}_2\text{O}_3)]^-$ (D) $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$
- C-3.** In dilute alkaline solution, MnO_4^- changes to :
 (A) MnO_4^{2-} (B) MnO_2 (C) Mn_2O_3 (D) MnO
- C-4.** Cl_2 gas is obtained by various reactions but not by :
 (A) $\text{KMnO}_4(\text{s}) + \text{conc. HCl} \xrightarrow{\Delta}$ (B) $\text{KCl}(\text{s}) + \text{K}_2\text{Cr}_2\text{O}_7(\text{s}) + \text{conc. H}_2\text{SO}_4 \xrightarrow{\Delta}$
 (C) $\text{MnO}_2(\text{s}) + \text{conc. HCl} \xrightarrow{\Delta}$ (D) $\text{KCl}(\text{s}) + \text{F}_2(\text{g}) \longrightarrow$
- C-5.** The developer used in photography is an alkaline solution of :
 (A) hydroquinol (B) glycerol (C) phenol (D) picric acid
- C-6.** When acidified solution of $\text{K}_2\text{Cr}_2\text{O}_7$ is shaken with aqueous solution of FeSO_4 , then :
 (A) $\text{Cr}_2\text{O}_7^{2-}$ ion is reduced to Cr^{3+} ions (B) $\text{Cr}_2\text{O}_7^{2-}$ ion is converted to CrO_4^{2-} ions
 (C) $\text{Cr}_2\text{O}_7^{2-}$ ion is reduced to Cr (D) $\text{Cr}_2\text{O}_7^{2-}$ ion is converted to CrO_3
- C-7.** Which of the following compounds is used as the starting material for the preparation of potassium dichromate?
 (A) $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (chrome alum) (B) PbCrO_4 (chrome yellow)
 (C) FeCr_2O_4 (chromite) (D) $\text{PbCrO}_4 \cdot \text{PbO}$ (chrome red)
- C-8.** CrO_3 dissolves in aqueous NaOH to give :
 (A) CrO_4^{2-} (B) $\text{Cr}(\text{OH})_3$ (C) $\text{Cr}_2\text{O}_7^{2-}$ (D) $\text{Cr}(\text{OH})_2$
- C-9.** The final products obtained for the following reaction is :
 $\text{KMnO}_4 (\text{excess}) + \text{H}_2\text{SO}_4 (\text{concentrated and cold}) \longrightarrow$
 (A) Mn_2O_7 (B) MnO (C) Mn_3O_4 (D) MnO_3^+

Section (D) : Lanthanoids and actinoids

- D-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
- D-2.** Among the lanthanoids the one obtained by synthetic method is :
 (A) Lu (B) Pm (C) Pr (D) Gd
- D-3.** The most common lanthanoid is :
 (A) lanthanum (B) cerium (C) samarium (D) plutonium
- D-4.** Across the lanthanide series, the basicity of the lanthanoid hydroxides :
 (A) increases (B) decreases
 (C) first increases and then decreases (D) does not change
- D-5.** Actinides :
 (A) are all synthetic elements (B) includes element 104
 (C) have only short lived isotopes (D) have variable valency
- D-6.** The lanthanoid contraction is responsible 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
- D-7.** Lanthanoid and actinides resemble in :
 (A) electronic configuration (B) oxidation state
 (C) ionization energy (D) formation of complexes
- D-8.** The separation of lanthanoids by ion exchange method is based on
 (A) sizes of the ions (B) oxidation state of the ions
 (C) the solubility of their nitrates (D) basicity of hydroxides of lanthanides



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)	ZnS + BaSO ₄ mixture	(p)	Lunar caustic
(B)	FeSO ₄ (NH ₄) ₂ SO ₄ · 6H ₂ O	(q)	Schwitzer's reagent.
(C)	AgNO ₃	(r)	Lithopone
(D)	[Cu(NH ₃) ₄]SO ₄	(s)	Mohr's salt

2. Match the reactions listed in column(I) with the characteristic(s) of the products/type of reactions listed in column(II).

	Column-I		Column-II
(A)	MnO ₄ ²⁻ + CO ₂ →	(p)	a pungent smelling gas is liberated.
(B)	CrO ₄ ²⁻ + H ⁺ →	(q)	Show disproportionation reaction.
(C)	FeSO ₄ $\xrightarrow{\Delta}$	(r)	Dimeric bridged tetrahedral metal ion.
(D)	K ₂ CrO ₄ + Cr ₂ O ₃ + O ₂ →	(s)	One of the products has central metal in its highest stable oxidation state.

3. 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 some magnetic moment but equal.
(B)	KMnO ₄ and K ₂ Cr ₂ O ₇	(q)	Pair of compounds which are diamagnetic but coloured.
(C)	Cu ₂ O and HgI ₂	(r)	Pair of compounds having metals in the highest stable oxidation states.
(D)	VOCl ₂ and CuCl ₂	(s)	Pair of compounds which show diamagnetism and are colourless.

Exercise-2

Marked questions are recommended for Revision.

PART - I : ONLY ONE OPTION CORRECT TYPE

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

	Column X	Column Y
I	[Cr(H ₂ O) 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
(C)	8	5	6	3

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

2. Standard reduction electrode potential of Zn²⁺ / Zn is -0.76 V. This means :

- (A) ZnO can't be reduced to Zn by H₂ under standard conditions.
 (B) Zn can't liberates H₂ with concentrated acids
 (C) Zn is generally the anode in an electrochemical cell
 (D) Zn is generally the cathode in an electrochemical cell

3. Of the ions Zn²⁺, Ni²⁺ and Cr³⁺ (atomic number Zn = 30, Ni = 28, Cr = 24) :

- (A) only Zn²⁺ is colourless and Ni²⁺ and Cr³⁺ are coloured.
 (B) all three are colourless.
 (C) all three are coloured.
 (D) only Ni²⁺ is coloured and Zn²⁺ and Cr³⁺ are colourless.





4. Which of the following group of ions is paramagnetic in nature :
(A) Cu^+ , Zn^{2+} , Sc^{3+} (B) Mn^{2+} , Fe^{3+} , Ni^{2+} (C) Cr^{2+} , Mn^{3+} , Sc^{3+} (D) Cu^{2+} , Ni^{2+} , Ti^{4+}
5. Which forms interstitial compounds?
(A) Fe (B) Co (C) Ni (D) All
6. When H_2O_2 is added to an acidified solution of $\text{K}_2\text{Cr}_2\text{O}_7$:
(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 $\text{CrO}(\text{O}_2)_2$ is formed
(D) solution gives green ppt of $\text{Cr}(\text{OH})_3$
7. Sodium thiosulphate is used in photography because of its :
(A) oxidising behaviour (B) reducing behaviour
(C) complexing behaviour (D) photochemical behaviour
8. Lanthanide contraction is due to increase in :
(A) shielding by 4f electrons (B) atomic number
(C) effective nuclear charge (D) size of 4f orbitals
9. Which of the following is not an actinide ?
(A) Curium (B) Californium (C) Uranium (D) Terbium
10. 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
11. Which of the following statements is not correct ?
(A) $\text{La}(\text{OH})_3$ is less basic than $\text{Lu}(\text{OH})_3$.
(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 : SINGLE AND DOUBLE VALUE INTEGER TYPE

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 1st 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. Chromite ore is processed through the following sequence :

$$\text{FeCr}_2\text{O}_4 \xrightarrow[\text{Fuse}]{\text{Na}_2\text{O}_2} \{(\text{A}) + (\text{B})\} \xrightarrow[\text{H}_2\text{O}]{\text{Boil}} (\text{B})_{\text{aq.}} \xrightarrow{\text{excess H}^+} (\text{C})$$

$$\downarrow \text{H}_2\text{O}_2$$

$$(\text{H}) \xleftarrow{\text{H}_2\text{O}_2} (\text{G}) \xleftarrow[\text{excess}]{\text{NaOH}} (\text{F}) \xleftarrow{\text{NH}_3 \text{ little}} (\text{E}) \xleftarrow[\text{-O}_2]{\text{warm H}^+} (\text{D})$$

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



7. $\text{KMnO}_4 \xrightarrow[\text{R.A.}]{\text{H}^+} \text{Mn}^x$
 $\text{KMnO}_4 \xrightarrow[\text{R.A.}]{\text{OH}^-} \text{Mn}^y$
 $\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{OH}^-} \text{Cr}^z$
 $x + y + z$ is :
8. The no. of electrons satisfying $n+l = 7$ for Lu (Atomic number : 71)

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. 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 ${}_{23}\text{V} < {}_{24}\text{Cr} > {}_{25}\text{Mn}$ and ${}_{28}\text{Ni} < {}_{29}\text{Cu} > {}_{30}\text{Zn}$
 (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.
4. 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
5. The less stable oxidation states of Cr are :
 (A) Cr^{2+} (B) Cr^{3+} (C) Cr^{4+} (D) Cr^{6+}
6. Which of the following statement is/are correct ?
 (A) Transition metals and their many compounds act as good catalyst.
 (B) The enthalpies of atomization of the transition metals are high.
 (C) The transition metals generally form interstitial compounds with small atoms like C, B, H etc.
 (D) All transition metal compounds are not paramagnetic.
7. Select correct statement (s).
 (A) PH_3 reduces AgNO_3 to metallic Ag.
 (B) Organic tissues turn AgNO_3 black by reducing it to Ag.
 (C) AgCN is soluble in KCN.
 (D) Zr and Ta have almost similar size due to lanthanide contraction.
8. 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
9. Which of the following chemical reaction(s) is/are involved in developing of photographic plate ?
 (A) $\text{C}_6\text{H}_4(\text{OH})_2 + 2\text{AgBr} \longrightarrow 2\text{Ag} + \text{C}_6\text{H}_4\text{O}_2 + 2\text{HBr}$
 (B) $\text{AgBr} + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2] + \text{NaBr}$
 (C) $2\text{AgNO}_3 + \text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Ag}_2\text{S}_2\text{O}_3 + 2\text{NaNO}_3$
 (D) $\text{AgNO}_3 + \text{KCN} \longrightarrow \text{AgCN} + \text{KNO}_3$



10. 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
11. 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.
12. 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
13. 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 passage carefully and answer the questions.

Comprehension # 1

Transition metals usually form coloured complexes and d-d transitions ($t_{2g} \longleftrightarrow e_g$) 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 $3d^0$ 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

Comprehension # 3

Answer Q.6, Q.7 and Q.8 by appropriately matching the information given in the three columns of the following table.

Observe the three columns in which column-1 Elements, Column-2 Property (Compare in given elements), while column-3 Aqueous solution of element salts show colours.			
Column-1 (Element)		Column-2 (Property compare in given element)	Column-3 (Aqueous solution of element salts show colour)
(I)	Fe	(i) Highest II nd I.E.	(P) Light pink
(II)	Ni	(ii) M in $\text{M}(\text{CO})_4$ is sp^3 hybridization	(Q) Green
(III)	Cu	(iii) (+3) oxidation state is more paramagnetic than (+2)	(R) Colour less
(IV)	Mn	(iv) Shows +7 oxidation state (highest)	(S) Green Pale

6. Which combination is correct :
 (A) (I) (i) (P) (B) (II) (ii) (Q) (C) (III) (iii) (S) (D) (IV) (iv) (R)
7. Which combination is/are not correct
 (A) (I) (ii) (Q) (B) (III) (i) (R) (C) (I) (iii) (S) (D) (IV) (iv) (P)
8. Which combination is correct for Ni.
 (A) (II) (i) (R) (B) (II) (ii) (Q) (C) (II) (iii) (S) (D) (II) (iv) (P)

Exercise-3

* Marked Questions may have more than one correct option.

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

1. Amongst the following identify the species with an atom in +6 oxidation state. [JEE 2000(S), 3/35]
 (A) MnO_4^- (B) $\text{Cr}(\text{CN})_6^{3-}$ (C) NiF_6^{2-} (D) CrO_2Cl_2
2. Write the balanced chemical equations for developing photographic films. [JEE 2000(M), 2/100]
3. In the standardization of $\text{Na}_2\text{S}_2\text{O}_3$ using $\text{K}_2\text{Cr}_2\text{O}_7$ by iodometry, the equivalent weight of $\text{K}_2\text{Cr}_2\text{O}_7$ is :
 (A) (molecular weight)/2, (molar mass)/2 (B) (molecular weight)/6
 (C) (molecular weight)/3 (D) same as molecular weight [JEE 2001(S), 3/35]
4. When MnO_2 is fused with KOH , a coloured compound is formed. The product and its colour is :
 [JEE 2003(S), 3/144]
 (A) K_2MnO_4 , green (B) Mn_2O_3 , brown (C) Mn_2O_4 , black (D) KMnO_4 , purple
5. The product of oxidation of I^- with MnO_4^- in alkaline medium is : [JEE 2004(S), 3/144]
 (A) IO_3^- (B) I_2 (C) IO^- (D) IO_4^-
6. The pair of compounds having metals in their highest oxidation state is : [JEE 2004(S), 3/144]
 (A) MnO_2 , FeCl_3 (B) $[\text{MnO}_4]^-$, CrO_2Cl_2
 (C) $[\text{Fe}(\text{CN})_6]^{2-}$, $[\text{Co}(\text{CN})_6]^{3-}$ (D) $[\text{NiCl}_4]^{2-}$, $[\text{Ni}(\text{CO})_4]$.
7. Which of the following pair of compounds is expected to exhibit same colour in aqueous solution ? [JEE 2005(S), 3/84]
 (A) FeCl_3 , CuCl_2 (B) VOCl_2 , CuCl_2 (C) VOCl_2 , FeCl_2 (D) FeCl_2 , MnCl_2
8. Give equations and describe the process for the developing of black and white photographic film. When sodium thiosulphate solution is treated with acidic solution turns milky white. Give the half reaction of the above described process. [JEE 2005(M), 4/60]



(A)
Colourless
liquid at room
temperature,
transition metal
↓
moist Air
↓
White fumes
(C)

Identify (A), (B) and (C). Also explain colour difference between MCl_4 and (B). [JEE 2005(M), 4/60]

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

[JEE 2007, 6/162]

	Column I		Column II
(A)	$O_2^- \rightarrow O_2 + O_2^{2-}$	(p)	Redox reaction
(B)	$CrO_4^{2-} + H^+ \rightarrow$	(q)	One of the products has trigonal planar structure
(C)	$MnO_4^- + NO_2^- + H^+ \rightarrow$	(r)	Dimeric bridged tetrahedral metal ion
(D)	$NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow$	(s)	Disproportionation

11. Among the following, the coloured compound is : [JEE 2008, 3/163]

- (A) $CuCl$ (B) $K_3[Cu(CN)_4]$ (C) CuF_2 (D) $[Cu(CH_3CN)_4]BF_4$

12. The oxidation number of Mn in the product of alkaline oxidative fusion of MnO_2 is. [JEE 2009, 4/160]

13.* 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

14. The colour of light absorbed by an aqueous solution of $CuSO_4$ is : [JEE 2012, 3/136]

- (A) orange-red (B) blue-green (C) yellow (D) violet

15.* Which of the following halides react(s) with $AgNO_3(aq)$ to give a precipitate that dissolves in $Na_2S_2O_3(aq)$? [JEE 2012, 4/136]

- (A) HCl (B) HF (C) HBr (D) HI

16. Consider the following list of reagents : 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 : [JEE(Advanced) 2014, 3/120]

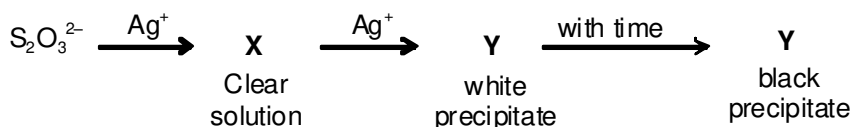
17.* The correct statement(s) about Cr^{2+} and Mn^{3+} is (are) : [JEE(Advanced) 2015, 4/168]

- [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.

18.* 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

19. In the following reaction sequence in aqueous solution, the species X, Y and Z, respectively, are [JEE(Advanced) 2016, 3/124]



- (A) $[Ag(SO_2O_3)_2]^{3-}$, $Ag_2S_2O_3$, Ag_2S (B) $[Ag(S_2O_3)_3]^{5-}$, Ag_2SO_3 , Ag_2S
(C) $[Ag(SO_3)_2]^{3-}$, $Ag_2S_2O_3$, Ag (D) $[Ag(SO_3)_3]^{3-}$, Ag_2SO_4 , Ag_s



20. Which of the following combination will produce H_2 gas ?
 (A) Fe metal and conc. HNO_3
 (B) Cu metal and conc. HNO_3
 (C) Au metal and $NaCN(aq)$ in the presence of air
 (D) Zn metal and $NaOH(aq)$

[JEE(Advanced) 2017, 3/122]

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

JEE(MAIN) OFFLINE PROBLEMS

- Number of electrons transferred in each case when $KMnO_4$ acts as an oxidising agent to give MnO_2 , Mn^{2+} , $Mn(OH)_3$ and MnO_4^{2-} are respectively :
 (1) 3, 5, 4 and 1 (2) 4, 3, 1 and 5 (3) 1, 3, 4 and 5 (4) 5, 4, 3 and 1
 [AIEEE 2002, 3/225]
- Which of the following ions has the maximum magnetic moment?
 (1) Mn^{2+} (2) Fe^{2+} (3) Ti^{2+} (4) Cr^{2+} .
 [AIEEE 2002, 3/225]
- Most common oxidation state of Ce (Cerium) are :
 (1) +3, +4 (2) +2, +3 (3) +2, +4 (4) +3, +5
 [AIEEE 2002, 3/225]
- What would happen when a solution of potassium chromate is treated with an excess of dilute HNO_3 ?
 (1) $Cr_2O_7^{2-}$ and H_2O are formed (2) CrO_4^{2-} is reduced to +3 state of Cr
 (3) CrO_4^{2-} is oxidised to +7 state of Cr (4) Cr^{3+} and $Cr_2O_7^{2-}$ are formed
 [AIEEE 2003, 3/225]
- Which one of the following nitrates will leave behind a metal on strong heating ?
 (1) Copper nitrate (2) Manganese nitrate (3) Silver nitrate (4) Ferric nitrate
 [AIEEE 2003, 3/225]
- The atomic numbers of V, Cr, Mn and Fe are respectively 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionization enthalpy ?
 (1) Cr (2) Mn (3) Fe (4) V
 [AIEEE 2003, 3/225]
- Which of the following group of transition metals is called coinage metals ?
 (1) Cu, Ag, Au (2) Ru, Rh, Pb (3) Fe, Co, Ni (4) Os, Ir, Pt
 [AIEEE 2003, 3/225]
- The number of d-electrons retained in Fe^{2+} (At. no. Fe = 26) ions are :
 (1) 3 (2) 4 (3) 5 (4) 6
 [AIEEE 2003, 3/225]
- Ammonia forms the complex ion $[Cu(NH_3)_4]^{2+}$ with copper ions in the alkaline solutions but not in acidic solutions. What is the Statement-2 for it ?
 (1) In acidic solutions hydration protects copper ions
 (2) In acidic solutions protons co-ordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available.
 (3) In alkaline solutions insoluble $Cu(OH)_2$ is precipitated which is soluble in excess of any alkali
 (4) Copper hydroxide is an amphoteric substance.
 [AIEEE 2003, 3/225]
- The radius of La^{3+} (Atomic number of La = 57) is 1.06\AA . Which one of the following given values will be closest to the radius of Lu^{3+} (Atomic number of Lu = 71) ?
 (1) 1.60\AA (2) 1.40\AA (3) 1.06\AA (4) 0.85\AA
 [AIEEE 2003, 3/225]
- Cerium (Z = 58) is an important member of the lanthanoids. Which of the following statement about cerium is incorrect?
 (1) The common oxidation state of cerium are +3 and +4.
 (2) The +3 oxidation state of cerium is more stable than +4 oxidation state.
 (3) The +4 oxidation state of cerium is not known in solution.
 (4) Cerium (IV) acts as an oxidizing agent.
 [AIEEE 2004, 3/225]
- The lanthanide contraction is responsible for the fact that
 (1) Zr and Y have about the same radius
 (2) Zr and Nb have similar oxidation state
 (3) Zr and Hf have about the same radius
 (4) Zr and Zn have same oxidation state.
 [AIEEE 2005, 3/225]



13. Which of the following factors may be regarded as the main cause of lanthanide contraction ?
 (1) Greater shielding of 5d electrons by 4f electrons [AIEEE 2005, 4½/225]
 (2) Poorer shielding of 5d electron by 4f electrons
 (3) Effective shielding of one of 4f electrons by another in the sub-shell
 (4) Poor shielding of one of 4f electron by another in the sub-shell.
14. The “spin-only” magnetic moment [in units of Bohr magneton, (μ_B) of Ni^{2+} in aqueous solution would be (atomic number of Ni = 28)
 (1) 2.84 (2) 4.90 (3) 0 (4) 1.73 [AIEEE 2006, 3/165]
15. Lanthanoid contraction is caused due to : [AIEEE 2006, 3/165]
 (1) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge
 (2) the appreciable shielding on outer electrons by 5f electrons from the nuclear charge
 (3) the same effective nuclear charge from Ce to Lu
 (4) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge
16. Identify the incorrect statement among the following. [AIEEE 2007, 3/120]
 (1) The chemistry of various lanthanoids is very similar.
 (2) 4f and 5f orbitals are equally shielded.
 (3) d-block elements show irregular and erratic chemical properties among themselves.
 (4) La and Lu have partially filled d orbitals and no other partially filled orbitals.
17. The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because [AIEEE 2007, 3/120]
 (1) The actinoids are more reactive than the lanthanoids.
 (2) The 5f orbitals extend farther from the nucleus than the 4f orbitals.
 (3) The 5f orbitals are more buried than the 4f orbitals
 (4) There is a similarity between 4f and 5f orbitals in their angular part of the wave function
18. Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being. [AIEEE 2008, 3/105]
 (1) lesser energy difference between 5f and 6d than between 4f and 5d orbitals
 (2) more energy difference between 5f and 6d than between 4f and 5d orbitals
 (3) more reactive nature of the actinoids than the lanthanoids
 (4) 4f orbitals more diffused than the 5f orbitals
19. In context with the transition elements, which of the following statements is incorrect? [AIEEE 2009, 4/144]
 (1) In the highest oxidation states, the transition metal show basic character and form cationic complexes.
 (2) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding.
 (3) Once the d^5 configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.
 (4) In addition to the normal oxidation states, the zero oxidation state is also shown by these elements in complexes.
20. Knowing that the Chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statement is incorrect ? [AIEEE 2009, 4/144]
 (1) The ionic sizes of Ln (III) decrease in general with increasing atomic number.
 (2) Ln (III) compounds are generally colourless.
 (3) Ln (III) hydroxides are mainly basic in character
 (4) Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character.
21. The correct order of $E_{M^{2+}/M}^0$ 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) $Cr > Mn > Fe > Co$



22. 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.
23. 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) $4f^{14} 5d^1 6s^2$
24. Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is incorrect ? [AIEEE 2012, 4/120]
 (1) Ferrous oxide is more basic in nature than the ferric oxide.
 (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.
25. Which of the following arrangements does not represent the correct order of the property stated against it? [JEE(Main) 2013, 4/120]
 (1) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behaviour
 (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
26. 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 $E_{M^{3+}/M^{2+}}^\circ$ value ? [JEE(Main) 2013, 4/120]
 (1) Cr(Z = 24) (2) Mn(Z = 25) (3) Fe(Z = 26) (4) Co(Z = 27)
27. Which series of reactions correctly represents chemical relations related to iron and its compound ?
 (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) $Fe \xrightarrow{O_2, \text{heat}} Fe_3O_4 \xrightarrow{CO, 600^\circ C} FeO \xrightarrow{CO, 700^\circ C} Fe$ [JEE(Main) 2014, 4/120]
28. The equation which is balanced and represents the correct product(s) is : [JEE(Main) 2014, 4/120]
 (1) $Li_2O + 2KCl \longrightarrow 2LiCl + K_2O$
 (2) $[CoCl(NH_3)_5]^{2+} + 5H^+ \longrightarrow Co^{2+} + 5NH_4^+ + Cl^-$
 (3) $[Mg(H_2O)_6]^{2+} + (EDTA)^{4-} \xrightarrow{\text{excess NaOH}} [Mg(EDTA)]^{2-} + 6H_2O$
 (4) $CuSO_4 + 4KCN \longrightarrow K_2[Cu(CN)_4] + K_2SO_4$
29. Match the catalysts to the correct processes : [JEE(Main)-2015, 4/120]
- | | Catalyst | | Process |
|-----|----------|-------|------------------------------|
| (A) | $TiCl_3$ | (i) | Wacker process |
| (B) | $PdCl_2$ | (ii) | Ziegler-Natta polymerization |
| (C) | $CuCl_2$ | (iii) | Contact process |
| (D) | V_2O_5 | (iv) | Deacon's process |
- (1) (A) - (iii), (B) - (ii), (C) - (iv), (D) - (i) (2) (A) - (ii), (B) - (i), (C) - (iv), (D) - (iii)
 (3) (A) - (ii), (B) - (iii), (C) - (iv), (D) - (i) (4) (A) - (iii), (B) - (i), (C) - (ii), (D) - (iv)
30. The colour of $KMnO_4$ is due to : [JEE(Main) 2015, 4/120]
 (1) $M \rightarrow L$ charge transfer transition (2) d - d transition
 (3) $L \rightarrow M$ charge transfer transition (4) $\sigma - \sigma^*$ transition

JEE(MAIN) ONLINE PROBLEMS

1. Chloro compound of Vanadium has only spin magnetic moment of 1.73 BM. This Vanadium chloride has the formula : (at. no. of V = 23) [JEE(Main) 2014 Online (09-04-14), 4/120]
 (1) VCl_2 (2) VCl_4 (3) VCl_3 (4) VCl_5
2. Which one of the following exhibits the largest number of oxidation states? [JEE(Main) 2014 Online (12-04-14), 4/120]
 (1) Ti (22) (2) V (23) (3) Cr (24) (4) Mn (25)



3. Copper becomes green when exposed to moist air for a long period. This is due to :
[JEE(Main) 2014 Online (12-04-14), 4/120]
(1) the formation of a layer of cupric oxide on the surface of copper.
(2) the formation of a layer of basic carbonate of copper on the surface of copper.
(3) the formation of a layer of cupric hydroxide on the surface of copper.
(4) the formation of basic copper sulphate layer on the surface of the metal.
4. Which of the following statements is false ? [JEE(Main) 2015 Online (11-04-15), 4/120]
(1) $\text{Na}_2\text{Cr}_2\text{O}_7$ is less soluble than $\text{K}_2\text{Cr}_2\text{O}_7$ (2) $\text{Na}_2\text{Cr}_2\text{O}_7$ is primary standard in volumetry
(3) CrO_4^{2-} is tetrahedral in shape (4) CrO_7^{2-} has a Cr—O—Cr bond
5. Which one of the following species is stable in aqueous solution?
[JEE(Main) 2016 Online (09-04-16), 4/120]
(1) MnO_4^{2-} (2) MnO_4^{3-} (3) Cu^+ (4) Cr^{2+}
6. The transition metal ions responsible for color in ruby and emerald are, respectively :
[JEE(Main) 2016 Online (10-04-16), 4/120]
(1) Cr^{3+} and Cr^{3+} (2) Co^{3+} and Co^{3+} (3) Co^{3+} and Cr^{3+} (4) Cr^{3+} and Co^{3+}
7. The pair of compounds having metals in their highest oxidation state is :
[JEE(Main) 2017 Online (08-04-17), 4/120]
(1) MnO_2 and CrO_2Cl_2 (2) $[\text{FeCl}_4]^-$ and Co_2O_3
(3) $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Cu}(\text{CN})_4]^{2-}$ (4) $[\text{NiCl}_4]^{2-}$ and $[\text{CoCl}_4]^{2-}$
8. When XO_2 is fused with an alkali metal hydroxide in presence of an oxidizing agent such as KNO_3 ; a dark green product is formed which disproportionates in acidic solution to afford a dark purple solution. X is :
[JEE(Main) 2018 Online (16-04-18), 4/120]
(1) Mn (2) Cr (3) V (4) Ti
9. The highest value of the calculated spin-only magnetic moment (in BM) among all the transition metal complexes is :
[JEE(Main) 2019 Online (09-01-19), 4/120]
(1) 4.90 (2) 6.93 (3) 3.87 (4) 5.92
10. The transition element that has lowest enthalpy of atomisation, is :
[JEE(Main) 2019 Online (09-01-19), 4/120]
(1) V (2) Fe (3) Zn (4) Cu
11. The 71st electron of an element X with an atomic number of 71 enters into the orbital:
[JEE(Main) 2019 Online (10-01-19), 4/120]
(1) 6s (2) 5d (3) 4f (4) 6p
12. The element that usually does NOT show variable oxidation states is :
[JEE(Main) 2019 Online (11-01-19), 4/120]
(1) Cu (2) Ti (3) Sc (4) V
13. $\text{A} \xrightarrow{4\text{KOH}, \text{O}_2} 2\text{B} + 2\text{H}_2\text{O}$
(Green)
 $3\text{B} \xrightarrow{4\text{HCl}} 2\text{C} + \text{MnO}_2 + 2\text{H}_2\text{O}$
(Purple)
 $2\text{C} \xrightarrow{\text{H}_2\text{O}_2, \text{KI}} 2\text{A} + 2\text{KOH} + \text{D}$
In the above sequence of reactions,
A and D, respectively, are : [JEE(Main) 2019 Online (11-01-19), 4/120]
(1) KIO_3 and MnO_2 (2) MnO_2 and KIO_3 (3) KI and K_2MnO_4 (4) KI and KMnO_4
14. The pair of metal ions that can give a spin-only magnetic moment of 3.9 BM for the complex $[\text{M}(\text{H}_2\text{O})_6]\text{Cl}_2$ is :
[JEE(Main) 2019 Online (12-01-19), 4/120]
(1) Cr^{2+} and Mn^{2+} (2) V^{2+} and Co^{2+} (3) V^{2+} and Fe^{2+} (4) Co^{2+} and Fe^{2+}
15. The correct order of atomic radii is : [JEE(Main) 2019 Online (12-01-19), 4/120]
(1) $\text{Eu} > \text{Ce} > \text{Ho} > \text{N}$ (2) $\text{N} > \text{Ce} > \text{Eu} > \text{Ho}$ (3) $\text{Ce} > \text{Eu} > \text{Ho} > \text{N}$ (4) $\text{Ho} > \text{N} > \text{Eu} > \text{Ce}$



Answers

EXERCISE - 1

PART - I

- A-1.** $(n-1)d^{1-10}ns^{1-2}$ (palladium is exception); $[\text{Kr}]^{36}4d^{10}5s^0$.
- A-2.** (i) $[\text{Ar}]3d^54s^0$ (ii) $[\text{Ar}]3d^54s^0$ (iii) $[\text{Ar}]3d^84s^0$ (iv) $[\text{Ar}]3d^34s^0$
- A-3.** Zn, Cd and Hg have $(n-1)d^{10}ns^2$ electron configuration in their atoms and $(n-1)d^{10}ns^0$ electron configuration in their most stable simple ions i.e. M^{2+} . So they do not have partially filled d-orbitals in their atoms or in their simple ions.
- A-4.** Lanthanide contraction phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called **Lanthanoid contraction**. This essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d-series exhibit similar radii and have very similar physical and chemical properties.
- A-5.** (i) Sc (ii) Os or Ir
- A-6.** (i) As Hg has weakest interatomic interaction on account of no unpaired electrons, $(n-1)d^{10}ns^2$ available for bonding.
(ii) As W has highest interatomic interaction on account of more number of unpaired electrons, $(n-1)d^5ns^1$ available for bonding.
- A-7.** In case of zinc, no electrons from 3d-orbitals are involved in the formation of metallic bonds.
- A-8.** 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.
- A-9.** The energies of $(n-1)d$ orbitals and ns orbitals are very close. Hence, electrons from both can participate in bonding.
- A-10.** +2
- B-1.** (i) enthalpy of sublimation (ii) ionisation energy (iii) enthalpy of hydration
- B-2.** Much larger third ionisation energy of Mn (change from $3d^5$ to $3d^4$) is responsible for this. This also explains why the +3 state of Mn is of little importance.
- B-3.** (i) Mn^{2+} is more stable than Fe^{3+} .
(ii) The order of getting oxidised is $\text{Mn} > \text{Cr} > \text{Fe}$.
- B-4.** (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 undergo d-d transition of electron according to CFT and, therefore, are colourless.
- B-5.** Electronic configuration of ${}_{22}\text{Ti}^{4+}$ is $[\text{Ar}]^{18}3d^04s^0$. So all electrons are paired and thus its all complexes are diamagnetic.
- B-6.** $\mu_B = 3.9 \text{ BM}$, $n = 3$
- B-7.** (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 interatomic interaction and hence stronger bonding between the atoms.
(c) May be attributed to the presence of unpaired electrons (d-d transition in most of the compounds)



- D-3.** Lanthanoids show limited number of oxidation state, viz, +2, +3 and +4 (out of which +3 is most common). This is because of large energy gap between 4f, 5d and 6s subshells, the dominant oxidation state of actinoids is also + 3 but they show a number of other oxidation states also, e.g. uranium ($Z = 92$) and plutonium ($Z = 94$), show +3 +4 +5 and +6 neptunium ($Z = 94$) shows +3 +4 +5 and +7 etc. This is due to small energy difference between 5f, 6d and 7s subshell of the actinoids
- D-4.** The most stable oxidation state of lanthanoides 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. (C) | A-2. (C) | A-3. (B) | A-4. (B) | A-5. (C) |
| A-6. (A) | B-1. (A) | B-2. (B) | B-3. (A) | B-4. (D) |
| B-5. (C) | B-6. (C) | B-7. (C) | B-8. (C) | B-9. (D) |
| C-1. (B) | C-2. (D) | C-3. (B) | C-4. (B) | C-5. (A) |
| C-6. (A) | C-7. (C) | C-8. (A) | C-9. (A) | D-1. (C) |
| D-2. (B) | D-3. (B) | D-4. (B) | D-5. (D) | D-6. (C) |
| D-7. (A) | D-8. (A) | | | |

PART - III

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

EXERCISE - 2

PART - I

- | | | | | |
|----------------|---------------|---------------|---------------|----------------|
| 1. (A) | 2. (A) | 3. (A) | 4. (B) | 5. (D) |
| 6. (C) | 7. (C) | 8. (C) | 9. (D) | 10. (A) |
| 11. (A) | | | | |

PART - II

- | | | | |
|--|-------------|--------------|--------------|
| 1. 3 | 2. 4 | 3. 2 | 4. 34 |
| 5. $(26 + 4 + (2 \times 5)) = 40$ | 6. 3 | 7. 12 | 8. 15 |

PART - III

- | | | | | |
|-------------------|-----------------|-------------------|----------------|------------------|
| 1. (ABC) | 2. (ABC) | 3. (ABC) | 4. (AC) | 5. (ACD) |
| 6. (ABCD) | 7. (ABC) | 8. (ABD) | 9. (AB) | 10. (ABD) |
| 11. (ABCD) | 12. (AB) | 13. (ABCD) | | |

PART - IV

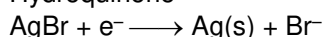
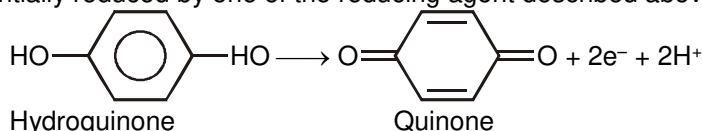
- | | | | | |
|---------------|---------------|---------------|---------------|---------------|
| 1. (C) | 2. (C) | 3. (A) | 4. (B) | 5. (B) |
| 6. (B) | 7. (B) | 8. (B) | | |



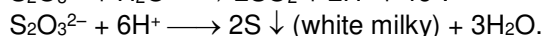
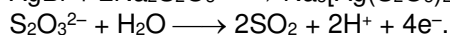
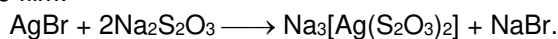
EXERCISE - 3

PART - I

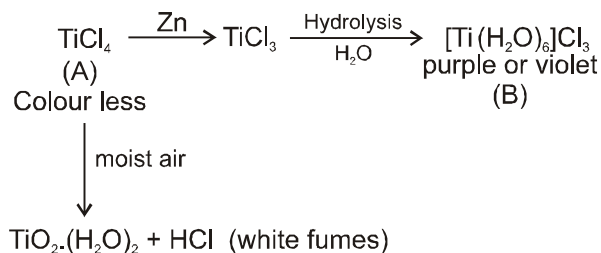
1. (D)
2. $C_6H_4(OH)_2 + 2AgBr \longrightarrow 2Ag + C_6H_4O_2 + 2HBr$
 $AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$
3. (B) 4. (A) 5. (A) 6. (B) 7. (B)
8. Developer is usually a weak reducing agent like potassium ferrous oxalate, an alkaline solution of pyrogallol or an alkaline solution of quinol.
 In the process of development of the photographic film, the exposed/activated AgBr grains are preferentially reduced by one of the reducing agent described above.



The photographic film is then fixed by washing with hypo solution to remove the unreacted AgBr grains from the film.



9. (A) is $TiCl_4$ as it has no unpaired electron and is liquid at room temperature on account of covalent character because of high polarising power of Ti^{+4} . $TiCl_4$ being covalent gets hydrolysed forming $TiO_2(H_2O)_2$ and HCl (B) which fumes in air.
 In $[Ti(H_2O)_6]Cl_3$ complex Ti(III) has one unpaired electron ($3d^1$) which gives violet / purple colour due to d-d transition.



10. (A – p, s); (B – r); (C – p, q); (D – p). 11. (C) 12. 6
- 13.* (ACD)/(AD) 14. (A) 15.* (ACD) 16. 7
- 17.* (ABC) 18.* (CD) 19. (A) 20. (D)

PART - II

JEE(MAIN) OFFLINE PROBLEMS

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (1) | 2. (1) | 3. (1) | 4. (1) | 5. (3) |
| 6. (1) | 7. (1) | 8. (4) | 9. (2) | 10. (4) |
| 11. (3) | 12. (3) | 13. (4) | 14. (1) | 15. (4) |
| 16. (2) | 17. (2) | 18. (1) | 19. (1) | 20. (2) |
| 21. (1) | 22. (4) | 23. (4) | 24. (4) | 25. (1) |
| 26. (4) | 27. (4) | 28. (2) | 29. (2) | 30. (3) |

JEE(MAIN) ONLINE PROBLEMS

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (2) | 2. (4) | 3. (2) | 4. (1) | 5. (1) |
| 6. (1) | 7. (3) | 8. (1) | 9. (4) | 10. (3) |
| 11. (2) | 12. (3) | 13. (2) | 14. (2) | 15. (1) |



Additional Problems for Self Practice (APSP)

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

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Time : 1 Hr.

Max. Marks : 120

Important Instructions

- The test is of **1 hour** duration.
- The Test Booklet consists of **30** questions. The maximum marks are **120**.
- Each question is allotted **4 (four)** marks for correct response.
- Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question. $\frac{1}{4}$ (**one fourth**) marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.

- The maximum oxidation state shown by V(Z = 23), Cr(Z = 24), Co(Z = 27), Sc(Z = 21) are respectively :
(1) +5, +6, +3, +3 (2) +3, +4, +5, +2 (3) +5, +3, +2, +1 (4) +4 in each case.
- Which oxide of manganese is most acidic in nature ?
(1) MnO (2) Mn₂O₇ (3) Mn₂O₃ (4) MnO₂
- The first ionisation energies of the elements of the first transition series :
(1) generally increases as the atomic numbers increase.
(2) decrease as the atomic number increase.
(3) do not show any change as the addition of electrons takes place in the inner (n – 1) d-orbitals.
(4) increase from Ti to Mn and then decrease from Mn to Cu.
- The ions from among the following which are colourless are :
(i) Ti⁴⁺, (ii) Cu⁺, (iii) Co³⁺, (iv) Fe²⁺.
(1) (i) and (ii) only (2) (i), (ii) and (iii) (3) (iii) and (iv) (4) (ii) and (iii).
- Which of the following transition metal ions has least magnetic moment ?
(1) Co³⁺ (2) Fe³⁺ (3) Cr²⁺ (4) V³⁺
- If a non metal is added to the interstitial sites of a metal, then the metal becomes :
(1) softer (2) less tensile (3) less malleable (4) more ductile.
- The pair of the compounds in which both the metals are in the highest possible oxidation state is,
(1) [Fe(CN)₆]³⁻, [Co(CN)₆]³⁻ (2) CrO₂Cl₂, MnO₄⁻
(3) TiO₂, MnO₂ (4) [Co(CN)₆]³⁻, Mn₂O₇
- Among the following statements, the incorrect is :
(1) Calamine and siderite are carbonate ores (2) Argentite and cuprite are oxide ores
(3) Zinc blende and pyrites are sulphide ores (4) Malachite and azurite are ores of copper.
- 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 :
(1) Fe₃O₄ (2) FeSO₄ (3) FeCl₃ (4) FeCl₂.
- Iron is rendered passive by treatment with concentrated :
(1) HCl (2) H₂SO₄ (3) HNO₃ (4) both (2) & (3)
- Which one of the following dissolves in hot concentrated NaOH ?
(1) Fe (2) Zn (3) Cu (4) Ag
- Hot copper wire reacts with oxygen to produce :
(1) Cu₂O (2) CuO₂ (3) Cu₂O₂ (4) CuO.



13. A compound is yellow when hot and white when cold. The compound is :
 (1) Al_2O_3 (2) PbO (3) CaO (4) ZnO
14. At 300°C , $\text{FeCl}_3(\text{s})$:
 (1) decomposes into FeCl_2 and Cl_2 . (2) decomposes into Fe and Cl_2 .
 (3) sublimes to give liquid FeCl_3 . (4) sublimes to give gaseous dimer $(\text{FeCl}_3)_2$.
15. When FeSO_4 is strongly heated, the number of acidic gases produced is :
 (1) One (2) Two (3) Three (4) Four
16. On heating $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$, the compound obtained is :
 (1) ZnCl_2 (2) $\text{Zn}(\text{OH})\text{Cl}$ (3) $\text{Zn}(\text{OH})_2$ (4) Zn
17. On heating KMnO_4 , one among the following is not formed :
 (1) K_2MnO_4 (2) O_2 (3) MnO_2 (4) MnO .
18. Reaction of KMnO_4 in neutral or very weakly alkaline solution can be represented as :
 (1) $\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$. (2) $2\text{MnO}_4^- + 2\text{OH}^- \rightarrow 2\text{MnO}_4^{2-} + 1/2\text{O}_2 + \text{H}_2\text{O}$.
 (3) $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$. (4) $\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$.
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 :
 (1) Mn_2O_7 , MnO_2 (2) Mn_2O_7 , Mn_2O_3 (3) MnSO_4 , Mn_2O_3 (4) Mn_2O_3 , MnO_2
20. Which of the following statement is wrong ?
 (1) An acidified solution of $\text{K}_2\text{Cr}_2\text{O}_7$ liberates iodine from iodides.
 (2) In acidic solution dichromate ions are converted to chromate ions.
 (3) Ammonium dichromate on heating undergo exothermic decomposition to give Cr_2O_3 .
 (4) Potassium dichromate is used as a titrant for Fe^{2+} .
21. The image on an exposed and developed photographic film is due to :
 (1) AgBr (2) $[\text{Ag}(\text{C}_2\text{O}_3)_2]^{3+}$ (3) Ag (4) Ag_2O .
22. The yellow colour solution of Na_2CrO_4 changes to orange red on passing CO_2 gas due to the formation of :
 (1) CrO_5 (2) CrO_3 (3) $\text{Na}_2\text{Cr}_2\text{O}_7$ (4) Na_3CrO_8 .
23. What happens when a molten mixture of K_2FeO_4 and K_2CrO_4 is acidified ?
 (1) FeO_4^{2-} is converted to H_2FeO_4
 (2) CrO_4^{2-} is reduced to Cr^{3+} liberating O_2
 (3) CrO_4^{2-} is converted to Cr^{3+}
 (4) FeO_4^{2-} is reduced to Fe^{3+} liberating O_2
24. Why silver chloride is used in photochromic spectacles ?
 (1) Silver halides darken in light owing to photochemical decomposition
 (2) Silver halides produced elemental silver in light.
 (3) If the halogen produced is kept in close proximity to finely divided silver chloride, the silver metal is formed.
 (4) All of these.
25. 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 ?
 (1) $\text{Ag} + \text{dilute HNO}_3$ (2) $\text{Ag} + \text{conc. HNO}_3$ (3) $\text{Ag} + \text{conc. H}_2\text{SO}_4$ (4) All of these
26. Which of the following can be used for the conversion of potassium manganate to potassium permanganate?
 (1) O_3 (2) Cl_2 (3) CO_2 (4) All.
27. Reaction of potassium chromate and CuSO_4 in aqueous solution produces :
 (1) CuCrO_4 only (2) $\text{Cu}_5[\text{CrO}_4]_2$ only
 (3) CuCr_2O_7 only (4) both CuCrO_4 and $\text{Cu}_2\text{Cr}_2\text{O}_7$.



28. 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.
 (1) 1 and 2 (2) 1 and 3 (3) 2 and 4 (4) 1 and 4
29. Transuranic elements begin with
 (1) Np (2) Cm (3) Pu (4) U
30. Lanthanide contraction is observed in :
 (1) Gd (2) At (3) Xe (4) Ac

Practice Test-1 (IIT-JEE (Main Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

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

PART - II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

1. 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.
2. Iron articles get rusted on weathering due to the formation of **[NSEC-2003]**
 (A) FeO (B) Fe₂O₃ (C) Fe₃O₄ (D) Fe(OH)₃
3. Chromium has the lowest oxidation state in **[NSEC-2003]**
 (A) chromium sulphate (B) chromium trioxide
 (C) potassium chromate (D) potassium dichromate.
4. Paramagnetism is not exhibited by **[NSEC-2004]**
 (A) CuSO₄·5H₂O (B) CuCl₂·5H₂O (C) CuI (D) NiSO₄·6H₂O.
5. 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.
6. The cation containing maximum number of unpaired electrons is **[NSEC-2005]**
 (A) Fe (II) (B) Fe (III) (C) Co (II) (D) Ni (II)
7. Chromium has the lowest oxidation state in **[NSEC-2005]**
 (A) potassium chromate (B) chromium sulphate
 (C) potassium dichromate (D) chromium oxide.

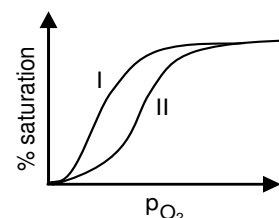




8. Which of the following statements concerning transition elements is false ? [NSEC-2006]
 (A) They are all metals.
 (B) They easily form coordination compounds.
 (C) Their ions are mostly coloured.
 (D) They show multiple oxidation states always differing by two units.
9. The magnetic moment of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ is: [NSEC-2007]
 (A) 1.73 BM (B) 3.87 BM (C) 4.09 BM (D) 5.92 BM
10. Which two of the following reactions are possible ? [NSEC-2007]
 (i) $2\text{FeCl}_3 + \text{SnCl}_2 \longrightarrow 2\text{FeCl}_2 + \text{SnCl}_4$ (ii) $2\text{FeCl}_2 + \text{SnCl}_4 \longrightarrow 2\text{FeCl}_3 + \text{SnCl}_2$
 (iii) $\text{PbCl}_2 + \text{SnCl}_4 \longrightarrow \text{SnCl}_2 + \text{PbCl}_4$ (iv) $\text{SnCl}_2 + \text{PbCl}_4 \longrightarrow \text{PbCl}_2 + \text{SnCl}_4$
 (A) i and ii (B) i and iii (C) i and iv (D) ii and iv
11. Europium forms stable Eu^{2+} ions because [NSEC-2007]
 (A) Europium is a lanthanide. (B) +2 is the common oxidation state of lanthanides.
 (C) Eu^{2+} has f^7 valence electronic configuration. (D) All of the above reasons.
12. 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]
13. How many unpaired electrons are in a Fe^{2+} ion in the ground state ? [NSEC-2008]
 (A) 0 (B) 2 (C) 4 (D) 6
14. In which of the following transition metal ion complexes, the colour is not due to d-d transition ? [NSEC-2008]
 (A) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{CoF}_6]^{3-}$ (B) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{MnO}_4]^-$
 (C) $[\text{CoF}_6]^{3-}$ and $[\text{CrO}_4]^{2-}$ (D) $[\text{MnO}_4]^-$ and $[\text{CrO}_4]^{2-}$
15. The compound with the lowest oxidation state of iron is – [NSEC-2009]
 (A) Fe_2O (B) Fe_3O_4 (C) $\text{K}_3\text{Fe}(\text{CN})_6$ (D) $\text{K}_4\text{Fe}(\text{CN})_6$
16. The aqua ion which will be almost colorless is – [NSEC-2009]
 (A) Cu^{2+} (B) Cr^{2+} (C) Ti^{4+} (D) Mn^{2+}
17. 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
18. 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.
19. The highest magnetic moment is shown by a transition metal ion with the outer electronic configuration [NSEC-2010]
 (A) $3d^2$ (B) $3d^5$ (C) $3d^7$ (D) $3d^9$
20. The compound in which Mn has oxidation state of +3 is [NSEC-2011]
 (A) KMnO_4 (B) $\text{K}_2[\text{Mn}(\text{CN})_6]$ (C) MnSO_4 (D) $\text{CsMn}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
21. 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
22. Which of the following ion is colourless ? [NSEC-2012]
 (A) Mn^{2+} (B) Cu^+ (C) Cr^{3+} (D) Fe^{2+}



23. The lanthanide compound which is used as a most powerful liquid laser after dissolving in selenium oxychloride is : [NSEC-2012]
 (A) Cerium oxide (B) Neodymium oxide
 (C) Promethium sulphate (D) Cerium sulphate
24. 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
25. In which of the following compounds is the oxidation number of the transition metal, zero ? [NSEC-2013]
 (A) $[\text{Fe}(\text{H}_2\text{O})_3](\text{OH})_2$ (B) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ (C) $[\text{Ni}(\text{CO})_4]$ (D) $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$
26. One of the constituents of German silver is [NSEC-2013]
 (A) Ag (B) Mg (C) Cu (D) Al
27. A mixture of acidified $\text{K}_2\text{Cr}_2\text{O}_7$ and 10% KI is titrated against $\text{Na}_2\text{S}_2\text{O}_3$ (Sodium thiosulphate) solution using starch indicator. The colour of the reaction mixture at the end point is [NSEC-2013]
 (A) Yellow (B) Blue (C) Green (D) Colourless
28. The colourless ion from among the following is [NSEC-2013]
 (A) Mn^{2+} (B) Cu^+ (C) Cr^{3+} (D) Fe^{2+}
29. Bell metal is an alloy of copper and [NSEC-2013]
 (A) Tin (B) Aluminium (C) Zinc (D) Nickel
30. 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
31. The pair of compounds that **will not** react with each other in an aqueous solution, at room temperature is [NSEC-2014]
 (A) FeCl_3 , SnCl_2 (B) HgCl_2 , SnCl_2 (C) FeCl_2 , SnCl_2 (D) FeCl_3 , KI
32. Four statements for Cr and Mn are given below. [NSEC-2015]
 (i) Cr^{2+} and Mn^{3+} have the same electronic configuration.
 (ii) Cr^{2+} is a reducing agent while Mn^{3+} is an oxidizing agent.
 (iii) Cr^{2+} is an oxidizing agent while Mn^{3+} is a reducing agent
 (iv) both Cr and Mn are oxidizing agents.
 The correct statements are
 (A) I, III, IV (B) I, II (C) I, II, IV (D) I, IV
33. The incorrect statement for lanthanides among the following statements is [NSEC-2015]
 (A) 4f and 5d orbitals are so close in energy that it is very difficult to locate the exact position of electrons in lanthanides
 (B) most common stable oxidation state is +3
 (C) tripositive lanthanide ions have characteristic color depending on nature of group with which they combine to form compounds
 (D) some lanthanide ions absorb either in infrared or ultraviolet region of electromagnetic spectrum
34. Which of the following statements is not true for Ce^{3+} and Yb^{3+} ? [NSEC-2016]
 (A) Both absorb in UV region (B) Both show f-f transition
 (C) Both show 4f to 5d transition (D) Both ions are colorless
35. Haemoglobin is a Fe containing protein responsible for oxygen transport in the blood. The curves given below indicate the percentage saturation of haemoglobin by O_2 as a function of partial pressure of O_2 . [NSEC-2017]
 Which of the following statement/s is /are correct for the given curves?
 I. In presence of CO_2 , higher P_{O_2} is needed for a given percentage saturation.
 II. In presence of CO_2 , lower P_{O_2} is needed for a given percentage saturation.
 III. The maximum percentage saturation is not affected by the presence of CO_2
 IV. In the absence of CO_2 , maximum saturation of haemoglobin occurs at lower p_{O_2}
 (A) I and IV (B) II and IV (C) I, III and IV (D) II and III





PART - III : HIGH LEVEL PROBLEMS (HLP)

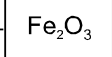
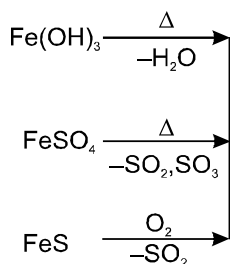
THEORY

1. Ferric Oxide, Fe_2O_3

Physical Properties :

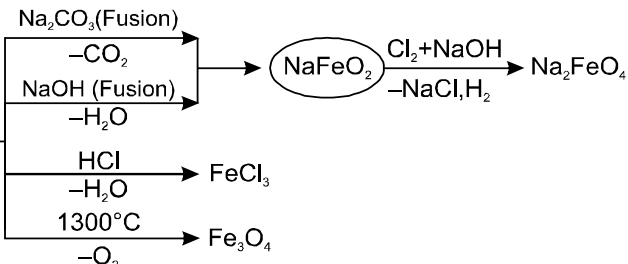
Deep red coloured powder and insoluble in water.

PREPARATION



Amphoteric
Nature

CHEMICAL PROPERTIES



Uses : It is used

- (i) as red pigment.
- (ii) an abrasive polishing powder.
- (iii) as a catalyst.

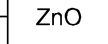
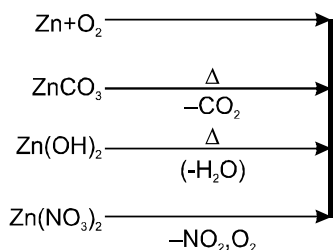
2. ZnO, Zinc oxide (Chinese white or Philosopher's wool)

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

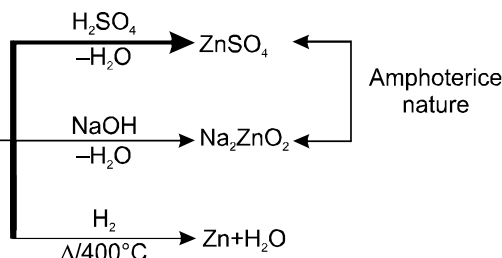
Physical Properties :

- (i) White powder which becomes yellow on heating due to change in the structure of lattice again turns white on cooling.
- (ii) Insoluble in water and sublimes at 400°C .

PREPARATION



CHEMICAL PROPERTIES



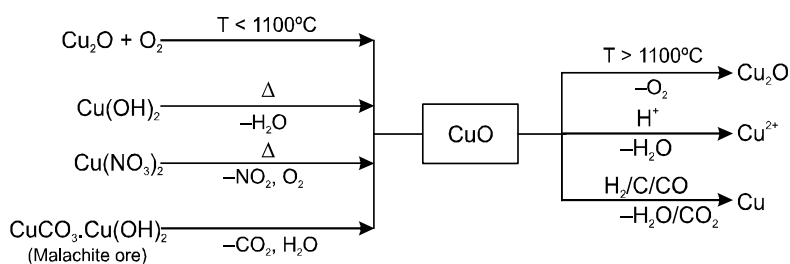
Uses : It is used

- (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 alcohol.
- (iv) for making soft rubber.

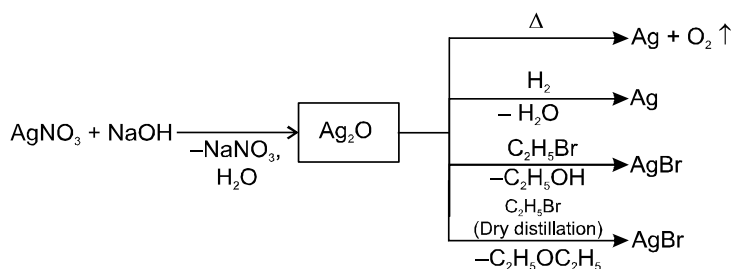
3. Cupric oxide, (CuO) :

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

Physical properties : Brown solid sparingly soluble in water properties.

PREPARATION**CHEMICAL PROPERTIES**

Uses : It is used

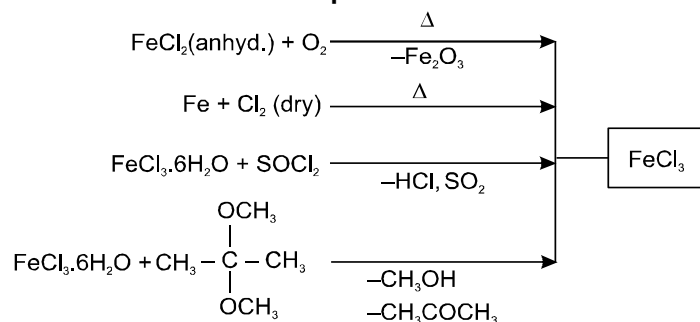
- as Tollen's reagent for detection of aldehydes, formic acid, and terminal alkynes.
- in the manufacturing of mirrors.

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

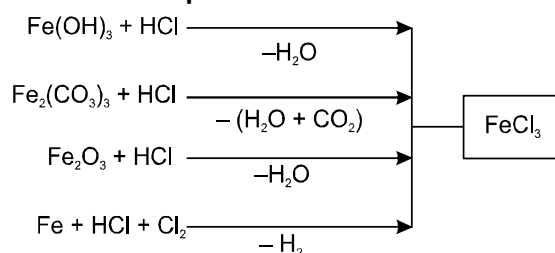
5. Ferric Chloride, FeCl_3

Preparation

(a) Anhydrous FeCl_3

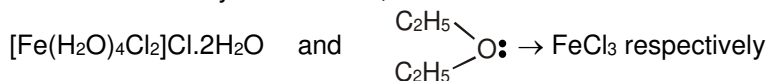
Preparation

(b) Hydrated FeCl_3

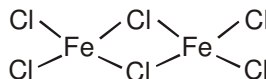
Preparation

**Properties :**

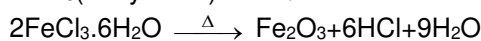
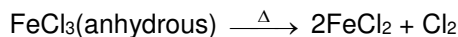
- Anhydrous FeCl_3 is dark black solid, while hydrated salt. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is yellowish-brown deliquescent crystalline liquid.
- Both hydrous FeCl_3 and hydrated FeCl_3 , are soluble in water as well as ether forming solvated species.



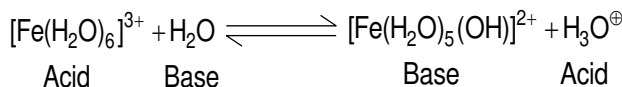
- It sublimes at 300°C giving a dimeric gas.

**Chemical Properties :**

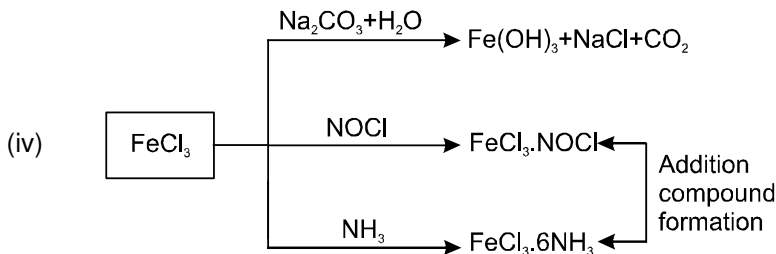
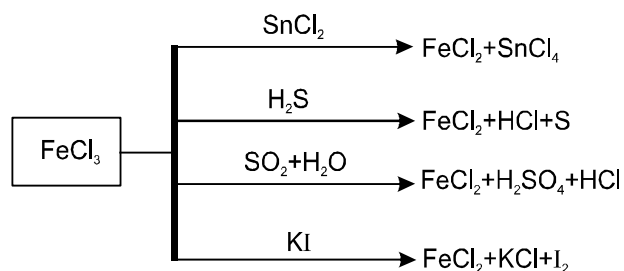
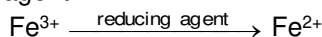
- (i) Action of heat :



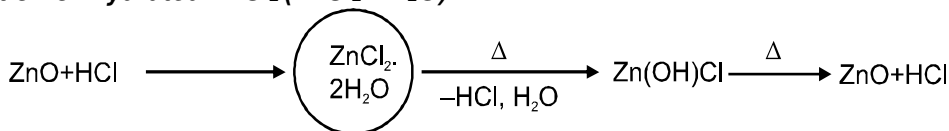
- (ii) Aqueous solution is acidic due to hydrolysis.



- (iii) As an oxidising agent.

**Uses :** It is used

- as a medicine.
- for detection of phenols.
- for making Prussian blue dyes.
- as an oxidising agent.

6. Zinc Chloride**Preparation of Hydrated $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$** **Anhydrous ZnCl_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.

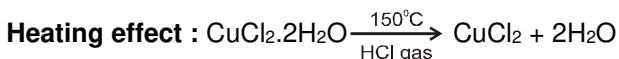
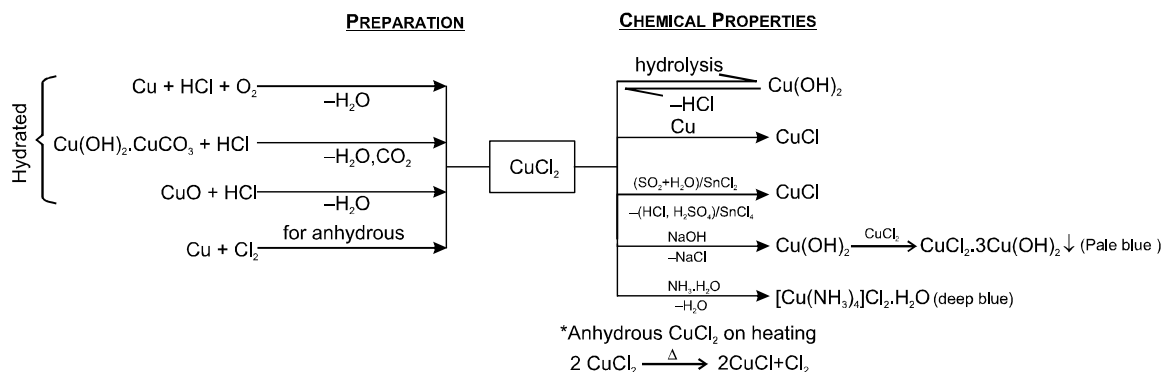
7. Cupric chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ **Physical Properties**

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 $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ and yellow colour due to complex anion $[\text{CuCl}_4]^{2-}$ and green when both are present.

**SUBJECTIVE QUESTIONS**

- K_2PtCl_6 compound whereas corresponding Ni compound is not known. Explain.
- What is meant by disproportionation of an oxidation state? Give an example.
- Most of transition metals can displace hydrogen from dilute acids. Why?
- Why do Mn(II) show maximum paramagnetic character amongst the bivalent ions of the 1st transition series?
- Explain why transition metals and their many compounds act as good catalyst.
- A transition metal forms alloys with other transition elements. Explain.
- What happens when CuSO_4 solution is treated with
(i) excess of ammonia solution and (ii) KI solution?
- What happens when silver nitrate solution is added to $\text{Na}_2\text{S}_2\text{O}_3$ solution and then content is allowed to keep for a longer period?
- What reaction will take place if a silver coin is put in dilute HNO_3 ?
- What happens when :
(a) FeSO_4 reacts with potassium ferricyanide.
(b) Fe_2O_3 is fused with soda ash.
(c) Salts of iron (III) reacts with NH_4SCN .
(d) Zinc oxide and cobalt oxide is fused.

ONLY ONE OPTION CORRECT TYPE

- Which ore contains both iron and copper?
(A) Cuprite (B) Chalcocite (C) Chalcopyrite (D) malachite



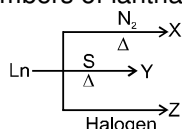
12. Atoms of the transition elements are smaller than those of the s-block elements, because :
 (A) there is increase in the nuclear charge along the period.
 (B) orbital electrons are added to the penultimate d-subshell rather than to the outer shell of the atom.
 (C) the shielding effect of d-electrons is small.
 (D) All of these
13. Which of the following statements is correct ?
 (A) The lesser number of oxidation states in 3d-series in the beginning of the series is due to the presence of too few electrons to loose or share
 (B) The lesser number of oxidation states in 3d-series towards the end of the series is due to the presence of too many electrons and thus fewer empty orbitals to share electrons with the ligands
 (C) (A) and (B) both
 (D) None is correct
14. E^\ominus values for the couples $\text{Cr}^{3+}/\text{Cr}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ are -0.41 and $+1.51$ volts respectively. Considering these values select the correct option from the following statements.
 (A) Cr^{2+} acts as a reducing agent and Mn^{3+} acts as an oxidising agent in their aqueous solutions.
 (B) Cr^{2+} (aq.) is more stable than Cr^{3+} (aq.).
 (C) Mn^{3+} (aq.) is more stable than Mn^{2+} (aq.).
 (D) None of these.
15. A metal ion from the first transition series has a magnetic moment (calculated) of 3.87 B.M. How many unpaired electrons are expected to be present in the ion ?
 (A) 1 (B) 2 (C) 3 (D) 4
16. Which one of the ionic species will impart colour to an aqueous solution ?
 (A) Ti^{4+} (B) Cu^+ (C) Zn^{2+} (D) Cr^{3+}
17. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is blue in colour because
 (A) It contains water of crystallization
 (B) SO_4^{2-} ions absorb red light
 (C) Cu^{2+} ions absorb red light
 (D) Cu^{2+} ions absorb all colours except red from the white light
18. When AgNO_3 (aq) reacts with excess of iodine, we get :
 (A) AgIO_3 (B) HIO_3 (C) AgO (D) HI
19. When $\text{K}_4[\text{Fe}(\text{CN})_6]$ is added to FeCl_3 , the complex compound formed is :
 (A) $\text{Fe}_3[\text{Fe}(\text{CN})_6]_4$ (B) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ (C) $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$ (D) $\text{K}_2\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$
20. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is actually :
 (A) $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_3$ (B) $[\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
 (C) $[\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (D) $[\text{Fe}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$
21. Aqueous solution of which of the following ions is green ?
 (A) V^{2+} (B) V^{3+} (C) VO^{2+} (D) VO_2^+
22. 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
23. In the reaction, $2\text{CuCl}_2 + 2\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{A} + \text{H}_2\text{SO}_4 + 2\text{HCl}$; A is
 (A) CuCl (B) Cu (C) CuSO_4 (D) CuS
24. German silver is an alloy of copper and :
 (A) $\text{Zn} + \text{Ni}$ (B) $\text{Al} + \text{Ag}$ (C) $\text{Zn} + \text{Ag}$ (D) $\text{Sn} + \text{Zn}$
25. 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) $\text{Cu}(\text{OH})_2$ (B) CuO (C) CuCO_3 (D) $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
26. FeCl_3 dissolves in :
 (A) water (B) ether (C) ammonia (D) (A) and (B) both



27. When AgNO_3 (aq) reacts with excess of iodine, we get :
 (A) AgIO_3 (B) HIO_3 (C) AgO (D) HI
28. $\text{ZnO} + \text{CoO} \xrightarrow{\Delta} \text{X}$; Product 'X' colour is :
 (A) Green (B) Blue (C) Pink (D) Bluish green
29. The compound that gets oxidised even on exposure to atmosphere is :
 (A) $\text{Co}_2(\text{SO}_4)_3$ (B) NiSO_4 (C) KMnO_4 (D) FeSO_4
30. The +3 ion of which one of the following has half filled 4f subshell ?
 (A) La (B) Lu (C) Gd (D) Ac

SINGLE AND DOUBLE VALUE INTEGER TYPE

31. $\text{FeC}_2\text{O}_4 \xrightarrow{\Delta} \text{products}$
 Number of diamagnetic products = x
 Number of unpaired electrons in paramagnetic product = y
 Report your answer as (x + y).
32. No. of following reagents in which ppt A is soluble is :
 $\text{AgNO}_3 + \text{NaCl} \longrightarrow \text{A} \downarrow$
 (i) aq. NH_3 (ii) aq. KCN (iii) $\text{Na}_2\text{S}_2\text{O}_3$
 (iv) Conc. HCl (v) aq. NaOH (iv) aq. KI
33. The number of water molecule(s) directly bonded to the metal centre in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is—
34. How many of the following statements are correct for green vitriol?
 1. It can be used for the preparation of Mohr's salt.
 2. It is a hydrated salt and its anhydrous form is white in colour.
 3. The decomposition reaction of its anhydrous form is redox in nature.
 4. It is used for making Fenton's reagent used as a catalyst in organic chemistry.
 5. It can be used for the preparation of Potassium ferrocyanide.
 6. It has same number of molecules of water of crystallization as white vitriol or blue vitriol.
 7. It turns brownish-yellow on exposure to atmosphere.
 8. Its aqueous solution is acidic in nature due to hydrolysis.
 9. Out of the decomposition products of its anhydrous form, only one can turn acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution green.
35. The heavier members of lanthanoid series metal react with following non-metal.



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

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

36. The less stable oxidation states of Cr are :
 (A) Cr^{2+} (B) Cr^{3+} (C) Cr^{4+} (D) Cr^{5+}
37. Which of the following is/are soluble in excess of NaOH .
 (A) $\text{Al}(\text{OH})_3$ (B) $\text{Cr}(\text{OH})_3$ (C) $\text{Fe}(\text{OH})_3$ (D) $\text{Zn}(\text{OH})_2$
38. 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
39. Which of the following reaction(s) is/are used for the preparation of anhydrous FeCl_3 ?
 (A) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + 6\text{SOCl}_2 \longrightarrow \text{FeCl}_3 + 12\text{HCl} + 6\text{SO}_2$
 (B) $\text{Fe}(\text{OH})_3 \downarrow + 3\text{HCl} \longrightarrow \text{FeCl}_3 + 3\text{H}_2\text{O}$
 (C) $2\text{Fe} + 4\text{HCl} (\text{aq.}) + \text{Cl}_2 \longrightarrow 2\text{FeCl}_3 + 2\text{H}_2$
 (D) $2\text{Fe} + 3\text{Cl}_2 (\text{dry}) \longrightarrow 2\text{FeCl}_3$





40. 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 .

PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.

Max. Marks : 66

Important Instructions

A. General :

- The test is of 1 hour duration.
- The Test Booklet consists of 22 questions. The maximum marks are 66.

B. Question Paper Format

- Each part consists of five sections.
- Section-1 contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
- Section-2 contains 5 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
- Section-3 contains 6 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
- Section-4 contains 1 paragraphs each describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a particular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
- Section-5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

C. Marking Scheme

- For each question in Section-1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (– 1) mark will be awarded.
- For each question in Section-2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
- For each question in Section-3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

SECTION-1 : (Only One option correct Type)

This section contains 7 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

- 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+}
- The pair of the compounds in which both the metals are in the highest possible oxidation state is,
 (A) $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{CN})_6]^{3-}$ (B) CrO_2Cl_2 , MnO_4^-
 (C) TiO_2 , MnO_2 (D) $[\text{Co}(\text{CN})_6]^{3-}$, Mn_2O_7
- 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+}
- 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^0 value for the $\text{Mn}^{3+} / \text{Mn}^{2+}$ couple is much more positive than that for $\text{Cr}^{3+} / \text{Cr}^{2+}$ or $\text{Fe}^{3+} / \text{Fe}^{2+}$.
 (A) T T F T (B) T F F T (C) T F T T (D) F F T F



5. Identify the incorrect statement.
 (A) CuSO_4 reacts with KCl in aqueous solution to give Cu_2Cl_2 .
 (B) CuSO_4 reacts with KI in aqueous solution to give Cu_2I_2 .
 (C) CuSO_4 reacts with NaOH and glucose in aqueous medium to give Cu_2O .
 (D) CuSO_4 on strong heating gives CuO .
6. $\text{CuFeS}_2 + \text{O}_2$ (excess) $\xrightarrow{\Delta}$ $\text{X(s)} + \text{Y(s)}$
Note : Corresponding sulphates of copper and iron are formed respectively.
 Which is correct choice for (X) and (Y) ?
 (A) (X) liberates iodine from soluble iodides like KI
 (B) (Y) on heating liberates SO_3 only
 (C) (X) forms bluish white precipitate with sodium hydroxide which redissolves in excess of sodium hydroxide.
 (D) (Y) on reaction with potassium ferricyanide gives brown precipitate.
7. $\text{FeCr}_2\text{O}_4 + \text{Na}_2\text{CO}_3 + \text{O}_2 \xrightarrow{\text{Fusion}} [\text{X}] \xrightarrow[\text{H}_2\text{O}]{\text{H}^+} [\text{Y}] \xrightarrow[\text{H}_2\text{O}_2]{\text{H}^+} [\text{Z}]$
 Which of the following statement is true for the compounds [X], [Y] and [Z] ?
 (A) In all three compounds, the chromium is in + 6 oxidation state.
 (B) [Z] is a deep blue-violet coloured compound which decomposes rapidly in aqueous solution into Cr^{3+} and dioxygen.
 (C) Saturated solution of [Y] gives bright orange compound, chromic anhydride, with cold and concentrated H_2SO_4 .
 (D) All of these.

Section-2 : (One or More than one options correct Type)

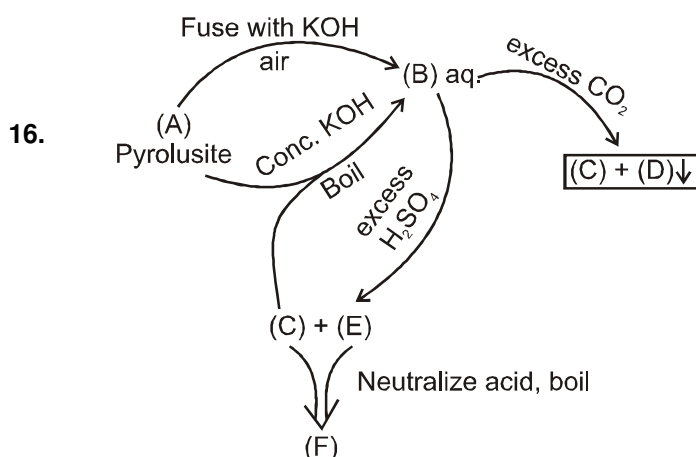
This section contains 5 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

8. 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 $\text{MnO} < \text{CrO} < \text{VO} < \text{TiO}$.
 (D) Vanadium(V) oxide does not react with acids but reacts with alkalis only.
9. Fenton's reagent is $\text{X} + \text{H}_2\text{O}_2$. 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) $\text{X} = \text{FeSO}_4$ (B) $\text{X} = \text{Fe}_2(\text{SO}_4)_3$ (C) $\text{Y} = (\text{NH}_4)_2\text{SO}_4$ (D) $\text{Z} = \text{FeSO}_4$
10. 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 .
11. 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 .
12. 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.

**Section-3 : (One Integer Value Correct Type.)**

This section contains 6 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

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 magnetic 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) $\text{CuSO}_4 + \text{NaOH}(\text{excess}) \longrightarrow$ (b) $\text{CuCl}_2 + \text{NH}_3(\text{excess}) \longrightarrow$
 (c) $\text{ZnSO}_4 + \text{NaOH}(\text{excess}) \longrightarrow$ (d) $\text{ZnSO}_4 + \text{NH}_3(\text{excess}) \longrightarrow$
 (e) $\text{FeSO}_4 + \text{NaOH}(\text{excess}) \xrightarrow[\text{air}]{\text{in air}}$ (f) $\text{FeCl}_3 + \text{NaOH}(\text{excess}) \longrightarrow$
 (g) $\text{CuSO}_4 + \text{KI}(\text{excess}) \longrightarrow$ (h) $\text{ZnSO}_4 + \text{NaHCO}_3 \longrightarrow$
 (i) $\text{CuCl}_2 + \text{NaNO}_3 \longrightarrow$



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 lanthanides 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 $\text{Ce}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$.
 (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 .

SECTION-4 : Comprehension Type (Only One options correct)

This section contains 1 paragraphs, each describing theory, experiments, data etc. 3 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

Paragraph for Questions 19 to 21

- (i) A powdered substance (A) on treatment with fusion mixture gives a green coloured compound (B).
 (ii) The solution of (B) in boiling water on acidification with dilute H_2SO_4 gives a pink coloured compound (C) and brown colour compound (D).
 (iii) The aqueous solution of (A) on treatment with NaOH and Br_2 -water gives the compound (D).



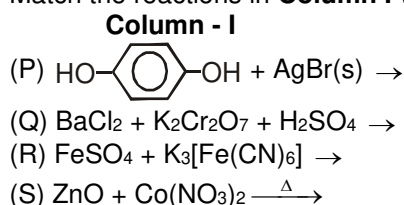
(iv) A solution of (D) in concentrated HNO_3 on treatment with lead peroxide at boiling temperature produced a compound (E) which was of the same colour at that of (C).
 (v) A solution of (A) on treatment with a solution of barium chloride gave a white precipitate of compound (F) which was insoluble in concentrated HNO_3 and concentrated HCl .

19. Which of the following is true for compound (C) ?
 (A) It oxidises ammonia to nitrogen dioxide in neutral medium.
 (B) It's pink colour is due to d-d transition.
 (C) It can be oxidised by ozone.
 (D) It is obtained by alkaline fusion of pyrolusite followed by electrolytic oxidation.
20. The oxidation state of central metal ions of (A), (B) and (C) compounds are respectively :
 (A) +II, +VI and +VII (B) +II, +VI and +VI (C) +II, +VII and +VII (D) +VI, +VII and +VII
21. Consider the following statements ;
 (I) anions of both (B) and (C) are diamagnetic and have tetrahedral geometry.
 (II) anions of both (B) and (C) are paramagnetic and have tetrahedral geometry.
 (III) anion of (B) is paramagnetic and that of (C) is diamagnetic but both have tetrahedral geometry.
 (IV) green coloured compound (B) in a neutral or acidic medium disproportionates to give (C) and (D).
 of these select the correct one from the codes given :
 (A) I and III only (B) II and III only (C) II and IV only (D) III and IV only

SECTION-5 : Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

22. Match the reactions in **Column I** with the types of products / the use of products in **Column II**.



Code :

	P	Q	R	S
(A)	1	3	2	4
(C)	4	3	1	2

- Column - II**
 (1) Turn bull's blue pigment
 (2) Rinmann's green pigment
 (3) Chromyl chloride test
 (4) Photography

	P	Q	R	S
(B)	3	2	4	1
(D)	4	1	2	3

Practice Test-2 ((IIT-JEE (ADVANCED Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22								
Ans.										



APSP Answers

PART - I

1.	(1)	2.	(2)	3.	(1)	4.	(1)	5.	(4)
6.	(3)	7.	(2)	8.	(2)	9.	(3)	10.	(4)
11.	(2)	12.	(4)	13.	(4)	14.	(4)	15.	(2)
16.	(2)	17.	(4)	18.	(1)	19.	(1)	20.	(2)
21.	(3)	22.	(3)	23.	(4)	24.	(4)	25.	(4)
26.	(4)	27.	(4)	28.	(4)	29.	(1)	30.	(1)

PART - II

1.	(C)	2.	(C)	3.	(A)	4.	(C)	5.	(B)
6.	(B)	7.	(B)	8.	(D)	9.	(D)	10.	(D)
11.	(C)	12.	(A)	13.	(C)	14.	(D)	15.	(A)
16.	(C)	17.	(C)	18.	(B)	19.	(B)	20.	(D)
21.	(D)	22.	(B)	23.	(B)	24.	(A)	25.	(C)
26.	(C)	27.	(C)	28.	(B)	29.	(A)	30.	(A)
31.	(C)	32.	(B)	33.	(C)	34.	(B)	35.	(C)

PART - III

- This is because Pt^{4+} is more stable than Ni^{4+} as the sum of four ionisation energies of Pt is less than those of Ni.
- When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher. It is said to undergo disproportionation,
e.g., $3\text{Mn}^{\text{VI}}\text{O}_4^{2-} + 4\text{H}^+ \longrightarrow 2\text{Mn}^{\text{VII}}\text{O}_4^- + \text{Mn}^{\text{IV}}\text{O}_2 + 2\text{H}_2\text{O}$
Mn (VI) is unstable relative to Mn (VII) and Mn (IV).
- Because most of the transition metals have negative oxidation potential and lie above hydrogen in electrochemical series.
- Mn^{2+} has maximum number of unpaired electrons i.e. $3d^5$.
- The transition metals form reaction intermediates due to the presence of vacant orbitals or their tendency to form variable oxidation states. These intermediates give reaction paths of lower activation energy and, therefore, increase the rate of the reaction. These reaction intermediates readily decompose yielding the products and regenerating the original substance.
- Transition metals form a large number of alloys. The transition metals are quite similar in size and, therefore, the atoms of one metal can substitute the atoms of other metal in its crystal lattice. Thus, on cooling a mixture solution of two or more transition metals, solid alloys are formed.
- (i) $\text{CuSO}_4 + 4\text{NH}_4\text{OH} \longrightarrow [\text{Cu}(\text{NH}_3)_4] \text{SO}_4$ (blue colour complex) + $4\text{H}_2\text{O}$
(ii) $\text{CuSO}_4 + 2\text{KI} \longrightarrow \text{CuI}_2 + \text{K}_2\text{SO}_4$
 $2\text{CuI}_2 \longrightarrow \text{Cu}_2\text{I}_2$ (white) + I_2 (violet vapours)
- White precipitate of $\text{Ag}_2\text{S}_2\text{O}_3$ is obtained which turns yellow, brown and finally black on keeping.
 $2\text{AgNO}_3 + \text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Ag}_2\text{S}_2\text{O}_3 \downarrow$ (white) + 2NaNO_3
 $\text{Ag}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \longrightarrow \text{Ag}_2\text{S} \downarrow$ (black) + H_2SO_4
- $3\text{Ag} + 4\text{HNO}_3 \longrightarrow 3\text{AgNO}_3 + \text{NO} + 2\text{H}_2\text{O}$



10. (a) $3\text{FeSO}_4 + 2\text{K}_3[\text{Fe}(\text{CN})_6] \longrightarrow \text{Fe}_3[\text{Fe}(\text{CN})_6]_2 + 3\text{K}_2\text{SO}_4$
 (b) $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{CO}_3 \longrightarrow 2\text{NaFeO}_2 + \text{CO}_2$
 (c) $\text{Fe(III)} + 3\text{NH}_4\text{SCN} \longrightarrow [\text{Fe}(\text{SCN})_3] + 3\text{NH}_4^+$
 (d) $\text{ZnO} + \text{CoO} \longrightarrow \text{CoZnO}_2$ (Rinmann's green)
11. (C) 12. (D) 13. (C) 14. (A) 15. (C)
 16. (D) 17. (C) 18. (B) 19. (B) 20. (C)
 21. (B) 22. (C) 23. (A) 24. (A) 25. (D)
 26. (D) 27. (B) 28. (A) 29. (D) 30. (C)
 31. 6 32. 4 (I, II, III, IV) 33. 4 34. 8 35. 11
 36. (ACD) 37. (ABD) 38. (ABCD) 39. (AD) 40. (ABC)

PART - IV

1. (D) 2. (B) 3. (A) 4. (B) 5. (A)
 6. (A) 7. (D) 8. (AB) 9. (AC) 10. (ABC)
 11. (BCD) 12. (BD) 13. 4 14. 2 15. 3
 16. 3 17. 9 18. 6 19. (D) 20. (A)
 21. (D) 22. (C)

APSP Solutions

PART - I

1. (1) Electron configuration of V is $[\text{Ar}] 3d^3 4s^2$ and thus maximum 5 electrons participate in bonding.
 (2) Electron configuration of Cr is $[\text{Ar}] 3d^5 4s^1$ and thus maximum 6 electrons participate in bonding.
 (3) Electron configuration of Co is $[\text{Ar}] 3d^7 4s^2$. In octahedral splitting in presence of ligands, half filled t_{2g}^6 has higher CFSE and thus +3 oxidation state is most stable.
 (4) Electron configuration of Sc is $[\text{Ar}] 3d^1 4s^2$ 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 $\text{Mn}_2\text{O}_7 > \text{MnO}_2 > \text{Mn}_2\text{O}_3 > \text{MnO}$.
3. First ionisation energies of 3d-series (first transition series) increase with increase in atomic number due to (1) increase in nuclear charge (2) decrease in atomic size.
4. (i) Valence shell electron configuration of Ti^{4+} is $3d^0 4s^0$. 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. (1) Valence shell electron configuration of Co^{3+} is $3d^6 4s^0$. So has 4 unpaired electrons.
 (2) Valence shell electron configuration of Fe^{3+} is $3d^5 4s^0$. So has 5 unpaired electrons.
 (3) Valence shell electron configuration of Cr^{2+} is $3d^4 4s^0$. So has 4 unpaired electrons.
 (4) 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. (1) 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.
 (2) Highest oxidation state of Cr in CrO_2Cl_2 is +6 and highest oxidation state of Mn in MnO_4^- is +7.
 (3) 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.
 (4) 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.
9. (3) 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 $\text{Fe}(\text{OH})_3$.

$$\text{FeCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 \text{ (Brown)} + 3\text{HCl}$$
11. $\text{Zn} + 2\text{NaOH} \longrightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2$
12. $2\text{Cu}(\text{hot}) + \text{O}_2(\text{g}) \rightarrow 2\text{CuO}$.
13. It is a white powder which becomes yellow on heating due to change in the structure of lattice (due to cation excess defect) but again turns white on cooling.
14. $2\text{FeCl}_3 \longrightarrow \begin{array}{c} \text{Cl} \quad \quad \text{Cl} \\ \diagdown \quad \diagup \\ \text{Fe} \quad \text{Fe} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \quad \text{Cl} \end{array} \text{ (gas)}$
15. SO_2 and SO_3
 $\text{FeSO}_4 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + \text{SO}_2\uparrow + \text{SO}_3\uparrow + \text{O}_2\uparrow$
 The acidic gases produced are SO_2 and SO_3
16. $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O} \xrightarrow{\Delta} \text{Zn}(\text{OH})\text{Cl} + \text{HCl} + \text{H}_2\text{O}$.
17. $2\text{KMnO}_4 \xrightarrow{750\text{K}} \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$.
18. $\text{MnO}_4^- + 3\text{e}^- + 2\text{H}_2\text{O} \longrightarrow \text{MnO}_2 + 4\text{OH}^-$ (neutral / weak alkaline medium)
19. $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow 2\text{KHSO}_4 + (\text{MnO}_3)_2\text{SO}_4 + 2\text{H}_2\text{O}$
 $(\text{MnO}_3)_2\text{SO}_4 + \text{H}_2\text{O} \longrightarrow \text{Mn}_2\text{O}_7 + \text{H}_2\text{SO}_4$
 $\text{Mn}_2\text{O}_7 \xrightarrow{\Delta} 2\text{MnO}_2 + \frac{3}{2}\text{O}_2$
20. (1) $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{I}^- \longrightarrow 2\text{Cr}^{3+} + 3\text{I}_2 + 7\text{H}_2\text{O}$.
 (2) In acidic solution, actually chromate is converted to dichromate.
 $2\text{CrO}_4^{2-} + 2\text{H}^+ \longrightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$.
 (3) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{N}_2 + 4\text{H}_2\text{O} + \text{Cr}_2\text{O}_3$.
 (4) $6\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \longrightarrow 6\text{Fe}^{3+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$.
21. Quinol developer (a reducing agent) reduces AgBr to Ag .
 $2\text{AgBr}^*(\text{s}) + 2\text{OH}^-(\text{aq}) + \text{C}_6\text{H}_5(\text{OH})_2(\text{aq}) \longrightarrow 2\text{Ag}(\text{s}) + 2\text{H}_2\text{O} + \text{C}_6\text{H}_4\text{O}_2(\text{aq}) + 2\text{Br}^-(\text{aq})$
 Where AgBr^* represents a molecules of AgBr exposed to light.
22. $\text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{CO}_3 \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}$; $\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}$ (orange red) + H_2O
23. In FeO_4^{2-} , Fe is in very high oxidation state (+6) and hence unstable, so it gets reduced to Fe^{3+} liberating O_2 . CrO_4^{2-} in acidic medium converted to $\text{Cr}_2\text{O}_7^{2-}$.



24. $\text{AgCl} \xrightarrow{h\nu} \text{Ag}\downarrow + 1/2 \text{Cl}_2$
(black)
If source of light is removed, we get back Ag and blackness due to Ag removed.
25. $\text{Ag} + \text{dilute HNO}_3 \rightarrow \text{AgNO}_3 + \text{NO (g)}$
 $\text{Ag} + \text{conc. HNO}_3 \rightarrow \text{AgNO}_3 + \text{NO}_2 \text{ (g)}$
 $\text{Ag} + \text{conc. H}_2\text{SO}_4 \rightarrow \text{Ag}_2\text{SO}_4 + \text{SO}_2 \text{ (g)}$
26. $2\text{K}_2\text{MnO}_4 + \text{Cl}_2 \rightarrow 2\text{KMnO}_4 + 2\text{KCl}$; $2\text{K}_2\text{MnO}_4 + \text{H}_2\text{O} + \text{O}_3 \rightarrow 2\text{KMnO}_4 + 2\text{KOH} + \text{O}_2$
 $3\text{K}_2\text{MnO}_4 + 2\text{CO}_2 \rightarrow 2\text{KMnO}_4 + \text{MnO}_2 + 2\text{K}_2\text{CO}_3$
27. Aqueous solution of CuSO_4 is acidic in nature, it converts some CuCrO_4 to CuCr_2O_7 .
28. In Co^{3+} ion, electronic configuration $[\text{Ar}]_{18} 3d^6 4s^0$. For octahedral complex 4 unpaired electrons get paired and in configuration become $t_{2g}^6 e_g^0$ and hybridization d^2sp^3 .
Os has maximum VIII oxidation state.
29. After uranium all elements are transuranic elements.

PART - III

12. The atomic radii of the transition metals lie in-between those of s- and p-block elements. In the beginning, the atomic radius decreases with the increase in nuclear charge (as atomic number increases), whereas the shielding effect of d-electrons is small and orbital electrons are added to the penultimate d-subshell rather than to the outer shell of the atom.
13. The lesser number of oxidation states in the beginning of series can be due to the presence of smaller number of electrons to lose or share (Sc, Ti). On the other hand, at the extreme right hand side end (Cu, Zn), lesser number of oxidation state is due to large number of d electrons so that only a few orbitals are available in which the electron can share with other for higher valence.
14. $\text{Cr}^{3+} + e^- \rightarrow \text{Cr}^{2+}$, $E^\ominus = -0.41$ volts and $\text{Mn}^{3+} + e^- \rightarrow \text{Mn}^{2+}$, $E^\ominus = +1.51$ volts
This shows that Cr^{2+} is unstable and has a tendency to acquire more stable Cr^{3+} state by acting as a reducing agent. On the other hand Mn^{3+} is unstable and is reduced to more stable Mn^{2+} state.
15. $3.87 = \sqrt{n(n+2)}$; n = number of unpaired electrons. So $n = 3$.
16. In Ti^{4+} , Cu^+ and Zn^{2+} , all have electrons paired so all are diamagnetic. Cr^{3+} with electron configuration $[\text{Ar}]_{18} 3d^3$ has three unpaired electrons. So it undergoes d-d transition of electrons in presence of ligands according to CFT and thus it is coloured.
17. Cu^{2+} ion ($3d^9$) absorbs red light from the visible region, for the promotion of 3d electrons, the ions reflect blue light and appear blue.
18. $5\text{AgNO}_3 + 3\text{I}_2 \text{ (excess)} + 3\text{H}_2\text{O} \rightarrow \text{HIO}_3 + 5\text{AgI} + 5\text{HNO}_3$.
19. $\text{Fe}^{3+} + [\text{Fe}(\text{CN})_6]^{4-} \rightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ (prussian blue)
20. Hydrated FeCl_3 exists as $[\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$; it is factual.
21. (A) V^{2+} violet (B) V^{3+} green
(C) VO^{2+} blue (D) VO_2^+ yellow
23. $2\text{CuCl}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{CuCl} + 2\text{HCl} + \text{H}_2\text{SO}_4$.
24. German silver contains Cu = 60% ; Zn = 20% ; and Ni = 20%.
25. $\text{Cu} + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$.
Green crust of basic copper carbonate is formed.
26. Dissolves in both ether and water forming solvated/ hydrated monomeric species,

$$\begin{array}{ccc} \text{C}_2\text{H}_5 & & \\ & \diagup & \\ & \text{O} & \longrightarrow \text{FeCl}_3 \\ & \diagdown & \\ \text{C}_2\text{H}_5 & & \end{array}$$
solvated FeCl_3

$$[\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$$
hydrated FeCl_3





PART - IV

- ${}_{22}\text{Ti} = 3d^2 4s^2$, $\text{Ti}^{2+} = 3d^2$; ${}_{23}\text{V} = 3d^3 4s^2$, $\text{V}^{3+} = 3d^2$.
 ${}_{24}\text{Cr} = 3d^5 4s^1$, $\text{Cr}^{4+} = 3d^2$; ${}_{25}\text{Mn} = 3d^5 4s^2$, $\text{Mn}^{5+} = 3d^2$.
- (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.
- It is an amphoteric in nature and it reacts with alkalies as well as with acids to give $\text{V}_4\text{O}_9^{2-}$ and VO_2^+ respectively.
- S₁** : It is because Mn^{2+} has $3d^5$ configuration which has extra stability.
S₂ : Not titanium but Copper, because with +1 oxidation state an extra stable configuration, $3d^{10}$ results.
S₃ : It is not stable as it undergoes disproportionation ; $2\text{Cu}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{Cu}(\text{s})$. The E° value for this is favourable.
S₄ : Much larger third ionisation energy of Mn (where the required change is d^5 to d^4) is mainly responsible for this.
- (A) CuSO_4 reacts with KI to give Cu_2I_2 (white precipitate) but not with KCl.
 (B) $2\text{Cu}^{2+} + 4\text{I}^- \longrightarrow \text{Cu}_2\text{I}_2 + \text{I}_2\uparrow$.
 (C) Fehling's solution mainly contains CuSO_4 and NaOH. When warmed with glucose (with – CHO group) gives red precipitate of Cu_2O . Glucose reduces the Cu^{2+} to Cu_2O (red).
 (D) CuSO_4 on heating gives CuO.

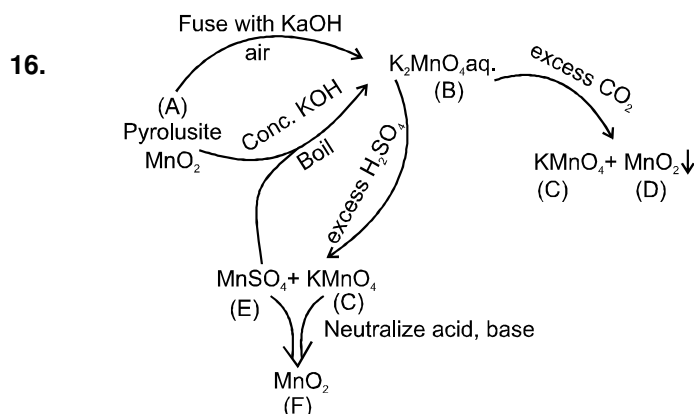
$$\text{CuSO}_4 \xrightarrow{1000\text{K}} \text{CuO} + \text{SO}_2 + \frac{1}{2} \text{O}_2.$$
- $\text{CuFeS}_2 + 4\text{O}_2 \xrightarrow{\Delta} \text{CuSO}_4 (\text{s}) + \text{FeSO}_4 (\text{s})$
 (A) $\text{CuSO}_4 + 4\text{KI} \longrightarrow \text{Cu}_2\text{I}_2 + \text{I}_2 + 2\text{K}_2\text{SO}_4$
 (B) $2\text{FeSO}_4 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$
 (C) $\text{CuSO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + \text{Cu}(\text{OH})_2\downarrow$ (insoluble in excess NaOH)
 (D) $\text{Fe}^{2+} + 2\text{K}_3[\text{Fe}(\text{CN})_6] \longrightarrow \text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ (deep blue)
- $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \xrightarrow{\text{Fusion}} \text{Na}_2\text{CrO}_4 \xrightarrow[\text{H}_2\text{O}]{\text{H}^+} \text{Na}_2\text{Cr}_2\text{O}_7 \xrightarrow[\text{H}_2\text{O}_2]{\text{H}^+} \text{CrO}(\text{O}_2)_2$ (deep blue
 violet) $\xrightarrow{\text{H}_2\text{O}} \text{O}_2 + \text{H}_2\text{O} + \text{Cr}^{3+}$. (X) (Y) (Z)
 $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow 2\text{CrO}_3$ (bright orange/red- chromic anhydride) + $\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$.
- (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 $\text{TiO} < \text{VO} < \text{CrO} < \text{MnO}$.
 (D) V_2O_5 reacts with alkalies as well as acids to give VO_4^{3-} and VO_2^+ respectively.
- Fenton's reagent is $\text{FeSO}_4 + \text{H}_2\text{O}$
 $\text{FeSO}_4 + (\text{NH}_4)_2\text{SO}_4 + 6\text{H}_2\text{O} \longrightarrow \text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
 (Y)
 $\text{FeS}_2 + \text{O}_2 + \text{H}_2\text{O} \longrightarrow \text{FeSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4$
 (Z)
 $\text{FeSO}_4 + \text{KMnO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{MnSO}_4 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$
 (X) (Z).



10. (A) $2\text{CuSO}_4 + 2\text{NaCl} + 2\text{H}_2\text{O} + \text{SO}_2 \longrightarrow \text{Cu}_2\text{Cl}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$
 (B) $\text{Cu} + \text{HCl} + [\text{O}] \longrightarrow \text{CuCl}_2 + \text{H}_2\text{O}$; $\text{CuCl}_2 + \text{Cu} \longrightarrow \text{Cu}_2\text{Cl}_2$
 (C) $\text{CuSO}_4 + 2\text{HCl} \longrightarrow \text{CuCl}_2 + \text{H}_2\text{SO}_4$; $\text{CuCl}_2 + \text{Cu} \longrightarrow \text{Cu}_2\text{Cl}_2$
 (D) $\text{CuO} + 2\text{HCl} \longrightarrow \text{CuCl}_2 + \text{H}_2\text{O}$; Cu_2Cl_2 is not formed.
11. (A) $5\text{HCHO} + \text{MnO}_4^- + 6\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 5\text{HCOOH} + 3\text{H}_2\text{O}$.
 (B) $4\text{KOH} + 2\text{MnO}_2$ (manganese dioxide) + $\text{O}_2 \rightarrow 2\text{K}_2\text{MnO}_4$ (potassium manganate) + $2\text{H}_2\text{O}$.
 (C) $\text{Mn}(\text{OH})_2 + \text{O}_2^{2-} \rightarrow \text{MnO}_4^{2-}$ (manganate) + 2OH^- .
 (D) $2\text{KMnO}_4 \xrightarrow{750\text{K}} \text{K}_2\text{MnO}_4$ (potassium manganate) + $\text{MnO}_2 + \text{O}_2$.
12. (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 $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, so it can not be weighed correctly for the preparation of standard solution.
 (C) $2\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} 2\text{K}_2\text{CrO}_4 + \text{Cr}_2\text{O}_3$ (green) + $3/2 \text{O}_2$.
 (D) $4\text{KMnO}_4 + 4\text{KOH} \xrightarrow{\Delta} 4\text{K}_2\text{MnO}_4$ (green) + $2\text{H}_2\text{O} + \text{O}_2$
13.

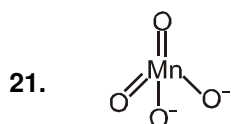
*NO ₂	Coloured & Paramagnetic
Cu ⁺¹	Colourless
*O ₂	Paramagnetic
O ₃	Diamagnetic
Hg ₂ ⁺²	Colourless
Cd ⁺²	Colourless
*Al	Paramagnetic
*C(graphite)	Paramagnetic
Sc ⁺³	Colourless or diamagnetic
14.

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) $\text{Cu}(\text{OH})_2 \downarrow$ (blue) (b) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ (aq.)
 (c) $\text{Na}_2[\text{Zn}(\text{OH})_4]$ (aq.) (d) $[\text{Zn}(\text{NH}_3)_4]^{2+}$ (aq.)
 (e) $\text{Fe}(\text{OH})_2 \downarrow$ (greenish) (f) $\text{Fe}(\text{OH})_3 \downarrow$ (reddish brown)
 (g) CuI (white) (h) $\text{ZnCO}_3 \downarrow$ (white)
 (i) $\text{Cu}(\text{NO}_3)_2 \downarrow$ (aq.)





17. Paramagnetic – 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), HgS (black), AgF (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 basicity decreases from $\text{Ce}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$ becomes of f-block rule.
 (6) Correct
 (7) Correct
 (8) All lanthanides have –ve S.R.P. hence all releases hydrogen.
19. (A) $2\text{MnO}_4^- + 2\text{NH}_3 \longrightarrow 2\text{MnO}_2 + \text{N}_2 + 2\text{OH}^- + 2\text{H}_2\text{O}$
 (B) It is due to charge transfer from O^{2-} to empty d-orbital of Mn(VII).
 (C) MnO_4^- is in highest oxidation state i.e. +VII and thus can not be oxidised further.
 (D) $\text{MnO}_2 + \text{OH}^- \longrightarrow \text{MnO}_2^{2-} \xrightarrow{[\text{e}^-]} \text{MnO}_4^-$
20. (A) In MnSO_4 , = +II ; (B) MnO_4^{2-} = +VI ; (C) MnO_4^- = +VII



(III) Electron configuration of Mn(VI) in MnO_4^{2-} is $[\text{Ar}]^{18} 3d^1$. So it is paramagnetic and tetrahedral. Electron configuration of Mn(VII) in MnO_4^- is $[\text{Ar}]^{18} 3d^0$. So it is diamagnetic and tetrahedral.

(IV) $3\text{MnO}_4^{2-} + 4\text{H}^+ \longrightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$.

(Solution : 19 to 21)

A = MnSO_4 , B = K_2MnO_4 , C = KMnO_4 , D = MnO_2 , E = HMnO_4 , F = BaSO_4 .

$\text{MnSO}_4(\text{A}) + 2\text{KNO}_3 + \text{K}_2\text{CO}_3 \longrightarrow \text{K}_2\text{MnO}_4(\text{B}) + 2\text{KNO}_2 + 2\text{CO}_2 + \text{K}_2\text{SO}_4$

$2\text{MnO}_4^{2-} + 4\text{H}^+ \longrightarrow \text{MnO}_4^- (\text{C}) + \text{MnO}_2 + 2\text{H}_2\text{O}$.

$\text{Mn}^{2+} + 2\text{OH}^- \longrightarrow \text{Mn}(\text{OH})_2 \downarrow$; $\text{Mn}(\text{OH})_2 + \text{Br}_2 + 2\text{NaOH} \longrightarrow \text{MnO}_2(\text{D}) + 2\text{NaBr} + 2\text{H}_2\text{O}$

$\text{MnO}_2 + 4\text{HNO}_3 \longrightarrow 2\text{Mn}(\text{NO}_3)_2 + 2\text{H}_2\text{O} + \text{O}_2$

$\text{Mn}(\text{NO}_3)_2 + 5\text{PbO}_2 + 6\text{HNO}_3 \longrightarrow 2\text{HMnO}_4(\text{E}) + 5\text{Pb}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$

$\text{SO}_4^{2-} + \text{Ba}^{2+} \longrightarrow \text{BaSO}_4 \downarrow (\text{white}) (\text{F})$

22. (P) $\text{HO}-\text{C}_6\text{H}_4-\text{OH} + 2\text{AgBr}(\text{s}) \longrightarrow \text{O}=\text{C}_6\text{H}_4=\text{O} + 2\text{HBr} + 2\text{Ag}(\text{black silver particles})$

Hydroquinone acts as developer

(Q) $\text{BaCl}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + 3\text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{CrO}_2\text{Cl}_2 + 2\text{BaSO}_4 + 3\text{H}_2\text{O}$

(R) $\text{FeSO}_4 + \text{K}_3[\text{Fe}(\text{CN})_6] \longrightarrow \text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6] + \text{K}_2\text{SO}_4$

(S) $\text{Co}(\text{NO}_3)_2 + \text{ZnO} \xrightarrow{\Delta} \text{CoZnO}_2 \text{ or } \text{CoO} \cdot \text{ZnO}$