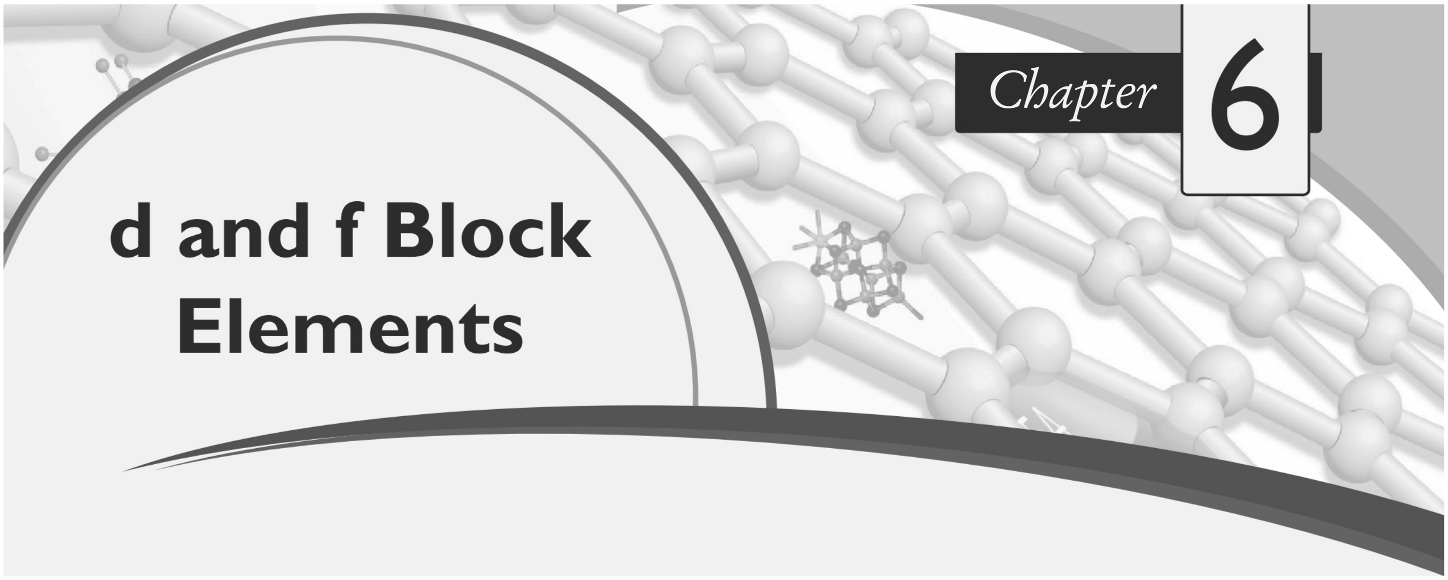
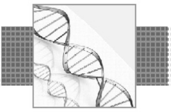


Chapter 6

d and f Block Elements

Key Concepts



TRANSITION ELEMENTS

- The elements lying in the middle of the periodic table between group 2 and group 13 are known as d-block elements.
- These d-block elements are called transition elements because they exhibit transitional behaviour between s-block and p-block elements.
- Depending upon the subshell (3d, 4d, 5d) involved, transition elements are mainly classified into three series.
  1. First transition series or 3d series.
  2. Second transition series or 4d series.
  3. Third transition series or 5d series.

Outer electronic configuration of the transition elements

3d-series or I transition series:-

Atomic number	21	22	23	24	25	26	27	28	29	30
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

4d-series or II transition series:-

Atomic number	39	40	41	42	43	44	45	46	47	48
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

5d-series or III transition series:-

Atomic number	57	72	73	74	75	76	77	78	79	80
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

Properties of transition elements

1. **Metallic character:-** All the transition elements are metallic in nature and nearly all of them have simple hcp, ccp or bcc lattices. Due to their greater effective nuclear charge and the large number of valence electrons, the metallic bond is quite strong and hence they are hard, posses high densities and high enthalpies of atomization.
2. **Oxidation states:-** Transition elements exhibit variable oxidation state due to the participation of ns as well as (n –1) d electrons.

   Except scadium, the most common oxidation state of the first row (3d series) elements is +2 which arises from the loss of two 4s electrons, which means that after scandium, d-orbital become stable than s-orbital.

   In the +2 and +3 oxidation states, bond formed are generally ionic while in higher oxidation states the bond formed are essentially convalent. For example in MnO_4^-, CrO_4^{2-}, etc. the bond formed between metal and oxygen are covalent.

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

Oxidation states of the first row of transition metals (the most common ones are in circles)

3. **Complex formation (complexation):-** Transition metal ions form variety of complex due to the following reasons:
   (i) Small size and high nuclear charge
   (ii) Availability of vacant d-orbital of suitable energy, which can accept lone pair of electrons donated by the molecule or ion (ligand).
4. **Magnetic Properties:-** Two types of magnetic behaviour are found in substances diamagnetism and paramagnetism. Paramagnetic substances are attracted by the magnetic field and weigh more while the diamagnetic substances are slightly repelled by the magnetic field and weight less.

   As the transition metal ions generally contain one or more unpaired electrons in them and hence their complexes are generally paramagnetic. Paramagnetic character increases with increase in number of unpaired electrons. Paramagnetism is expressed in terms of magnetic moment.

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

   n – number of unpaired electrons

   More the magnetic moment, more will be the paramagnetic character.
5. **Formation of Alloys:-** As the transition elements have similar atomic sizes hence in the crystal lattice, one metal can be readily replaced by another metal giving solid solution and smooth alloys. The alloys so formed are hard and have often high melting point.
6. **Interstitial compound:-** Transition metal form number of interstitial compounds, in which they take up atoms of small size, e.g., H, C and N in the vacant spaces in the their lattices. The presence of these atoms results in decrease in ductility and malleability of the metals but increases their tensile strength.
7. **Catalytic properties:-** Transition metals and their compounds are known to act as a good catalyst due to the following reasons:
   (i) Due to their variable oxidation state, they form unstable intermediate compounds and provide a new path with lower activation energy for the reaction (intermediate compound formation theory).
   (ii) In some cases the finely divided metal or their compounds provide a large surface area for adsorption and the adsorbed reactants react faster due to the closer contact (Adsorption theory).
8. **Ionization energy:-** The ionization energies of transition elements are higher than those of S-block elements but lower than p-block elements.
   - In a particular transition series, ionization energy increases gradully as we move from left to right, and it is due to the increase in nuclear charge.
   - Further the magnitudes of ionization energies provide an indication of the energy needed to raise the metal to a particular oxidation state in a compound. From the knowledge of values of ionization energies of the metal it is possible to rationalize the relative stabilities of various oxidation state.
   - Ni(II) compounds are thermodynamically more stable than Pt(II) compounds, on the other hand Pt(IV) compounds are more stable than Ni(IV) compounds. It is due to that sum of first four ionization energies is less for platinum whereas sum of the first two ionization energies is less for nickel.
9. **Coloured compounds:-** Compounds of transition elements are usually coloured due to the promotion of an electron from one d-orbital to another by the absorption of visible light. It can be clearly explained as follows:

   In the transition elements which have partly filled d-orbitals, the transition of electron can take from one of the lower d-orbitals to some higher d-orbital within the same subshell. The energy required for this transition falls in the visible region. So when white light falls on these complexes they absorb a particular colour from the radiation for the promotion of electron and the remaining colours are emitted. The colour of the complex is due to this emitted radiation.

   A few of the transition metal ions such as Cu^+, Ag^+, Sc^{3+} are colourlesss. In these ions, the d-orbital are either completely filled or empty.

Oxides, chlorides and sulphates of Iron, copper and Zinc

(A) Ferric Oxide, Fe_2O_3

Preparation:

1. In lab, it can be prepared by heating ferrous sulphate or ferric hydroxide.

$$2\,FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2\uparrow + SO_3\uparrow$$

$$2Fe\,(OH)_3 \xrightarrow{\Delta} Fe_2O_3 + 3H_2O$$

$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3\uparrow$$

2. $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

$$4FeS + 7O_2 \longrightarrow 2Fe_2O_3 + 4SO_2$$

3. Hydrolysis of $FeCl_3$ actually gives a red-brown gelatinous precipitute of the hydrous oxide $Fe_2O_3(H_2O)_n$ which on heating at 200°C gives red-brown Fe_2O_3 (which occurs as the mineral haematite).

Properties:

1. It is reddish brown powder, insoluble in water but soluble in acid. Amphoteric in nature and reacts with acids and alkalies.

$$Fe_2O_3 + 6HCl \longrightarrow 2\,FeCl_3 + 3H_2O$$

$$Fe_2O_3 + Na_2CO_3 \longrightarrow \underset{\text{Sodium ferrite}}{2NaFeO_2} + CO_2$$

$$Fe_2O_3 + 2NaOH \longrightarrow 2NaFeO_2 + H_2O$$

2. It liberates oxygen at 1300° C.

$$6Fe_2\,O_3 \xrightarrow{1300°C} 4Fe_3O_4 + O_2$$

3. It is reduced to Fe as:

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

$$Fe_2O_3 + 3H_2 \longrightarrow 2Fe + 3H_2O$$

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

(B) Zinc Oxide (ZnO)

Preparation:

1. It is prepared by burning zinc metal in air or by heating the zinc carbonate, zinc nitrate or zinc hydroxide.

$$2Zn + O_2 \longrightarrow 2ZnO$$

$$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$$

$$2Zn(NO_3)_2 \xrightarrow{\Delta} 2ZnO + 4NO_2 + O_2$$

$$Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O$$

2. $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$

Properties:

1. It is a white, light powder insoluble in water and known as philospher's wool. On heating it becomes yellow and on cooling it becomes white (this is due to change in the structure of lattice).
2. It is reduced to Zn by the reaction of charcoal or dry H_2.

$$ZnO + H_2 \longrightarrow Zn + H_2O$$

$$ZnO + C \longrightarrow Zn + CO$$

3. It dissolves readily in mineral acids forms the corresponding salts and with alkalies, it forms zincates $[Zn\,(OH)_4]^{2-}$ or ZnO_2^{2-}.

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

$$ZnO + 2NaOH + H_2O \longrightarrow Na_2\,[Zn(OH)_4]$$

$$ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$$

(C) Ferric chloride ($FeCl_3$)

Preparation:

1. Anhydrous ferric chloride is obtained by passing dry chlorine gas over heated iron filling

$$2Fe + 3Cl_2 \xrightarrow{\Delta} Fe_2Cl_6 \text{ or } 2FeCl_3$$

(anhydrous)

2. Hydrated $FeCl_3.6H_2O$ can be prepared by dissolving iron in aqua regia or iron oxide in hydrochloride acid then the crystallization of the solution.

$$2Fe + 4HCl + Cl_2 \longrightarrow 2FeCl_3 + 2H_2$$

$$Fe_2O_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$$

Properties:

1. Anhydrous $FeCl_3$ is deep red-black flaky crystals but hydrated $FeCl_3.6H_2O$ is yellowish brown, deliquescent solid, soluble in water, alcohol and ether.
2. It dissociates on heating above 973 K first into $FeCl_3$ and then into $FeCl_2$ and Cl_2

$$Fe_2Cl_6 \xrightarrow{973\,K} FeCl_3 \xrightarrow{\Delta} FeCl_2 + Cl_2\uparrow$$

3. Its aqueous solution is acidic in nature due to hydrolysis.

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$$

4. Fe^{3+} solution gives deep blue ppt. of Prussian blue with $K_4[Fe(CN)_6]$, potassium ferrocyanide:

$$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

$$FeCl_3 + K_4[Fe(CN)_6] \longrightarrow KFe[Fe(CN)_6] + 3KCl$$

5. $2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$ (oxidizing)
6. Fe^{3+} solution gives blood red colour with SCN^- ions:

$$Fe^{3+} + SCN^- \longrightarrow [Fe(SCN)]^{2+}$$

(D) Zinc Chloride, ($ZnCl_2.2H_2O$)

Preparation:

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

$$ZnCO_3 + 2HCl \longrightarrow ZnCl_2 + CO_2 + H_2O$$
$$Zn(OH)_2 + 2HCl \longrightarrow ZnCl_2 + 2H_2O$$

The solution on concentration and cooling give hydrated zinc chloride crystals $ZnCl_2.2H_2O$.

2. Anhydrous $ZnCl_2$ is obtained by heating zinc in the atmosphere of dry Cl_2 or Dry HCl gas.

$$Zn + Cl_2 \longrightarrow ZnCl_2$$
$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

3. Anhydrous $ZnCl_2$ can also be formed by distilling zinc powder with mercuric chloride.

$$Zn + HgCl_2 \longrightarrow ZnCl_2 + Hg$$

Properties:

1. Anhydrous zinc chloride is white solid, deliquescent and soluble in water. It melts at 660° and boils at 730°C.
2. Hydrated $ZnCl_2$ on heating from zinc hydroxychloride or zinc oxychloride.

$$ZnCl_2.2H_2O \longrightarrow Zn(OH)\,Cl + HCl + H_2O$$
$$2ZnCl_2.2H_2O \longrightarrow \underset{\text{Zinc oxychloride}}{Zn_2OCl_2} + 2HCl + 3H_2O$$

3. $4ZnCl_2 + 4Na_2CO_3 + 3H_2O \longrightarrow ZnCO_3.3Zn(OH)_2 + 8NaCl + 3CO_2$

$$ZnCl_2 + 2NaHCO_3 \longrightarrow ZnCO_3 + 2NaCl + H_2O + CO_2$$

4. $ZnCl_2 + 4NH_3 \longrightarrow ZnCl_2.4NH_3$

(E) Ferrous sulphate ($FeSO_4.7H_2O$) or green vitriol

Preparation:

1. It is prepared by the action of dil. H_2SO_4 on iron.

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

This should be mode in a reducing atmosphere in order to prevent the oxidation of Fe^{2+} into Fe^{3+}.

2. $FeCO_3 + H_2SO_4 \longrightarrow FeSO_4 + H_2O + CO_2$
3. $FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$ (kipp's apparatus)

Properties:

1. It is pale green crystalline solid, soluble in water. It turns brown due to oxidation into the ferric compound by atmospheric oxygen.
2. It is an effloresccent substance, and in isomorphous with Epson salt ($MgSO_4.7H_2O$) and white vitriol ($ZnSO_4.7H_2O$).
3. On heating, green $FeSO_4$ $7H_2O$ gives a white anhydrous salt. On strong heating it forms Fe_2O_3, SO_2 and SO_3.

$$FeSO_4.7H_2O \xrightarrow{\Delta} \underset{\text{White}}{FeSO_4} + 7H_2O$$
$$2FeSO_4 \xrightarrow{\Delta} \underset{\text{Brown}}{Fe_2O_3} + SO_2\uparrow + SO_3\uparrow$$

4. $FeSO_4 + (NH_4)_2SO_4 + 6H_2O \longrightarrow FeSO_4.(NH_4)_2SO_4.6H_2O$ (Mohr salt)
5. Aqueous solution of $FeSO_4$ is acidic due to hydrolysis of Fe^{2+}:

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

6. Acidified MnO_4^- and $Cr_2O_7^{2-}$ oxidize Fe^{2+} to Fe^{3+}.

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$
$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

(F) Copper sulphate($CuSO_4.5H_2O$) or Blue vitriol

Preparation:

1. It is prepared by dissolving copper (II) oxide or copper (II) carbonate in dil Sulphuric acid.

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$
$$CuCO_3 + H_2SO_4 \longrightarrow Cu\,SO_4 + CO_2 + H_2O$$

On evaporation, solution is concentrated, blue crystal of $CuSO_4.5H_2O$ separate out on cooling.

2. On a large scale, copper (II) sulphate is obtained by passing air through a hot mixture of copper and dil H_2SO_4

$$2Cu + 4H^+ + O_2 \longrightarrow 2Cu^{2+} + 2H_2O$$

3. $CuFeS_2 + 4O_2 \longrightarrow CuSO_4 + FeSO_4$

Properties:

1. On heating $CuSO_4 . 5H_2O$ looses water molecules as follows.

$$CuSO_4.5H_2O \xrightarrow{373\,K} CuSO_4.H_2O \xrightarrow{432\,K} CuSO_4 \xrightarrow[\text{heating}]{\text{strong}} CuO + SO_3$$

2. $CuSO_4 + 6NH_4OH \longrightarrow \underset{\text{Schweitzer's reagent}}{[Cu(NH_3)_4](OH)_2} + (NH_4)_2SO_4 + 4H_2O$
3. $2CuSO_4 + 4KI \longrightarrow Cu_2I_2\downarrow + I_2\uparrow + 2K_2SO_4$ (CuI is not formed)
4. A mixture of copper sulphate and lime, under the name of Bordeaux mixture is used as fungicide in agriculture.

5. $2CuSO_4 + 2KSCN + SO_2 + 2H_2O \longrightarrow 2CuSCN\downarrow + K_2SO_4 + 2H_2SO_4$

(G) Zinc sulphate: $ZnSO_4.7H_2O$ (white vitriol)

Prepareation:

1. It is prepared by the action of dil. H_2SO_4 on Zn metal or its oxide or carbonate

$$ZnCO_3 + H_2SO_4 \longrightarrow ZnSO_4 + H_2O + CO_2$$
$$2ZnS + 3.5O_2 \xrightarrow{\Delta} ZnO + ZnSO_4 + SO_2$$
$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$

Properties:

1. It is highly soluble in water. The solution is acidic in nature due to hydrolysis.

$$ZnSO_4 + 2H_2O \longrightarrow Zn(OH)_2 + H_2SO_4$$

2. $ZnSO_4.7H_2O \xrightarrow[\Delta]{100^\circ C} ZnSO_4.6H_2O \xrightarrow[\Delta]{280^\circ C} ZnSO_4$
3. $ZnSO_4 \xrightarrow{760^\circ C} ZnO + SO_3$
4. It is isomorphous with Epsom salt and green vitriol.

(H) Silver Nitrate, $AgNO_3$ (Lunar Caustic):-

Preparation:

1. It is prepared by dissolving the metal in dilute nitric acid and crystallizing the solution

$$3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + 2H_2O + NO\uparrow$$

Properties:

1. It is a colourless crystalline solid, soluble in water and alcohol; melting point 212°C.
2. On heating, it gives metallic silver and nitrogen dioxide.

$$2AgNO_3 \xrightarrow[450^\circ C]{\Delta} 2Ag + 2NO_2 + O_2$$

3. It reacts with iodine in two ways

$$5AgNO_3 + 3I_2\,(\text{excess}) + 3H_2O \longrightarrow HIO_3 + 5AgI + 5HNO_3$$
$$6AgNO_3\,(\text{excess}) + 3I_2 + 3H_2O \longrightarrow AgIO_3 + 5AgI + 6HNO_3$$

4. It gives turbidity with tap water (Cl^-) and turbidity is soluble in NH_4OH.

$$AgNO_3 + \underset{\text{tap water}}{Cl^-} \longrightarrow \underset{\text{turbidity}}{AgCl\downarrow} + NO_3$$
$$AgCl + 2NH_4OH \longrightarrow \underset{\text{(soluble)}}{Ag(NH_3)_2Cl} + 2H_2O$$

5. When treated with alkali, it gives precipitate of silver oxide, which dissolves in excess of NH_4OH.

$$2AgNO_3 + 2NaOH \longrightarrow \underset{\text{Brown ppt.}}{Ag_2O\downarrow} + 2NaNO_3 + H_2O$$
$$2AgNO_3 + 2NH_4OH \longrightarrow Ag_2O\downarrow + 2NH_4NO_3 + H_2O$$
$$Ag_2O + 4NH_4OH \longrightarrow 2[Ag(NH_3)_2]OH + 3H_2O$$

6. Ammonical $AgNO_3$ is called Tollen's reagent and is used to identify reducing sugars (including aldehydes). It is called silver mirror test of aldehydes and reducing sugar (like glucose, fructose).
7. It dissolves in excess of KCN:

$$AgNO_3 + KCN \longrightarrow \underset{\text{White ppt.}}{AgCN} + KNO_3$$
$$AgCN + KCN \longrightarrow \underset{\text{Soluble potassium argentocyanide}}{K[Ag(CN)_2]}$$

(I) Silver (I) oxide (Ag_2O)

Preparation:

$$2AgNO_3 + 2NaOH \longrightarrow Ag_2O\downarrow + 2NaNO_3 + H_2O$$

Properties:

1. It is brownish powder, insoluble in water, thermally unstable and soluble in aqueous ammonia.
2. It decomposes to silver and oxygen.

$$2Ag_2O \longrightarrow 4Ag + O_2$$

(J) Silver thiosulphate ($Ag_2S_2O_3$)

Preparation:

1. With $Na_2S_2O_3$,

$$2AgNO_3 + Na_2S_2O_3 \longrightarrow \underset{\text{white ppt.}}{Ag_2S_2O_3\downarrow} + 2NaNO_3$$
$$2AgBr + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3\downarrow + 2NaBr$$

Properties:

1. $Ag_2S_2O_3 + 3Na_2S_2O_3 \longrightarrow \underset{\text{sodium argentothiosulphate}}{2Na_3[Ag(S_2O_3)_2]}$

(K) Potassium Dichromate ($K_2Cr_2O_7$)

Preparation:

1. It is prepared from chromite ore ($FeCr_2O_4$)

$$4FeCr_2O_4 + 16NaOH + 7O_2(\text{air}) \longrightarrow \underset{\text{Sodium chromate}}{8Na_2CrO_4} + 2Fe_2O_3 + 8H_2O$$

Or, $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

$$2Na_2CrO_4 + \text{dil. } H_2SO_4 \longrightarrow \underset{\text{Sodium dichromate}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$
$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Properties:

1. It is orange-red crystalline compound having melting point 670 K.
2. It is moderately soluble in cold water but readily soluble in hot water.
3. $4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2\uparrow$

   Potassium chromate chromic acid
4. $\underset{\substack{\text{chromate}\\\text{(yellow)}}}{2CrO_4^{2-}} + 2H^+ \underset{\text{alkali}}{\overset{\text{acid}}{\rightleftharpoons}} \underset{\substack{\text{Hydrogen}\\\text{chromate}}}{2HCrO_4^-} \underset{\text{alkali}}{\overset{\text{acid}}{\rightleftharpoons}} \underset{\substack{\text{dichromate}\\\text{(orange)}}}{Cr_2O_7^{2-}} + H_2O$
5. Action with HCl:

   $K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2\uparrow$

   Chlorine
6. Chromyl chloride Test (This is the test of chloride):

   $K_2Cr_2O_7 + 6H_2SO_4 + 4NaCl \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$

   chromyl chloride

   $4NaOH + CrO_2Cl_2 \longrightarrow \underset{\substack{\text{yellow solution}\\\text{(sod. Chromate)}}}{Na_2CrO_4} + 2NaCl + 2H_2O$
7. Oxidising character:
   - (a) Both $Na_2Cr_2O_7$ and $K_2Cr_2O_7$ are oxidizing agents but $K_2Cr_2O_7$ is preferred since it is not hygroscopic and can be used as primary standard.
   - (b) The dichromates act as powerful oxidising agent in acidic medium.

     $K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$

     nascent oxygen
   - (c) Some examples are:

     $K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$

     $K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$

     $K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3S + 7H_2O$

     $K_2Cr_2O_7 + \underset{\text{(sod. Sulphite)}}{3Na_2SO_3} + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + \underset{\text{(sod. Sulphate)}}{3Na_2SO_4} + 4H_2O$

     $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

(L) Potassium Permanganate ($KMnO_4$)

Preparation:

1. Potassium permanganate is prepared from mineral pyrolusite (MnO_2).
2. Steps involved are:
   - (a) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} \underset{\substack{\text{Pot. Manganate}\\\text{(Green mass)}}}{2K_2MnO_4} + 2H_2O$

     or, $2MnO_2 + 2K_2CO_3 + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2CO_2$
   - (b) $2K_2MnO_4 + Cl_2 \longrightarrow 2KCl + 2KMnO_4$

     or, $2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$

     or, $2K_2MnO_4 + 2CO_2 \longrightarrow 2K_2CO_3 + 2MnO_2\downarrow + 2KMnO_4$

Properties:

1. It is a dark violet crystalline solid having a metallic luster (meeting point 523 K). It is fairly soluble in water giving a purple solution.
2. $2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2\uparrow$
3. Action of alkalies:

   $4KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + 2H_2O + O_2\uparrow$
4. Oxidizing character:

   Potassium permanganate acts as an oxidizing agent in neutral, alkaline and acidic solutions.
   - (a) In neutral medium MnO_2 is formed.

     $2KMnO_4 + 3H_2S \longrightarrow 2KOH + 2MnO_2 + 3S + 2H_2O$

     $2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$

     $2KMnO_4 + 3Na_2S_2O_3 + H_2O \longrightarrow 2MnO_2 + 3Na_2SO_4 + 2KOH + 3S$
   - (b) In alkaline medium, MnO_2 is formed.

     $2KMnO_4 + KI + H_2O \longrightarrow 2MnO_2 + 2KOH + KIO_3$
   - (c) In acidic medium, Mn^{2+} is formed.

     $2KMnO_4 + 10\,FeSO_4 + 8H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

     $2KMnO_4 + 8H_2SO_4 + 10\,KI \longrightarrow 2MnSO_4 + 6K_2SO_4 + 8H_2O + 5I_2$

     $2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5S$

     $2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

$$2KMnO_4 + 3H_2SO_4 + 5KNO_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 5KNO_3 + 3H_2O$$

$$2KMnO_4 + 10HI + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$$

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

LANTHANIDES AND ACTINIDES

The elements from atomic number 58 (cerium) to 71 (lutetium) are known as lanthanides as they follow the element lanthanum (atomic number 57). These elements are placed together at the bottom of the periodic table. These elements are characterized by the filling up of the antipenultimate 4f energy levels. The compound of these elements show +III oxidation state and form ionic compounds. Some of the elements also show +II and +IV oxidation states.

Many trivalent lanthanide ions are coloured both in the solid state and in aqueous solution. The colour seems to depend on the number of unpaired electrons. Elements with nf electrons offer a similar colour to those with (14-n) f electrons. The atomic and ionic sizes of lanthanides progressively decreases from the first element to the last element. The contraction is about 20 pm and is known as the lanthanide contraction. This is due to the poor shielding effect of 4f electrons causing more and more attraction between the nucleus and the outer electrons.

The properties of an ion depends on its size and its charge. Because of the very small decrease in ionic size, the chemical properties of lanthanides are very similar. The sizes of the last four elements of the lanthanide series become lower than that of the element Y of the preceding trasition series. Also the elements which follows in the third transition series are considerable smaller than the expected value. The pairs Zr-Hf, Nb-Ta and Mo-W have almost identical sizes. The sizes of the third row of transition elements are very similar to those of the second row elements.

The elements from atomic numeber 90 (Thorium) to 103 (Lawrencium) are known as actinides as they follow the element actinium (atomic number 89). The actiinides also have an oxidation state of +III but this state is not always the most stable state. All the actinides are very reactive and show the phenomenon of radioactivity. Their melting points are moderating high but are considerable low as compared to those of transition elements. They also show actinide contraction to the lanthanide contraction.

Outer Electronic configuration of Lanthanum and Lanthanides

Atomic Number	Element Name	Electronic Configuration
57	La	$5d^1 6s^2$
58	Ce	$4f^1 5d^1 6s^2$
59	Pr	$4f^3 6s^2$
60	Nd	$4f^4 6s^2$
61	Pm	$4f^5 6s^2$
62	Sm	$4f^6 6s^2$
63	Eu	$4f^7 6s^2$
64	Gd	$4f^7 5d^1 6s^2$
65	Tb	$4f^9 6s^2$
66	Dy	$4f^{10} 6s^2$
67	Ho	$4f^{11} 6s^2$
68	Er	$4f^{12} 6s^2$
69	Tm	$4f^{13} 6s^2$
70	Yb	$4f^{14} 6s^2$
71	Lu	$4f^{14} 5d^1 6s^2$

Outer Electronic configuration of Actinium and Actinoids

Atomic Number	Element Name	Electronic Configuration
89	Ac	$6d^1 7s^2$
90	Th	$6d^2 7s^2$
91	Pa	$5f^2 6d^1 7s^2$
92	U	$5f^3 6d^1 7s^2$
93	Np	$5f^4 6d^1 7s^2$
94	Pu	$5f^6 7s^2$
95	Am	$5f^7 7s^2$
96	Cm	$5f^7 6d^1 7s^2$
97	Bk	$5f^9 7s^2$
98	Cf	$5f^{10} 7s^2$
99	Es	$5f^{11} 7s^2$
100	Fm	$5f^{12} 7s^2$
101	Md	$5f^{13} 7s^2$
102	No	$5^{14} 7s^2$
103	Lr	$5f^{14} 6d^1 7s^2$

Solved Examples

1. The oxidation number is changed in which of the following case-

(a) SO_2 gas is passed into $Cr_2O_7^{2-}/H^+$

(b) Aqueous solution of CrO_4^{2-} is acidified

(c) CrO_2Cl_2 is dissolved in NaOH

(d) $Cr_2O_7^{2-}$ solution is made alkaline

Sol.(a)

(a) $\overset{+6}{Cr_2O_7^{2-}} + \overset{+4}{SO_2} + 2H^+ \rightarrow \overset{+3}{2Cr^{3+}} + \overset{+6}{3SO_4^{2-}} + H_2O$

(b) $\overset{+6}{2CrO_4^{2-}} + 2H^+ \rightarrow \overset{+6}{Cr_2O_7^{2-}} + H_2O$

(c) $\overset{+6}{CrO_2Cl_2} + 2NaOH \rightarrow \overset{+6}{Na_2CrO_4}$

(d) $\overset{+6}{CrO_7^{2-}} + 2OH^- \rightarrow \overset{+6}{2CrO_4^{2-}} + H_2O$

2. What happen when $FeSO_4$(X) is subjected to heating, compound R,S,T are obtained. R is red-brown solid, S can be oxidized to (T). Identify R,S,T.

Sol. $\underset{(X)}{2FeSO_4} \xrightarrow{\Delta} \underset{\substack{(R)\\ \text{Red-Brown}}}{Fe_2O_3} + \underset{(S)}{SO_2} + \underset{(T)}{SO_3}$

3. Heating of Ag with dil. HNO_3 give

(a) NO (b) NO_2

(c) N_2O (d) N_2O_3

Sol.(a) $2HNO_3(\text{dil.}) \rightarrow 2NO + H_2O + 3[O]$

$6Ag + 8HNO_3 \longrightarrow 6AgNO_3 + 2NO + 4H_2O$

4. When excess of $SnCl_2$ is added to $HgCl_2$, the substance formed is –

(a) Hg_2Cl_2 (b) Sn

(c) Hg (d) Cl_2

Sol.(c) $SnCl_2$ reduces $HgCl_2$ to Hg_2Cl_2 and finally to Hg-

$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$

$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$

5. A mixture of Mn^{2+} & Zn^{2+} can be separated by using an excess of-

(a) NH_4OH (b) NaOH

(c) H_2SO_4 (d) HNO_3

Sol.(b) $Mn^{2+} + 2NaOH \longrightarrow \underset{(\text{ppt.})}{Mn(OH)_2} + 2Na^+$

$Zn^{2+} + 2NaOH \longrightarrow \underset{\substack{(\text{ppt.})\\ (\text{Amphoteric in nature})}}{Zn(OH)_2} + 2Na^+$

$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Soluble}}{Na_2[Zn(OH)_4]}$

6. Black coloured solid (A) $\xrightarrow[\Delta]{KNO_3+KOH}$ green coloured solution (B) $\xrightarrow{CO_2}$ $\underset{\text{Pink}}{(C)}$ + (A)

(C) is decolorised by Fe^{2+}. Identify (A), (B) and (C). Explain the reaction.

Sol. (A) MnO_2 (B) K_2MnO_4 (C) $KMnO_4$

$MnO_2 + KOH + O_2\ (KNO_3) \xrightarrow{\Delta}$
$\underset{(B)}{K_2MnO_4} \xrightarrow{CO_2} \underset{(C)}{MnO_4^-} + \underset{(A)}{MnO_2}$

$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$

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

7. Explain why mercury (I) ion exists as Hg_2^{2+} ion white copper (I) ion exists as Cu^+ ion.

Sol. $Hg(Z = 80) \Rightarrow 4f^{14}\,5d^{10}\,6s^2$; $Hg^{\oplus} \Rightarrow 4f^{14}\,5d^{10}\,6s^1$

Hg^+ has one electron in its valence 6s-orbital, due to this, Hg^+ compounds should be paramagnetic but actually they are diamgnetic. Hence, the single filled 6s-orbitals of the two $Hg^{\oplus}$ ions overlap from a Hg–Hg covalent bond. Thus, $Hg^{\oplus}$ ions exist as dimeric species, i.e., Hg_2^{2+}.

$Cu(Z = 29) \Rightarrow 3d^{10}\,4s^1$

$Cu^{\oplus} \Rightarrow 3d^{10}$

Therefore, $Cu^{\oplus}$ ion has no unpaired electron to form dimeric species. i.e., Cu_2^{2+} and hence, it always exists as $Cu^{\oplus}$ ion.

8. Why hydrated copper sulphate is blue while unhydrous copper sulphate is white?

Sol. In $CuSO_4$. $5H_2O$, four water molecules are present as ligand. In the presence of these ligands d-orbitals are no longer degenerate in energy. Hence d-d transition takes place absorbing red wavelength. The complementary colour, viz, blue is reflected. In anhydrous $CuSO_4$, d-orbitals remain degenerate. Hence, no d-d transition can occur. The white light is completely reflected back. Hence, it looks white.

9. (a) Of the lanthanides, cerium (Z = 58) forms a tetrapositive ion, Ce^{4+} in aqueous solution. Why?

(b) The +3 oxidation states of lanthanum (Z = 57), gadolinium (Z = 64) and lutetium (Z = 71) are especially stable. Why?

(c) Why do Zr and Hf or Nb and Ta exhibit similar properties ?

(d) Which out of the two, $La(OH)_3$ and $Lu(OH)_3$, is more basic and why?

Sol. (a) Ce^{3+} having the configuration $4f^1 5d^0 6s^0$ can easily loose an electron to acquire the configuration $4f^0$ and form Ce^{4+}. In fact, this is the only +4 state lanthanide which exists in solution.

(b) This is because they have empty, half-filled and completely filled 4f subshells respectively.

(c) Due to the consequence of lanthnoid contraction, Hf (Z = 72) has size similar to that of Zr (Z = 40). Hence, their properties are similar. For the same reason. Nb and Ta have similar size and hence similar properties.

(d) $La(OH)_3$ is more basic than $Lu(OH)_3$. As the size of the lanthanid ions decreases from La^{3+} to Lu^{3+}, the covalent chracter of the hydroxides increases (Fajan's rules). Hence, the basic strength decreases from $La(OH)_3$ to $Lu(OH)_3$.

10. Identify A to F.

(a) A powdered substance A on fusion with (Na_2CO_3 + KNO_3) mixture gives a green coloured compound B.

(b) The solution of B in boiling water on acidification with dilute H_2SO_4 gives a pink coloured compound C.

(c) The aqueous solution of A on treatement with NaOH and Br_2 - water gives a compound D.

(d) A solution of D in conc. HNO_3 on treatment with lead peroxide at boiling temperature produced a compound E which was of the same colour as that of C.

(e) A solution of A in dilute HCl on treatment with a solution of barium chloride gave a white precipitate of compound F which was insoluble in conc. HNO_3 and conc. HCl.

Sol. A is $MnSO_4$

(a) $\underset{(A)}{MnSO_4} + Na_2CO_3 + 2KNO_3 \rightarrow \underset{\text{(B) Green coloured}}{Na_2MnO_4} + 2KNO_2$

(b) $3Na_2MnO_4 + 2H_2SO_4 \rightarrow \underset{\text{(C) Pink coloured}}{2NaMnO_4} + MnO_2 + 2Na_2SO_4 + 2H_2O$

(c) $MnSO_4 + 4NaOH + Br_2 \rightarrow \underset{(D)}{MnO_2} + Na_2SO_4 + 2NaBr + 2H_2O$

(d) $2MnO_2 + 10HNO_3 + 5PbO_2 \rightarrow \underset{\text{(E) Pink coloured}}{2HMnO_4} + 5Pb(NO_3)_2$

(e) $MnSO_4 + BaCl_2 \rightarrow \underset{\text{(F) (Insoluble in conc. } HNO_3 \text{ and conc. HCl)}}{BaSO_4 + MnCl_2}$

Exercise

LEVEL I

1. Which of the following statements concerning transition elements, is not true?

(a) They are all metals.

(b) They easily form complexes.

(c) Compounds containing their ions are coloured.

(d) They show multiple oxidation states always differing by two units.

2. The stability of particular oxidation state of a metal in aqueous solution is determined by:

(a) Enthalpy of sublimation of the metal

(b) Ionization energy

(c) Enthalpy of hydration of the metal ion

(d) All of these

3. Which of the following is likely to form white salts?

(a) Cu^{2+} (b) Sc^{3+}

(c) Ti^{3+} (d) Fe^{2+}

4. Brass is an alloy of

(a) Silver and copper (b) Copper and zinc

(c) Copper and tin (d) Copper, zinc and tin

5. Zr and Hf have almost equal atomic and ionic radii because:

(a) of diagonal relationship.
(b) both are in the same group.
(c) of lanthanide contraction.
(d) they have same outermost shell.

6. Which of the following compounds is expected to be coloured?

(a) Ag_2SO_4 (b) CuF_2
(c) MgF_2 (d) CuCl

7. Stainless steel contains

(a) Fe + Cr + Cu (b) Fe + C + Ni
(c) Fe + Cr + Ni (d) Fe + Ni + Cu

8. The catalytic activity of the transition metals and their compounds is ascribed to

(a) Their chemical reactivity
(b) Their magnetic behavior
(c) Their unfilled d-orbitals
(d) Their ability to adopt multiple oxidation states and their complexing ability.

9. In the reaction $Zn + NaOH \xrightarrow{\Delta} X$, the product X is:

(a) Na_2ZnO_2 (b) $2NaZnO_2$
(c) $Zn\ (OH)_2$ (d) None of these

10. Which of the following is not correctly matched?

(a) SiC – Covalent carbide
(b) WC – Interstitial carbide
(c) Al_4C_3 – Ionic carbide
(d) B_4C – Molecular carbide

11. Which of the following is not a property of intersitial compounds?

(a) Neither ionic nor covalent
(b) High chemically reactivity
(c) Retain metallic conductivity
(d) Non-stoichiometric compound

12. K_2MnO_4 can be converted into $KMnO_4$ by:

(a) Passing CO_2 gas
(b) By passing Cl_2
(c) Electrolytic oxidation
(d) All of these

13. Which of the following metals of 3d series do not show variable oxidation state?

(a) Sc, Ti (b) Ti, Cu
(c) Sc, Zn (d) Co, Ni

14. The metals which are present in insulin and vitamin B_{12} respectively are:

(a) Zn, Co (b) Fe, Cr
(c) Co, Fe (d) Zn, Fe

15. $CrO_4^{2-} \underset{pH\ =\ Y}{\overset{pH\ =\ X}{\rightleftharpoons}} Cr_2O_7^{2-}$

The pH values of X and Y are respectively:

(a) 4 and 5 (b) 4 and 8
(c) 8 and 4 (d) 8 and 9

16. In which of the following oxoanions, the oxidation state of the central atom is not the same as that of its group number in the periodic table?

(a) MnO_4^{-} (b) $Cr_2O_7^{2-}$
(c) VO_4^{3-} (d) FeO_4^{2-}

17. Interstitial compounds are not formed by:

(a) Co (b) Ni
(c) Fe (d) Ca

18. Which compound does not exist?

(a) MnF_6 (b) MnF_4
(c) MnO_3F (d) MnO_4^{-2}

19. The incorrect match is:

(a) CrO_5 peroxide
(b) Mn_2O_7 Acidic oxide
(c) CrO_3 Amphoteric
(d) FeO Basic oxide

20. Solder is an alloy of:

(a) Pb + Sn (b) Mg + Al
(c) Cu + Sn (d) Al + Mn + Cu

21. Most common oxidation states are matched below with the elements. Which one is mismatched ?

(a) Iron (+2, +3)
(b) Chromium (+1, +2)
(c) Manganese (+2, +7)
(d) Titanium (+3, +4)

22. Which of the following pair of ions has same value of “spin-only" magnetic moment:

(a) Cu^{+}, Cu^{2+} (b) Co^{3+}, Fe^{2+}
(c) Ti^{2+}, Cu^{2+} (d) Sc^{2+}, Zn^{+2}

23. CO_2 and SO_2 gas can be distinguish by:

(a) Slaked lime (b) Beryta water
(c) Acidified $KMnO_4$ (d) All of these

24. Acidified $K_2Cr_2O_7$ can not oxidise:

(a) Green vitriol (b) Mohr's salt

(c) Ferric oxalate (d) Ferric sulphate

25. In which of the following oxo-anion, all M–O bond length are not identical?

(a) MnO_4^- (b) MnO_4^{-2}

(c) $Cr_2O_7^{-2}$ (d) CrO_4^{-2}

26. Which of the following is not a similarity between sulphur and chromium?

(a) Both exhibit hexacovalency

(b) Sulphate and chromate of Ba^{2+} are water insoluble

(c) Trioxide (MO_3) both are acidic

(d) Sulphate (SO_4^{2-}) and chromate (CrO_4^{2-}) have same colouration

27. Copper (II) ions gives reddish brown precipitate with potassium ferrcroyanide. The formula of the precipitate is:

(a) $Cu[Fe(CN)_6]$ (b) $Cu_2[Fe(CN)_6]$

(c) $Cu_3[Fe(CN)_6]$ (d) $Cu_3[Fe(CN)_6]_2$

28. CeO_2 is:

(a) A good oxidising agent

(b) Diamagnetic in nature

(c) Colourless compound

(d) All of these

29. Which of the following show highest oxidation state?

(a) Cl (b) Mn

(c) Np (d) All of these

30. Which of the following ion has maximum complex forming tendency?

(a) La^{+3} (b) Ce^{+3}

(c) Eu^{+3} (d) Lu^{+3}

LEVEL II

1. Number of Cr—O bonds in dichromate ion ($Cr_2O_7^{2-}$) is:

(a) 6 (b) 7

(c) 8 (d) 4

2 Potassium permanganate acts as an oxidant in neutral, alkaline as well as acidic media. The final products obtained from it in the three conditions are, respectively

(a) MnO_4^{2-}, Mn^{3+} and Mn^{2+}

(b) MnO_2, MnO_4^{2-} and Mn^{2+}

(c) MnO_2, MnO_2^+ and Mn^{3+}

(d) MnO_2 , MnO_2 and Mn^{3+}

3. Amongst TiF_6^{2-}, CoF_6^{3-}, Cu_2Cl_2 and $NiCl_4^{2-}$ (Atomic numbers : Ti = 22, Co = 27, Cu = 29, Ni = 28) the colourless species are

(a) TiF_6^{2-} and Cu_2Cl_2

(b) Cu_2Cl_2 and $NiCl_4^{2-}$

(c) TiF_6^{2-} and CoF_6^{3-}

(d) CoF_6^{3-} and $NiCl_4^{2-}$

4. CrO_3 dissolves in aqueous NaOH to give:

(a) CrO_4^{2-} (b) $Cr(OH)_3$

(c) $Cr_2O_7^{2-}$ (d) $Cr(OH)_2$

5. A compound of a metal ion M^{x+} (Z = 24) has a spin only magnetic moment of $\sqrt{15}$ Bohr Magnetons. The number of unpaired electrons in the compound are:

(a) 2 (b) 4

(c) 5 (d) 3

6. Which one of the following statement is not correct?

(a) $La(OH)_3$ is less basic than $Lu(OH)_3$.

(b) In lanthanide series, ionic radius of Ln^{3+} ions decreases.

(c) La is actually an element of transition series rather than lanthanide series.

(d) Atomic radii of Zr and Hf are same because of lanthanide contraction.

7. Which of the following compounds has colour but no unpaired electrons?

(a) $KMnO_4$ (b) K_2MnO_4

(c) $MnSO_4$ (d) $MnCl_2$

8. Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO_3 because:

(a) Zn acts as an oxidising agent when react with HNO_3.

(b) HNO_3 is weaker acid than H_2SO_4 and HCl.

(c) In electrochemical series Zn is above hydrogen.

(d) NO_3^- ion is reduced in preference to hydronium ion.

9. Which of the following is incorrectly matched?

	Catalyst	**Process**
(a)	V_2O_5	Contact process
(b)	Cu_2Cl_2	Sandmeyer reaction
(c)	Finely divided Fe	Vegatable oil to ghee
(d)	$TiCl_4 + Al(CH_3)_3$	Zieglar Natta Catalyst

10. An inorganic molecule X on heating gives green colouration and evolve O_2 gas. The X is:

(a) $(NH_4)_2Cr_2O_7$ (b) $K_2Cr_2O_7$

(c) $RbCrO_4$ (d) CrO_2Cl_2

11. Consider the following reaction:

$2Cu^{2+} + X^- \longrightarrow Cu_2X_2(s) + X_2$

Then X^- can be:

(a) F^- (b) Cl^-

(c) Br^- (d) I^-

12. In which reaction no colour change will be observed?

(a) $K_2Cr_2O_7 \xrightarrow{CO_2}$

(b) $K_2Cr_2O_7 \xrightarrow{SO_2}$

(c) $Na_2CrO_4 \xrightarrow{CO_2}$

(d) $Na_2S \xrightarrow{Na_2[Fe(CN)_5NO]}$

13. Which of the following property first increases then decreases on moving from Sc to Zn?

(a) Paramagnetism

(b) Heat of atomisation

(c) Maximum oxidation state

(d) All of these

14. Coloured and paramagnetic oxoanion is:

(a) MnO^-_4 (b) CrO_4^{-2}

(c) MnO_4^{-2} (d) $Cr_2O_7^{-2}$

15. Product formed when Au react with aquaregia is:

(a) AuCl (b) $AuCl_3$

(c) $Au(NO_3)_3$ (d) $HAuCl_4$

16. When $KMnO_4$ react with H_2O_2 in slightly alkaline and acidic medium, the respective products obtained:

(a) K_2MnO_4 and Mn^{2+}(aq)

(b) MnO_2 and MnO_2

(c) MnO_2 and Mn^{2+}(aq)

(d) Mn^{2+} (aq) and MnO_2

17. $K_2Cr_2O_7$ when reacts cold conc. H_2SO_4 gives red crystal of:

(a) CrO_4^{-2} (b) CrO_3

(c) $Cr_2(SO_4)_3$ (d) Cr_2O_3

18. $(X) + K_2CO_3 + \text{Air} \xrightarrow{\text{Heat}} (Y)$.

$(Y) + Cl_2 \longrightarrow (Z)$ Pink.

Which of the following is correct?

(a) X = Black, MnO_2, Y = Blue, K_2CrO_4, Z = $KMnO_4$.

(b) X = Green, Cr_2O_3, Y = Yellow, K_2CrO_4, Z = $K_2Cr_2O_7$.

(c) X = Black, MnO_2, Y = Green, K_2MnO_4, Z = $KMnO_4$.

(d) X = Black, Bi_2O_3, Y = Colourless, $KBiO_2$, Z = $KBiO_3$.

19. When acidified $KMnO_4$ is added to hot oxalic acid solution, the decolourization is slow in the beginning but becomes very rapid after some time. This is because:

(a) Mn^{+2} acts as autocatalyst

(b) CO_2 is formed as the product

(c) Reaction is exothermic

(d) MnO_4^- catalyses the reaction

20. 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) a deep red vapour is evolved.

(B) the vapour when passed into NaOH solution gives a yellow solution of Na_2CrO_4

(C) Chlorine gas is evolved

(D) chromyl chloride is formed

(a) A, B, D (b) A, B, C

(c) B, C, D (d) all are correct

21. Mercury (II) chloride solution on reaction with gaseous ammonia forms:

(a) $Hg(NH_2)Cl.HgO$

(b) $Hg(NH_3)Cl_2$

(c) $[Hg(NH_3)_4]Cl_2$

(d) $[Hg(NH_3)_2]Cl$

22. $AgNO_3 \xrightarrow{\Delta} (W) + (X) + O_2$

$(X) + H_2O \longrightarrow HNO_2 + HNO_3$

$(W) + HNO_3 \longrightarrow Y + NO + H_2O$

$(Y) + Na_2S_2O_3 \text{ (excess)} \longrightarrow (Z) + NaNO_3$

Identify (W) to (Z).

(a) W = Ag; X = N_2O; Y = $AgNO_3$; Z = $Na_2[Ag(S_2O_3)_2]$

(b) W = Ag_2O; X = NO; Y = $AgNO_3$; Z = $Na_3[Ag(S_2O_3)_2]$

(c) W = Ag; X = NO_2; Y = $AgNO_3$; Z = $Na_3[Ag(S_2O_3)_2]$

(d) W = AgO ; X = N_2; Y = $AgNO_3$; Z = $Na[Ag(S_2O_3)_2]$

23. Which of the following electronic configuration is associated with the highest stable oxidation state?

(a) [Ar] $3d^1 4s^2$ (b) [Ar] $3d^5 4s^1$

(c) [Ar] $3d^5 4s^2$ (d) [Ar] $3d^6 4s^2$

24. A white precipitate of AgCl dissolves in excess of:

(I) NH_3(aq) (II) $Na_2S_2O_3$

(III) NaCN

(a) III only (b) I, II, III

(c) I, II (d) I only

25. Zinc (II) ion on reaction with NaOH first gives a white precipitate which dissolves in excess of NaOH due to the formation of:

(a) ZnO (b) $Zn(OH)_2$

(c) $[Zn(OH)_4]^{2-}$ (d) $[Zn(H_2O)_4]^{2+}$

26. Dilute nitric acid on reaction with silver liberates:

(a) NO gas (b) NO_2

(c) N_2 gas (d) O_2 gas

27. Acidified permanganate solution does not oxidize:

(a) $C_2O_4^{2-}$ (aq.) (b) NO_2^- (aq.)

(c) S^{2-}(aq.) (d) F^-(aq.)

28. Which of the following characteristic is not the point of resemblance between lanthanoids and actinoids?

(a) Reducing property

(b) Oxidation state of +3

(c) Trends of ionic radii for M^{+3} ions

(d) Radioactivity

29. Which of the following statement is not correct?

(a) Lu^{+3} has the strongest tendency toward complex formation among trivalent lanthanoid ions.

(b) Ce has maximum composition in misch metal.

(c) f-block elements can have electrons from f^0 to f^{14}.

(d) Nd, Np and Nb all are f-block elements.

30. Which of the following lanthanoid has one electron in 6d subshell?

(a) La (b) Ce

(c) Gd (d) None of these

LEVEL III

One or more than one correct type

1. The metal oxide which decomposes on heating is/are:

(a) ZnO (b) Al_2O_3

(c) Ag_2O (d) HgO

2. Which of the following acids attack(s) on copper and silver?

(a) dilute HNO_3 (b) dilute HCl

(c) conc. H_2SO_4 (d) aqua regia

3. Which statements are correct regarding copper sulphate?

(a) It reacts with NaOH and glucose to give Cu_2O.

(b) It reacts with KCl to give Cu_2O.

(c) It gives CuO on strong heating in air.

(d) It reacts with KI to give brown colouration.

4. Pick out the correct statements (s):

(a) MnO_2 dissolves in conc. HCl, but does not form Mn^{4+} ions.

(b) Decomposition of acidic $KMnO_4$ is not catalysed by sunlight.

(c) MnO_4^{2-} is strongly oxidising and stable only in very strong alkali. In dilute alkali, water or acidic solutions, it disproportionates.

(d) $KMnO_4$ does not act as oxidising agent in alkaline medium.

5. The species that undergoes disproportionation in an alkaline medium are:

(a) Cl_2 (b) MnO_4^{2-}

(c) NO_2 (d) ClO_4^-

6. Mercuric chloride is converted into mercury by:

(a) Placing copper metal in aqueous solution of $HgCl_2$.

(b) Treating aqueous solution of $HgCl_2$ with excess of stannous chloride.

(c) Treating aqueous solution of $HgCl_2$ with $PbCl_4$ solution.

(d) None of these.

7. Choose correct statement (s) regarding the following reaction:

$$Cr_2O^{2-}_{7(aq.)} + 3SO^{2-}_{3(aq.)} + 8H^+ \rightarrow 2Cr^{3+}_{(aq.)} + 3SO^{2-}_{4(aq.)} + 4H_2O$$

(a) $Cr_2O_7^{2-}$ is an oxidising agent.

(b) SO_3^{2-} is a reducing agent.

(c) The oxidation number of per S-atom in SO_3^{2-} is increased by two.

(d) The oxidation number of per Cr-atom in is $Cr_2O^{2-}_{7(aq.)}$ decreased by three.

8. 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

9. Which of the following ions give(s) coloured aqueous solution?

(a) Ni^{2+} (b) Fe^{2+}

(c) Cu^{2+} (d) Cu^{+}

10. 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

11. 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 forming a yellow solution.

(c) Greenish yellow gas is liberated

(d) Deep red vapours dissolve in water forming yellow solution

PASSAGE-BASED QUESTIONS

Passage # 1 (Q. 12 and 13)

$$\text{Light green (Compound 'A')} \xrightarrow{\Delta} \text{White Residue (B)} \xrightarrow[\text{Temp.}]{\text{High}} C + D + E$$

(i) 'D' and 'E' are two acidic gas.

(ii) 'D' is passed through $HgCl_2$ solution to give yellow precipitate.

(iii) 'E' is passed through water first and then H_2S is passed, white turbidity is obtained.

(iv) A is water soluble and addition of $HgCl_2$ in it, white ppt is obtained but white ppt does not turn into grey on addition of excess solution of 'A'.

12. 'D' and 'E' are respectively.

(a) SO_2 and SO_3 (b) SO_3 and SO_2

(c) SO_2 and CO_2 (d) CO_2 and CO

13. Yellow ppt in the above observation is :

(a) Mercuric oxide

(b) Basic mercury (II) sulphite

(c) Basic mercury (II) sulphate

(d) Mercuric iodide

Passage # 2 (Q. 14 and 15)

MnO_2 is the most important oxide of maganese. It occurs naturally as the black coloured mineral pyrolusite. It is an oxidising agent, and decomposes to Mn_3O_4 on heating to 530°C. It is used in the preparation of potassium permanganate and in the production of Cl_2 gas. Over half a million tonnes per year of MnO_2 is used in dry batteries.

14. When MnO_2 is fused with KOH in the presence at air, the product formed is:

(a) purple colour $KMnO_4$

(b) green colour K_2MnO_4

(c) colourless MnO_4^-

(d) purple colour K_2MnO_4

15. In which of the following species, the colour is due to charge transfer.

(I) $[Mn(OH)_4]^{2-}$ (II) MnO_4^{2-}

(III) MnO_2 (IV) $KMnO_4$

(a) I, II, III (b) II, IV

(c) I, II (d) Only IV

Passage # 3 (Q. 16 and 17)

Iron forms iron halide salts by reacting the metal directly with halogen. FeI_3 does not exist. FeF_3 is white solid inspite of five unpaired electrons with d^5 configuration. $FeCl_3$ is soluble in water and is used as a mordant in dyeing industry.

16. FeI_3 does not exist because:

(a) of its large size.

(b) Fe^{3+} oxidises I^- to I_2.

(c) of low lattice energy.

(d) iodine is not highly electronegative enough to oxidise Fe to Fe^{3+}.

17. $FeCl_3$ solution added to $K_4[Fe(CN)_6]$ gives A while with KSCN gives B. A and B respectively are:

(a) $Fe_3[Fe(CN)_6]_2$, $Fe(CNS)_3$

(b) $Fe_4[Fe(CN)_6]_3$, $KFe(CNS)_3$

(c) $Fe_4[Fe(CN)_6]_3$, $K_3[Fe(CNS)_6]$

(d) $Fe_4[Fe(CN)_6]_3$, $K_3[Fe(SCN)_6]$

Passage # 4 (Q. 18 and 19)

Pyrolusite ore on oxidation with $KClO_3/KNO_3$ in basic medium produces dark green coloured compounds (A), which on electrolysis produces a purpule coloured compound (B). The purple coloured compound can be crystallisd 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 give another compound (D) along with oxygen.

18. The nature of compound (C) is:

(a) basic (b) acidic

(c) neutral (d) amphoteric

19. Identify (D)

(a) Mn_2O_7 (b) MnO_2

(c) $MnSO_4$ (d) Mn_2O_3

INTEGER VALUE TYPE QUESTIONS

20. Sum of highest stable oxidation states of following elements is:

Sc, Zn, Ti, Mn, Cr

21. Determine total number of unpaired electrons in following ions.

Ti^{3+}, V^{3+}, Cr^{3+}, Cr^{2+}, Mn^{3+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}

22. $FeC_2O_4 \xrightarrow{\Delta}$ products

Number of dimagnetic products = x

Number of unpaired electrons in paramagnetic product = y

Report your answer as (x + y).

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

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

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

x + y + z is:

(here x, y and z are oxidation states)

COLUMN MATCHING TYPE QUESTIONS

24.

	Column I		Column II
(A)	Kipp's apparatus waste	(P)	$(NH_4)_2SO_4.FeSO_4.6H_2O$
(B)	Green coloured compound	(Q)	$Cu(OH)_2$. $CuCO_3$
(C)	Leave(s) brown residue on heating	(R)	$FeSO_4$
(D)	Leave(s) black residue on heating	(S)	$CuCl_2.2H_2O$

25.

	Column I		Column II
(A)	Cu(I) and Zn(II) complexes	(P)	Pair of compounds having similar colour and same but non- zero magnetic moment.
(B)	$KMnO_4$ and $K_2Cr_2O_7$	(Q)	Pair of compounds which are diamagnetic but coloured.
(C)	Cu_2O and HgI_2	(R)	Pair of compounds having metals in the highest stable oxidation states.
(D)	$VOCl_2$ and $CuCl_2$	(S)	Pair of compounds which show diamagnetism and are colourless.

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. Match the reactions in column-I with nature of the reaction/type of the products in column-II

	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)	(s) Disproportionation

[IIT-2007]

2. Among the following, the coloured compound is:

(a) CuCl (b) $K_3[Cu(CN)_4]$

(c) CuF_2 (d) $[Cu(CH_3CN)_4]BF_4$

[IIT-2008]

3. The oxidation number of Mn in the product of alkaline oxidation fusion of MnO_2 is:

[IIT-2009]

4. Reduction of the metal centre in aqueous permanganate ion involves :

(a) 3 electrons in neutral medium

(b) 5 electrons in neutral medium

(c) 3 electrons in alkaline medium

(d) 5 electrons in acidic medium

[IIT-2011]

5. The colour of light abosrbed by an aqueous solution of $CuSO_4$ is:

(a) orange-red (b) blue-green

(c) yellow (d) violet

[IIT-2012]

6. The correct statement(s) about Cr^{2+} and Mn^{3+} is/are:

[Atomic numbers of Cr = 24 and Mn = 25]

(a) Cr^{2+} is a reducing agent

(b) Mn^{3+} is an oxdizing 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.

[JEE (Advanced) 2015]

7. Fe^{3+} is reduced to Fe^{2+} by using

(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

[JEE (Advanced) 2015]

8. The "spin-only" magnetic moment [in units of Bohr magneton, (μ_s) of Ni^{2+} in aqueous solution would be (atomic number of Ni = 28)

(a) 2.84 (b) 4.90

(c) 0 (d) 1.73

[AIEEE-2006]

9. Lanthanoid contraction is caused due to:

(a) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge.

(b) the appreciable shielding on outer electrons by 5f 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.

[AIEEE-2006]

10. Identify the incorrect statements among the following:

(a) The chemistry of various lanthanoids is very similar.

(b) 4f and 5f orbitals are equally shielded.

(c) d-block elements show irregular and erratic chemical properties among themselves.

(d) La and Lu have partially filled d orbitals and no other partially filled orbitals.

[AIEEE-2007]

11. The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because:

(a) The actinoids are more reactive than the lanthanoids.

(b) The 5f orbitals extend farther from the nucleus than the 4f orbitals.

(c) The 5f orbitals are more buried than the 4f orbitals

(d) There is a similarity between 4f and 5f orbitals in their angular part of the wave function.

[AIEEE-2007]

12. Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being:

(a) lesser energy difference between 5f and 6d than between 4f and 5d orbitals

(b) more energy difference between 5f and 6d than between 4f and 5d orbitals

(c) more reactive nature of the actinoids than the lanthanoids

(d) 4f orbitals more diffusion than the 5f orbitals.

[AIEEE-2008]

13. In context with transition elements, which of the following statements is incorrect?

(a) In the highest oxidation states, the transition metal show basic character and forms cationic complexes.

(b) In the highest oxidation states, of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding.

(c) Once the d^5 configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.

(d) In addition to the normal oxidation states, the zero oxidation state is also shown by these elements in complexes.

[AIEEE-2009]

14. Knowing that the chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements is incorrect?

(a) The ionic sizes of Ln(III) decreases in general with increasing atomic number.

(b) Ln(III) compounds are generally colourless.

(c) Ln(III) hydroxides are mainly basic in character.

(d) Because of the large size of the Ln(III) ions the bonding in its compounds is predominently ionic character.

[AIEEE-2009]

15. In context of the lanthanoids, which of the following statement is not correct?

(a) There is a gradual decreases in the radii of the members with increasing atomic number in the series.

(b) All the member exhibit +3 oxidation state.

(c) Because of similar properties the separation of lanthanoids is not easy.

(d) Availability of 4f electrons results in the formation of compounds in +4 state for all the members of the series.

[AIEEE-2011]

16. The outer electron configuration of Lu (Atomic number : 71) is:

(a) $4f^3\ 5d^5\ 6s^2$ (b) $4f^8\ 5d^{10}\ 6s^2$

(c) $4f^4\ 5d^4\ 6s^2$ (d) $4f^{14}\ 5d^1\ 6s^2$

[AIEEE-2011]

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

(a) Ferrous oxide is more basic in nature than the ferric oxide.

(b) Ferrous compounds are relatively more ionic than the corresponding ferric compounds

(c) Ferrous compounds are less volatile than the corresponding ferric compounds.

(d) Ferrous compouds are more easily hydrolysed than the corresponding ferric compounds.

[AIEEE-2012]

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

(a) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$; paramagnetic behaviour

(b) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size

(c) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution

(d) Sc < Ti < Cr < Mn: number of oxidation states

[JEE-Main - 2014]

19. Which series of reactions correctly represents chemical relations related to iron and its compound?

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

(b) $Fe \xrightarrow{O_2,\ \text{heat}} FeO \xrightarrow{\text{dil } H_2\ SO_4} FeSO_4 \xrightarrow{\text{heat}} Fe$

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

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

[JEE-Main - 2014]

20. The colour of $KMnO_4$ is due to:

(a) M → L charge transfer transition

(b) d → d transition

(c) L → M charge transfer transition

(d) σ → σ transition

[JEE-Main - 2015]

Answer Key

LEVEL I

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

LEVEL II

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

LEVEL III

1. (c, d) 2. (a, c, d) 3. (a, c, d) 4. (a, c) 5. (a, b, c) 6. (a, b) 7. (a, b, c, d) 8. (a, b, c)
9. (a,b,c) 10. (a,b,c,d) 11. (a, b, d) 12. (b) 13. (c) 14. (b) 15. (b) 16. (b)
17. (d) 18. (b) 19. (b) 20. (6) 21. (29) 22. (6) 23. (12)
24. A → R; B → P, Q,R,S; C → P, R; D → Q
25. A → S; B → Q, R; C → Q; D → P

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. A → p. s; B → r; C → p, q; D → p
2. (c) 3. (6) 4. (a, c, d) 5. (a) 6. (a, b, c) 7. (a, b) 8. (a) 9. (d) 10. (b)
11. (b) 12. (a) 13. (a) 14. (b) 15. (d) 16. (d) 17. (d) 18. (a) 19. (d) 20. (c)

Hints and Solutions

LEVEL I

1. **(d)** Unlike p-block elements, the various oxidation states of d-block elements differ by one unit.

2. **(d)** $M_{(s)} \rightarrow M^{+n}_{(aq)} + ne^-$

The above change involves sublimation, ionization and hydration.

3. **(b)** Sc^{3+} ([Ar] $4s^0$ $3d^0$) has no electrons in d-sub shell and hence, d-d transitions are not possible.

4. **(b)** Brass (Cu and Zn)

5. **(c)** Due to lanthanide contraction, elements in 5d-series have almost equal atomic and ionic radii with 4d- series elements.

6. **(b)** CuF_2 (Cu^{+2} = [Ar] $4s^0$ $3d^9$)

Due to d-d transitions, this compound is coloured.

7. **(c)** Stainless steel (Fe + Cr + Ni)

8. **(d)** Transition metals and their compound show catalytic activity because they can show variable oxidation state and they have tendency to form complex.

9. **(a)** $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2\uparrow$

10. **(d)** B_4C is a covalent network carbide.

11. **(b)** Interstitial compound do not have high chemical reactivity.

12. **(d)** K_2MnO_4 can be converted into $KMnO_4$ by passing Cl_2 (oxidizing agent) or by electrolytic oxidation or by disproportionation in acidic or in neutral medium.

13. **(c)** Sc and Zn show fixed oxidation state +3 and +2 respectively.

14. **(a)** Zn and Co are present in insulin and vitamin B_{12} respectively.

15. **(b)** $CrO_4^{2-} \underset{pH>7}{\overset{pH<7}{\rightleftharpoons}} Cr_2O_7^{2-}$

X will be less than 7 and Y will be more than 7.

16. **(d)**

$\overset{+7}{MnO_4^-}$ (VII group)

$\overset{+6}{Cr_2O_7^{2-}}$ (VI group)

$\overset{+5}{VO_4^{3-}}$ (V group)

$\overset{+6}{FeO_4^{2-}}$ (VIII group)

17. **(d)** S-block elements (Ca) are not formed interstitial compounds.

18. **(a)** MnF_6 does not exist.

19. **(c)** Mn_2O_7 and CrO_3 are acidic oxides.

20. **(a)** Solder (Pb + Sn)

21. **(b)** Chromium (+3, +6)

22. **(b)** Co^{+3} = [Ar] $4s^0$ $3d^6$ (4 unpaired e-)

Fe^{+2} = [Ar] $4s^0$ $3d^6$ (4 unpaired e-)

23. **(c)** SO_2 can decolorize acidified $KMnO_4$ but CO_2 cannot decolorize acidified $KMnO_4$.

24. **(d)** $Fe_2(SO_4)_3$ [Ferric sulphate] does not behave as reducing agent.

25. **(c)** In $Cr_2O_7^{-2}$, Six Cr-O bonds are identical while other two Cr-O bonds are identical but all eight Cr-O bonds are not identical.

26. **(d)** Sulphate (SO_4^{2-}) and chromate (CrO_4^{2-}) do not have same colour.

27. **(b)** $2Cu^{+2} + K_4[Fe(CN)_6] \rightarrow \underset{\text{Reddish-brown}}{Cu_2[Fe(CN)_6]\downarrow} + 4K^+$

28. **(d)** $Ce^{+4} = [Xe]\ 6s^0\ 5d^0$ (No unpaired e^-)

Hence, CeO_2 is colourless and diamagnetic in nature. The more common oxidation state of Ce is +3 hence, CeO_2 acts as a good oxidizing agent.

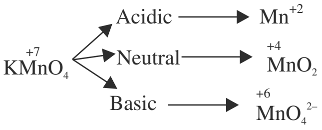
29. **(d)** Cl, Mn and Np all can show +7 oxidation state.

30. **(d)** Order of complex forming tendency:

$La^{+3} < Ce^{+3} < Eu^{+3} < Lu^{+3}$

LEVEL II

1. **(c)** Total number of Cr-O bonds in dichromate ion is 8.

2. **(b)** 

3. **(a)** $\overset{+4}{TiF_6^{2-}}$

$Ti^{+4} = [Ar]\ 4s^0\ 3d^0$ (No unpaired e- hence, no d-d transition)

$\overset{+1}{Cu_2Cl_2}$

$Cu^+ = [Ar]\ 4s^0\ 3d^{10}$ (No unpaired e- hence, no d-d transition)

4. **(a)** $\underset{\text{acid}}{CrO_3} + \underset{\text{base}}{2NaOH} \rightarrow \underset{\text{salt}}{Na_2CrO_4} + H_2O$

5. **(d)** 'Spin only' magnetic moment (μ_s) = $\sqrt{15}$ BM

$\mu_s = \sqrt{n(n+2)} = \sqrt{15}$

Here, n = 3 (unpaired e^-)

$M = [Ar]\ 4s^1\ 3d^5$

$M^{+3} = [Ar]\ 4s^0\ 3d^3$ (3 unpaired e^-)

6. **(a)** As atomic number increases, basic strength of hydroxides of lanthanides decreases.

7. **(a)** In $KMnO_4$, oxidation state of Mn is +7.

$Mn^{+7} = [Ar]\ 4s^0\ 3d^0$ (No unpaired e^-)

Colour in $KMnO_4$ is due to L → M charge transfer.

8. **(d)** $Zn + HNO_3\ (conc.) \rightarrow Zn(NO_3)_2 + NO_2 + H_2O$

NO_3^- ion is reduced in preference to H^+ ion.

9. **(c)** In process vegetable oil to ghee, the catalyst used is finely divided Ni.

10. **(b)** The X is $K_2Cr_2O_7$.

$K_2Cr_2O_7 \xrightarrow{\Delta} K_2CrO_4 + Cr_2O_3 + O_2\uparrow$

11. **(d)** X^- ion is I^-

$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2\downarrow + I_2$

12. **(a)** CO_2 does not react with $K_2Cr_2O_7$.

13. **(d)** As we move from Sc to Zn, number of unpaired e- increases upto Cr and then decreases.

14. **(c)** MnO_4^{-2} is green coloured due to L → M charge transfer. Oxidation state of Mn^{+6}.

$Mn^{+6} = [Ar]\ 4s^0\ 3d^1$ (1 unpaired e^-)

15. **(d)** $\underbrace{3HCl+HNO_3}_{\text{Aqura regia}} \rightarrow NOCl + 2H_2O + 2[Cl]$

$Au \xrightarrow{3[Cl]} AuCl_3 \xrightarrow{HCl} HAuCl_4$

16. **(c)** $KMnO_4 \xrightarrow{\text{Slightly alkaline}} MnO_2$

$KMnO_4 \xrightarrow{\text{Acidic}} Mn^{+2}$

17. **(b)** $K_2CrO_7 + H_2SO_4$ (Cold and Conc.) → CrO_3

18. **(c)** $\underset{(X)}{MnO_2} + K_2CO_3 + Air \xrightarrow{\text{Heat}} \underset{(Y)}{K_2MnO_4}$

$K_2MnO_4 + Cl_2 \longrightarrow \underset{(Z)}{KMnO_4}$

19. **(a)** When acidified $KMnO_4$ reacts with oxalic acid then reaction is slow in the beginning but becomes very rapid because Mn^{+2} acts as autocatalyst.

20. **(a)** $NaCl + K_2Cr_2O_7 + H_2SO_{4(Conc)} \rightarrow NaHSO_4 + KHSO_4 + H_2O + \underset{\text{deep-red}}{CrO_2Cl_2}\uparrow$

$CrO_2Cl_2 + NaOH \rightarrow \underset{\text{Yellow}}{Na_2CrO_4} + NaCl + H_2O$

21. **(a)** $HgCl_2 + NH_3 \rightarrow Hg(NH_2)Cl.\ HgO$

22. **(c)** $AgNO_3 \rightarrow \underset{(W)}{Ag} + \underset{(X)}{NO_2} + O_2$

$NO_2 + H_2O \rightarrow HNO_2 + HNO_3$

$HNO_3 + Ag \rightarrow AgNO_3 + NO + H_2O$

$AgNO_3 + Na_2S_2O_3\ (excess) \rightarrow \underset{(Z)}{Na_3[Ag(S_2O_3)_2]}$

23. **(c)** $Mn = [Ar]\ 3d^5\ 4s^2$

Mn shows +7 oxidation state.

24. **(b)** $AgCl + NH_3 \rightarrow \underset{\text{soluble}}{[Ag(NH_3)_2]Cl}$

$AgCl + Na_2S_2O_3 \rightarrow \underset{\text{soluble}}{Na_3[Ag(S_2O_3)_2]}$

$AgCl + NaCN \rightarrow \underset{\text{soluble}}{Na[Ag(CN)_2]}$

25. **(c)** $Zn^{+2} + NaOH \rightarrow Zn(OH)_2\downarrow$

$Zn(OH)_2 + NaOH(excess) \rightarrow \underset{\text{soluble}}{Na_2[Zn(OH)_4]}$

26. **(a)** $HNO_{3(dil)} + Ag \rightarrow AgNO_3 + NO + H_2O$

27. **(d)** $C_2O_4^{2-}$, NO_2^- and S^{2-} can behave as reducing agent while F^- ion cannot behave as reducing agent.

28. **(d)** Actinoids are radioactive while lanthanoids are not radioactive.

29. **(d)** Nb is a d-block element.

30. **(d)** No lanthanoids have electron in 6d-subshell.

LEVEL III

1. **(c, d)** $2Ag_2O \xrightarrow{\Delta} 4Ag + O_2$

$2HgO \xrightarrow{\Delta} 2Hg + O_2$

2. **(a, c, d)**

$Cu + HNO_3\ (dil) \longrightarrow Cu(NO_3)_2 + NO + H_2O$

$Cu + H_2SO_4\ (conc.) \longrightarrow CuSO_4 + SO_2 + H_2O$

$Cu + \text{Aqua regia}\ (3HCl + HNO_3) \longrightarrow CuCl_2$

3. **(a, c, d)**

$$\underset{\text{Oxidizing agent}}{\overset{+2}{Cu}SO_4} + NaOH + \underset{\text{reducing agent}}{\text{Glucose}} \rightarrow \underset{\text{red}}{\overset{+1}{Cu_2}O}$$

4. **(a, c)**

$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

Decomposition of acidic $KMnO_4$ is catalysed by sunlight.

$4MnO_4^- + 4H^+ \rightarrow 4MnO_2 + 2H_2O + 3O_2$

$3K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + MnO_2 + 4KOH$

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

($KMnO_4$ also acts as oxidizing agent in alkaline medium).

5. **(a, b, c)**

$Cl_2 + OH^- \rightarrow Cl^- + ClO_3^- + H_2O$

$MnO_4^{2-} + OH^- \rightarrow MnO_4^- + MnO_2 + H_2O$

$NO_2 + OH^- \rightarrow NO_2^- + NO_3^- + H_2O$

6. **(a, b)**

$Cu + HgCl_2 \rightarrow CuCl_2 + Hg$

$SnCl_2 + 2HgCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$

$Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg + SnCl_4$

7. **(a, b, c, d)**

$$\underset{\text{Oxidizing agent}}{\overset{+6}{Cr_2}O_7^{-2}} + \underset{\text{Reducing agent}}{3\overset{+4}{S}O_3^{2-}} + 8H^+ \rightarrow 2\overset{3+}{Cr} + 3\overset{+6}{S}O_4^{2-} + 4H_2O$$

8 **(a, b, c)**

Conditions required to form complexes are:

(a) Metal ion must have vacant orbitals.

(b) Metal ion must have small size or high charge density or higher nuclear charge.

9 **(a, b, c)**

$Ni^{+2} = [Ar]\ 4s^0 3d^8$

$Fe^{+2} = [Ar]\ 4s^0 3d^6$

$Cu^{+2} = [Ar]\ 4s^0 3d^9$

$Cu^+ = [Ar]\ 4s^0 3d^{10}$

Conditions required for d-d transition is electronic configuration of central metal from d^1 to d^9 hence, aqueous solution of Cu^+ is colourless.

10. **(a, b, c, d)**

$$\underset{\text{(green vitriol)}}{FeSO_4.7H_2O} \xrightarrow{\text{Strongly heated}} Fe_2O_3 + SO_2 + SO_3 + H_2O$$

Fe_2O_3 is basic oxide

H_2O is neutral oxide

SO_2 and SO_3 are acidic oxide

SO_2 is a reducing agent

11. **(a, b, d)**

$NaCl + K_2Cr_2O_7 + H_2SO_{4\,(conc.)} \longrightarrow \underset{\text{(Deep red)}}{CrO_2Cl_2\uparrow}$

$CrO_2Cl_2 + NaOH \longrightarrow \underset{\text{Yellow}}{Na_2CrO_4} + NaCl + H_2O$

$CrO_2Cl_2 + H_2O \longrightarrow \underset{\text{Yellow}}{H_2CrO_4} + HCl$

12. **(b)** $\underset{(A)}{FeSO_4.7H_2O} \xrightarrow{\Delta} \underset{(B)}{FeSO_4} \xrightarrow{\Delta} \underset{(C)}{Fe_2O_3} + \underset{(D)}{SO_3} + \underset{(E)}{SO_2}$

$SO_3 + HgCl_2 \longrightarrow HgO.HgSO_4\downarrow$

(Basic yellow mercury (II) sulphate)

$SO_2 + 2H_2S \longrightarrow \underset{\text{(turbidity)}}{3S} + 2H_2O$

13. **(c)** $SO_3 + HgCl_2 \longrightarrow HgO.\ HgSO_4\downarrow$

14. **(b)** $MnO_2 + KOH + O_2 \longrightarrow \underset{\text{green}}{K_2MnO_4} + H_2O$

15. **(b)** Cause of colour in MnO_4^{2-} and $KMnO_4$ is L → M charge transfer.

16. **(b)** I^- is very good reducing agent. It oxidizes into I_2 and reduces Fe^{3+} into Fe^{2+}.

17. **(d)** $FeCl_3 + K_4[Fe(CN)_6] \rightarrow Fe_4[Fe(CN)_6]_3$

$FeCl_3 + KSCN \rightarrow K_3[Fe(SCN)_6]$

18. **(b)** $\underset{(A)}{MnO_4^{2-}} \xrightarrow{\text{electrolysis}} \underset{(B)}{MnO_4^-}$

$\underset{(A)}{MnO_4^-} + H_2SO_{4\,(conc.)} \xrightarrow{\Delta} \underset{(C)}{Mn_2O_7}$

Mn_2O_7 is an acidic oxide.

19. **(b)** $Mn_2O_7 \xrightarrow{\Delta} \underset{(D)}{MnO_2} + O_2\uparrow$

20. **(22)**

Element	Higher stable oxidation state
Sc	+3
Zn	+2
Ti	+4
Mn	+7
Cr	+6

21. **(29)**

Element	No. of unpaired e^-
Ti^{3+}	1
V^{3+}	2
Cr^{3+}	3
Cr^{2+}	4
Mn^{3+}	4
Fe^{3+}	5
Fe^{2+}	4
Co^{2+}	3
Ni^{2+}	2
Cu^{2+}	1

22. $$FeC_2O_4 \xrightarrow{\Delta} \underset{\text{(Paramagnetic)}}{FeO} + \underbrace{CO + CO_2}_{\text{diamagnetic}}$$

Number of diamagnetic products (x) = 2

Number of unpaired e^- in FeO (y) = 4

$x + y = 6$

23. $KMnO_4 \xrightarrow[R.A.]{H^+} Mn^{+2}$

$KMnO_4 \xrightarrow[R.A.]{OH-} Mn^{+4}$

$K_2Cr_2O_7 \xrightarrow{OH^-} Cr^{+6}$

$x + y + z = 12$

24. (A → R ; B → P, Q, R, S ; C → P, R ; D → Q)

25. (A → S ; B → Q, R ; C → Q ; D → P)

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. (A → p, s ; B → r ; C → p, q ; D → p]

2. **(c)** $\overset{+2}{Cu}F_2$

$\overset{+2}{Cu} = [Ar]\ 4s^\circ 3d^9$

(due to d-d transition, CuF_2 is coloured)

3. $MnO_2 + KOH + O_2 \xrightarrow{\Delta} K_2\overset{+6}{Mn}O_4 + H_2O$

4. **(a, c, d)** $\overset{+7}{MnO_4^-} \xrightarrow{\text{acidic}} Mn^{+2}$

$MnO_4^- \xrightarrow{\text{neutral}} \overset{+4}{Mn}O_2$

$MnO_4^- \xrightarrow{\text{alkaline}} \overset{+4}{Mn}O_2$

5. **(a)** Colour of aqueous solution of $CuSO_4$ is blue green. It absorbs orange-red colour.

6. **(a, b, c)** $\underset{\text{Reducing agent}}{Cr^{2+}} \xrightarrow{\text{Oxidation}} Cr^{3+}$

$\underset{\text{Oxidizing agent}}{Mn^{3+}} \xrightarrow{\text{Reduction}} Mn^{2+}$

$Cr^{2+} = [Ar]\ 4s^0 3d^4$

$Mn^{3+} = [Ar]\ 4s^0 3d^4$

7. **(a, b)**

H_2O_2 in alkaline medium acts as reducing agent, reduces Fe^{3+} to Fe^{2+}.

8. **(a)** $Ni^{2+} = [Ar]\ 4s^0\ 3d^8$ (2 unpaired e^-)

$\mu_S = \sqrt{2(2+2)} \approx 2.84$

9. **(d)** Cause of lanthanoid contraction is the imperfect shielding on outer electrons by 4f electrons from the nuclear charge.

10. **(b)** 4f and 5f are not equally shielded.

11. **(b)** The 5f orbitals of actinoids extend farther from the nucleus than the 4f orbitals of lanthanoids. Hence, removal of e^- from 5f-orbitals is easier than 4f-orbitals.

12. **(a)** Antinoids show larger number of oxidation states than lanthanoids. It is due to lesser energy difference between 5f and 6d than 4f and 5d orbitals.

13. **(a)** In the highest oxidation states, the transition metal show acidic character and form cationic complexes.

14. **(b)** In general, due to presence of partially filled f-orbitals, Ln(III) compounds are coloured.

15. **(d)** All the members of lanthanoids exhibit +3 oxidation state not + 4 oxidation state.

16. **(d)** The outer electronic configuration of Lu is $4f^{14}$ $5d^1$ $6s^2$

17. **(d)** As the positive oxidation state increases, tendency of hydrolysis increases.

Ferric salts (Fe^{+3}) are more easily hydrolysed than the corresponding ferrous salts (Fe^{+2}).

18 **(a)**

Ions	Number of unpaired e^-
V^{+2}	3
Cr^{+2}	4
Mn^{+2}	5
Fe^{+2}	4

Order of paramagnetic behaviour :

$V^{+2} < Fe^{+2} = Cr^{+2} < Mn^{+2}$

19. **(d)** CO acts as a reducing agent to reduce FeO into Fe.

20. **(c)** Cause of colour of $KMnO_4$ is L → M charge transfer.