

## CHAPTER

## 22

## The d-and f-Block Elements

- Most common oxidation states of Ce (cerium) are [2002]
  - +2, +3
  - +2, +4
  - +3, +4
  - +3, +5.
- Arrange  $\text{Ce}^{+3}$ ,  $\text{La}^{+3}$ ,  $\text{Pm}^{+3}$  and  $\text{Yb}^{+3}$  in increasing order of their ionic radii. [2002]
  - $\text{Yb}^{+3} < \text{Pm}^{+3} < \text{Ce}^{+3} < \text{La}^{+3}$
  - $\text{Ce}^{+3} < \text{Yb}^{+3} < \text{Pm}^{+3} < \text{La}^{+3}$
  - $\text{Yb}^{+3} < \text{Pm}^{+3} < \text{La}^{+3} < \text{Ce}^{+3}$
  - $\text{Pm}^{+3} < \text{La}^{+3} < \text{Ce}^{+3} < \text{Yb}^{+3}$ .
- Which of the following ions has the maximum magnetic moment? [2002]
  - $\text{Mn}^{+2}$
  - $\text{Fe}^{+2}$
  - $\text{Ti}^{+2}$
  - $\text{Cr}^{+2}$ .
- The most stable ion is [2002]
  - $[\text{Fe}(\text{OH})_3]^{3-}$
  - $[\text{Fe}(\text{Cl})_6]^{3-}$
  - $[\text{Fe}(\text{CN})_6]^{3-}$
  - $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ .
- When  $\text{KMnO}_4$  acts as an oxidising agent and ultimately forms  $[\text{MnO}_4]^{-2}$ ,  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}^{+2}$  then the number of electrons transferred in each case respectively is [2002]
  - 4, 3, 1, 5
  - 1, 5, 3, 7
  - 1, 3, 4, 5
  - 3, 5, 7, 1.
- The radius of  $\text{La}^{3+}$  (Atomic number of La = 57) is  $1.06 \text{ \AA}$ . Which one of the following given values will be closest to the radius of  $\text{Lu}^{3+}$  (Atomic number of Lu = 71)? [2003]
  - $1.40 \text{ \AA}$
  - $1.06 \text{ \AA}$
  - $0.85 \text{ \AA}$
  - $1.60 \text{ \AA}$
- Ammonia forms the complex ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  with copper ions in alkaline solutions but not in acidic solutions. What is the reason for it? [2003]
  - In acidic solutions protons coordinate with ammonia molecules forming  $\text{NH}_4^+$  ions and  $\text{NH}_3$  molecules are not available
  - In alkaline solutions insoluble  $\text{Cu}(\text{OH})_2$  is precipitated which is soluble in excess of any alkali
  - Copper hydroxide is an amphoteric substance
  - In acidic solutions hydration protects copper ions
- A red solid is insoluble in water. However it becomes soluble if some KI is added to water. Heating the red solid in a test tube results in liberation of some violet coloured fumes and droplets of a metal appear on the cooler parts of the test tube. The red solid is [2003]
  - $\text{HgI}_2$
  - $\text{HgO}$
  - $\text{Pb}_3\text{O}_4$
  - $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
- A reduction in atomic size with increase in atomic number is a characteristic of elements of [2003]
  - d-block
  - f-block
  - radioactive series
  - high atomic masses
- What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid? [2003]
  - $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{H}_2\text{O}$  are formed
  - $\text{CrO}_4^{2-}$  is reduced to +3 state of Cr
  - $\text{CrO}_4^{2-}$  is oxidized to +7 state of Cr
  - $\text{Cr}^{3+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  are formed
- Which one of the following nitrates will leave behind a metal on strong heating? [2003]

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- (a) Copper nitrate (b) Manganese nitrate  
(c) Silver nitrate (d) Ferric nitrate
12. Of the following outer electronic configurations of atoms, the highest oxidation state is achieved by which one of them ? [2004]  
(a)  $(n-1)d^3 ns^2$  (b)  $(n-1)d^5 ns^1$   
(c)  $(n-1)d^8 ns^2$  (d)  $(n-1)d^5 ns^2$
13. The soldiers of Napoleon army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White metallic tin buttons got converted to grey power. This transformation is related to [2004]  
(a) a change in the partial pressure of oxygen in the air  
(b) a change in the crystalline structure of tin  
(c) an interaction with nitrogen of the air at very low temperature  
(d) an interaction with water vapour contained in the humid air
14. Among the properties (a) reducing (b) oxidising (c) complexing, the set of properties shown by  $CN^-$  ion towards metal species is [2004]  
(a) c, a (b) b, c  
(c) a, b (d) a, b, c
15. Cerium ( $Z = 58$ ) is an important member of the lanthanoids. Which of the following statements about cerium is **incorrect**? [2004]  
(a) The +4 oxidation state of cerium is not known in solutions  
(b) The +3 oxidation state of cerium is more stable than the +4 oxidation state  
(c) The common oxidation states of cerium are +3 and +4  
(d) Cerium (IV) acts as an oxidizing agent
16. The correct order of magnetic moments (spin only values in B.M.) among is [2004]  
(a)  $[Fe(CN)_6]^{4-} > [MnCl_4]^{2-} > [CoCl_4]^{2-}$   
(b)  $[MnCl_4]^{2-} > [Fe(CN)_6]^{4-} > [CoCl_4]^{2-}$   
(c)  $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [Fe(CN)_6]^{4-}$   
(d)  $[Fe(CN)_6]^{4-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$   
(Atomic nos. : Mn = 25, Fe = 26, Co = 27)
17. Heating mixture of  $Cu_2O$  and  $Cu_2S$  will give [2005]  
(a)  $Cu_2SO_3$  (b)  $CuO + CuS$   
(c)  $Cu + SO_3$  (d)  $Cu + SO_2$
18. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is: [2005]  
(a) +3 (b) +2  
(c) +6 (d) +4
19. Calomel ( $Hg_2Cl_2$ ) on reaction with ammonium hydroxide gives [2005]  
(a)  $HgO$   
(b)  $Hg_2O$   
(c)  $NH_2 - Hg - Hg - Cl$   
(d)  $HgNH_2Cl$
20. The lanthanide contraction is responsible for the fact that [2005]  
(a) Zr and Zn have the same oxidation state  
(b) Zr and Hf have about the same radius  
(c) Zr and Nb have similar oxidation state  
(d) Zr and Y have about the same radius
21. The value of the 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The correct one is [2005]  
(a)  $d^5$  (in strong ligand field)  
(b)  $d^3$  (in weak as well as in strong fields)  
(c)  $d^4$  (in weak ligand fields)  
(d)  $d^4$  (in strong ligand fields)
22. Which of the following factors may be regarded as the main cause of lanthanide contraction? [2005]  
(a) Greater shielding of 5d electrons by 4f electrons  
(b) Poorer shielding of 5d electrons by 4f electrons  
(c) Effective shielding of one of 4f electrons by another in the subshell  
(d) Poor shielding of one of 4f electron by another in the subshell

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Chemistry

23. A metal, M forms chlorides in its +2 and +4 oxidation states. Which of the following statements about these chlorides is correct? [2006]
- $\text{MCl}_2$  is more ionic than  $\text{MCl}_4$
  - $\text{MCl}_2$  is more easily hydrolysed than  $\text{MCl}_4$
  - $\text{MCl}_2$  is more volatile than  $\text{MCl}_4$
  - $\text{MCl}_2$  is more soluble in anhydrous ethanol than  $\text{MCl}_4$
24. Lanthanoid contraction is caused due to [2006]
- the same effective nuclear charge from Ce to Lu
  - the imperfect shielding on outer electrons by 4f electrons from the nuclear charge
  - the appreciable shielding on outer electrons by 4f electrons from the nuclear charge
  - the appreciable shielding on outer electrons by 5d electrons from the nuclear charge
25. The "spin-only" magnetic moment [in units of Bohr magneton, ( $\mu_B$ )] of  $\text{Ni}^{2+}$  in aqueous solution would be (At. No. Ni = 28) [2006]
- 6
  - 1.73
  - 2.84
  - 4.90
26. The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence [2007]
- $\text{PbX}_2 \ll \text{SnX}_2 \ll \text{GeX}_2 \ll \text{SiX}_2$
  - $\text{GeX}_2 \ll \text{SiX}_2 \ll \text{SnX}_2 \ll \text{PbX}_2$
  - $\text{SiX}_2 \ll \text{GeX}_2 \ll \text{PbX}_2 \ll \text{SnX}_2$
  - $\text{SiX}_2 \ll \text{GeX}_2 \ll \text{SnX}_2 \ll \text{PbX}_2$
27. Identify the incorrect statement among the following: [2007]
- 4f and 5f orbitals are equally shielded.
  - d-Block elements show irregular and erratic chemical properties among themselves.
  - La and Lu have partially filled d-orbitals and no other partially filled orbitals.
  - The chemistry of various lanthanoids is very similar.
28. The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because [2007]
- the 5f orbitals extend further from the nucleus than the 4f orbitals
  - the 5f orbitals are more buried than the 4f orbitals
  - there is a similarity between 4f and 5f orbitals in their angular part of the wave function
  - the actinoids are more reactive than the lanthanoids.
29. Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being [2008]
- 4f orbitals more diffused than the 5f orbitals
  - lesser energy difference between 5f and 6d than between 4f and 5d orbitals
  - more energy difference between 5f and 6d than between 4f and 5d orbitals
  - more reactive nature of the actinoids than the lanthanoids
30. Amount of oxalic acid present in a solution can be determined by its titration with  $\text{KMnO}_4$  solution in the presence of  $\text{H}_2\text{SO}_4$ . The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl [2008]
- gets oxidised by oxalic acid to chlorine
  - furnishes  $\text{H}^+$  ions in addition to those from oxalic acid
  - reduces permanganate to  $\text{Mn}^{2+}$
  - Oxidises oxalic acid to carbon dioxide and water
31. Knowing that the chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements is incorrect? [2009]
- The ionic size of Ln (III) decrease in general with increasing atomic number
  - Ln (III) compounds are generally colourless.
  - Ln (III) hydroxide are mainly basic in character.
  - Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character.
32. Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is incorrect? [2012]

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- (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 compounds are more easily hydrolysed than the corresponding ferric compounds.
33. Which of the following arrangements does not represent the correct order of the property stated against it? [2013]  
 (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
34. Which series of reactions correctly represents chemical reactions related to iron and its compound? [2014]  
 (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)  $Fe \xrightarrow{O_2, \text{heat}} FeO \xrightarrow{\text{dil. } H_2SO_4} FeSO_4 \xrightarrow{\text{heat}} Fe$   
 (c)  $Fe \xrightarrow{Cl_2, \text{heat}} FeCl_3 \xrightarrow{\text{heat, air}} FeCl_2 \xrightarrow{Zn} Fe$   
 (d)  $Fe \xrightarrow{O_2, \text{heat}} Fe_3O_4 \xrightarrow{CO, 600^\circ C} FeO \xrightarrow{CO, 700^\circ C} Fe$
35. The equation which is balanced and represents the correct product(s) is: [2014]  
 (a)  $Li_2O + 2KCl \longrightarrow 2LiCl + K_2O$   
 (b)  $[CoCl(NH_3)_5]^+ + 5H^+ \longrightarrow CO^{2+} + 5NH_4^+ + Cl^-$   
 (c)  $[Mg(H_2O)_6]^{2+} + (EDTA)^{4-} \xrightarrow{\text{excess NaOH}} [Mg(EDTA)]^{2-} + 6H_2O$   
 (d)  $CuSO_4 + 4KCN \longrightarrow K_2[Cu(CN)_4] + K_2SO_4$
36. Match the catalysts to the correct processes : [JEE M 2015]
- | Catalyst     | Process                             |
|--------------|-------------------------------------|
| (A) $TiCl_4$ | (i) Wacker process                  |
| (B) $PdCl_2$ | (ii) Ziegler - Natta polymerization |
| (C) $CuCl_2$ | (iii) Contact process               |
| (D) $V_2O_5$ | (iv) Deacon's process               |
- (a) (A) - (ii), (B) - (iii), (C) - (iv), (D) - (i)  
 (b) (A) - (iii), (B) - (i), (C) - (ii), (D) - (iv)  
 (c) (A) - (iii), (B) - (ii), (C) - (iv), (D) - (i)  
 (d) (A) - (ii), (B) - (i), (C) - (iv), (D) - (iii)
37. The color of  $KMnO_4$  is due to : [JEE M 2015]  
 (a)  $L \rightarrow M$  charge transfer transition  
 (b)  $\sigma - \sigma^*$  transition  
 (c)  $M \rightarrow L$  charge transfer transition  
 (d)  $d - d$  transition
38. Which of the following compounds is metallic and ferromagnetic? [JEE M 2016]  
 (a)  $VO_2$  (b)  $MnO_2$   
 (c)  $TiO_2$  (d)  $CrO_2$
39. In the following reactions,  $ZnO$  is respectively acting as a/an: [2017]  
 (A)  $ZnO + Na_2O \rightarrow Na_2ZnO_2$   
 (B)  $ZnO + CO_2 \rightarrow ZnCO_3$   
 (a) base and acid (b) base and base  
 (c) acid and acid (d) acid and base

**Answer Key**

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
(c)	(a)	(a)	(c)	(c)	(c)	(a)	(a)	(b)	(a)	(c)	(d)	(b)	(a)	(a)
16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
(c)	(d)	(a)	(d)	(b)	(d)	(d)	(a)	(b)	(c)	(d)	(a)	(a)	(b)	(c)
31	32	33	34	35	36	37	38	39						
(b)	(d)	(a)	(c)	(b)	(d)	(a)	(d)	(d)						

## SOLUTIONS

- (c) Common oxidation states of Ce (Cerium) are +3 and +4
- (a) In lanthanides there is a regular decrease in the atomic radii as well as ionic radii of trivalent ions as the atomic number increases from Ce to Lu. This decrease in size of atoms and ions is known as **lanthanide contraction**. Although the atomic radii do show some irregularities but ionic radii decreases from La to Lu. Thus the correct order is.  
 $\text{Yb}^{+3} < \text{Pm}^{+3} < \text{Ce}^{+3} < \text{La}^{+3}$   
 86.8pm 97pm 102pm 103pm
- (a)  $\text{Mn}^{++}$  – 5 unpaired electrons  
 $\text{Fe}^{++}$  – 4 unpaired electrons  
 $\text{Ti}^{++}$  – 2 unpaired electrons  
 $\text{Cr}^{++}$  – 4 unpaired electrons  
 hence maximum no. of unpaired electron is present in  $\text{Mn}^{++}$ .  
**NOTE** Magnetic moment  $\propto$  number of unpaired electrons
- (c) The cyano and hydroxo complexes are far more stable than those formed by halide ion. This is due to the fact that  $\text{CN}^-$  and  $\text{OH}^-$  are strong lewis bases (nucleophiles). Further  $[\text{Fe}(\text{OH})_5]^{3-}$  is not formed. hence most stable ion is  $[\text{Fe}(\text{CN})_6]^{3-}$
- (c)  $\text{Mn}_2\text{O}_3 \xrightarrow{-4e^-} [\text{KMnO}_4]^{+7} \xrightarrow{-e^-} [\text{MnO}_4]^{2-}$   
 $\swarrow -5e^- \quad \searrow -3e^-$   
 $\text{Mn}^{2+} \quad \text{MnO}_2$
- (c) Ionic radii  $\propto \frac{1}{z}$   
 Thus,  $\frac{z_2}{z_1} \Rightarrow \frac{1.06}{(\text{Ionic radii of } \text{Lu}^{3+})} = \frac{71}{57}$   
 $\Rightarrow$  Ionic radii of  $\text{Lu}^{3+} = 0.85 \text{ \AA}$
- (a)  $\ddot{\text{N}}\text{H}_3 + \text{H}^+ (\text{acid medium}) \rightleftharpoons \text{N}^+\text{H}_4$
- (a) When KI is added to mercuric iodide it dissolves in it and forms a complex.  

$$\underset{\substack{\text{red, solid} \\ \text{(insoluble)}}}{\text{HgI}_2} + \text{KI} \rightarrow \underset{\substack{\text{(soluble)}}}{\text{K}_2[\text{HgI}_4]}$$
  
 On heating  $\text{HgI}_2$  decomposes as  

$$\text{HgI}_2 \rightleftharpoons \text{Hg} + \text{I}_2$$

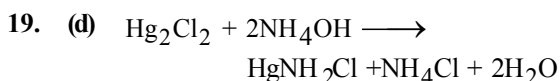
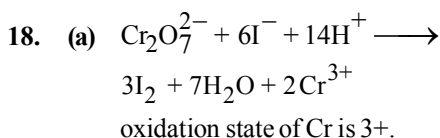
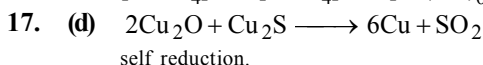
(violet vapours)
- (b) *f*-block elements show a regular decrease in atomic size due to lanthanide/actinide contraction.
- (a) When a solution of potassium chromate is treated with an excess of dilute nitric acid. Potassium dichromate and  $\text{H}_2\text{O}$  are formed.  
 $2\text{K}_2\text{CrO}_4 + 2\text{HNO}_3 \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{KNO}_3 + \text{H}_2\text{O}$   
 Hence  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{H}_2\text{O}$  are formed.
- (c)  $\text{AgNO}_3$  on heating till red **hot** decomposes as follows:  

$$\text{AgNO}_3 \rightarrow \text{Ag} + \text{NO}_2 + \frac{1}{2}\text{O}_2$$
- (d)  $(n-1)d^5ns^2$  attains the maximum O.S. of +7
- (b) Grey tin  $\rightleftharpoons$  white tin  
 Grey tin is brittle and crumbles down to powder in very cold climate  
 The conversion of grey tin to white tin is accompanied by increase in volume. This is known as **tin plaque** or **tin disease**.
- (a)  $\text{CN}^-$  ion acts as a good complexing as well as a reducing agent.
- (a) The +4 oxidation state of cerium is also known in solution.
- (c)  $[\text{Fe}(\text{CN})_6]^{4-} \rightarrow \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow} \boxed{:} \boxed{:} \boxed{:} \boxed{:}$   
 – no of unpaired electron = 0  
 $[\text{MnCl}_4]^{2-} \rightarrow \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow} \boxed{:} \boxed{:} \boxed{:} \boxed{:}$   
 – no of unpaired electron = 5  
 $[\text{CoCl}_4]^{2-} \rightarrow \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow} \boxed{:} \boxed{:} \boxed{:} \boxed{:}$   
 – no of unpaired electron = 3

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**NOTE** The greater the number of unpaired electrons, greater the magnitude of magnetic moment. Hence the correct order will be



20. (b) **NOTE** In vertical columns of transition elements, there is an increase in size from first member to second member as expected but from second member to third member, there is very small change in size and some times sizes are same. This is due to lanthanide contraction this is the reason for Zr and Hf to have same radius.

21. (d)  $d^5$  — strong ligand field

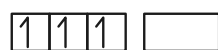


$t_{2g}$

$e_g$

$$\mu = n\sqrt{n+2} = \sqrt{3} = 1.73\text{BM}$$

$d^3$  — in weak as well as in strong field



$t_{2g}$

$e_g$

$$\mu = \sqrt{3(5)} = \sqrt{15} = 3.87\text{ B.M.}$$

$d^4$  — in weak ligand field



$t_{2g}$

$e_g$

$$\mu = \sqrt{4(8)} = \sqrt{24} = 4.89$$

$d^4$  — in strong ligand field



$t_{2g}$

$e_g$

$$\mu = \sqrt{2(4)} = \sqrt{8} = 2.82.$$

22. (d) In lanthanides, there is poorer shielding of  $5d$  electrons by  $4f$  electrons resulting in greater attraction of the nucleus over  $5d$  electrons and contraction of the atomic radii.

23. (a) Metal atom in the lower oxidation state forms the ionic bond and in the higher oxidation state the covalent bond. because higher oxidation state means small size and great polarizing power and hence greater the covalent character. Hence  $\text{MCl}_2$  is more ionic than  $\text{MCl}_4$ .

24. (b) The configuration of Lanthanides show that the additional electron enters the  $4f$  subshell. The shielding of one  $4f$  electron by another is very little or imperfect. The imperfect shielding of  $f$  electrons is due to the shape of  $f$  orbitals which is very much diffused. Thus as the atomic number increases, the nuclear charge increases by unity at each step. While no comparable increase in the mutual shielding effect of  $4f$  occurs. This causes a contraction in the size of the  $4f$  subshell. as a result atomic and ionic radii decreases gradually from La to Lu.

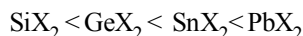
25. (c) The number of unpaired electrons in  $\text{Ni}^{2+}(\text{aq}) = 2$

Water is weak ligand hence no pairing will take place spin magnetic moment

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

$$= \sqrt{8} = 2.82$$

26. (d) Reluctance of valence shell electrons to participate in bonding is called inert pair effect. The stability of lower oxidation state (+2 for group 14 element) increases on going down the group. So the correct order is




27. (a)  $4f$  orbital is nearer to nucleus as compared to  $5f$  orbital therefore, shielding of  $4f$  is more than  $5f$ .

28. (a) **NOTE** More the distance between nucleus and outer orbitals, lesser will be force of attraction on them. Distance



between nucleus and  $5f$  orbitals is more as compared to distance between  $4f$  orbital and nucleus.

So actinoids exhibit more number of oxidation states in general than the lanthanoids.

29. (b)  **NOTE** The main reason for exhibiting larger number of oxidation states by actinoids as compared to lanthanoids is lesser energy difference between  $5f$  and  $6d$  orbitals as compared to that between  $4f$  and  $5d$  orbitals.

In case of actinoids we can remove electrons from  $5f$  as also from  $6d$  and due to this actinoids exhibit larger number of oxidation state than lanthanoids. Thus the correct answer is option (b)

30. (c) The titration of oxalic acid with  $\text{KMnO}_4$  in presence of  $\text{HCl}$  gives unsatisfactory result because of the fact that  $\text{KMnO}_4$  can also oxidise  $\text{HCl}$  along with oxalic acid.  $\text{HCl}$  on oxidation gives  $\text{Cl}_2$  and  $\text{HCl}$  reduces  $\text{KMnO}_4$  to  $\text{Mn}^{2+}$  thus the correct answer is (c).

31. (b) Most of the  $\text{Ln}^{3+}$  compounds except  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$  are coloured due to the presence of  $f$ -electrons.

32. (d)  $\text{Fe}^{3+}$  is easily hydrolysed than  $\text{Fe}^{2+}$  due to more positive charge.

33. (a)

- (a)  $\text{V} = 3d^3 4s^2$ ;  $\text{V}^{2+} = 3d^3 = 3$  unpaired electrons  
 $\text{Cr} = 3d^5 4s^1$ ;  $\text{Cr}^{2+} = 3d^4 = 4$  unpaired electrons  
 $\text{Mn} = 3d^5 4s^2$ ;  $\text{Mn}^{2+} = 3d^5 = 5$  unpaired electrons

$\text{Fe} = 3d^6 4s^2$ ;  $\text{Fe}^{2+} = 3d^6 = 4$  unpaired electrons  
 Hence the correct order of paramagnetic behaviour

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

- (b) For the same oxidation state, the ionic radii generally decreases as the atomic number increases in a particular transition series. hence the order is

$$\text{Mn}^{++} > \text{Fe}^{++} > \text{Co}^{++} > \text{Ni}^{++}$$

- (c) In solution, the stability of the compound depends upon electrode potentials, SEP of the transitions metal ions are given as

$$\text{Co}^{3+} / \text{Co} = +1.97, \text{Fe}^{3+} / \text{Fe} = +0.77;$$

$\text{Cr}^{3+} / \text{Cr}^{2+} = -0.41$ ,  $\text{Sc}^{3+}$  is highly stable as it does not show +2 O. S.

- (d)  $\text{Sc} - (+2), (+3)$

$$\text{Ti} - (+2), (+3), (+4)$$

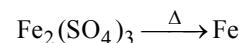
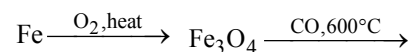
$$\text{Cr} - (+1), (+2), (+3), (+4), (+5), (+6)$$

$$\text{Mn} - (+2), (+3), (+4), (+5), (+6), (+7)$$

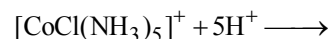
$$\text{i.e. Sc} < \text{Ti} < \text{Cr} = \text{Mn}$$

34. (c) In equation (i)  $\text{Fe}_2(\text{SO}_4)_3$  and in equation (ii)  $\text{Fe}_2(\text{SO}_4)_3$  on decomposing will form oxide instead of Fe.

The correct sequence of reactions is



35. (b) The complex  $[\text{CoCl}(\text{NH}_3)_5]^+$  decomposes under acidic medium, so



36. (d) (A) - (ii), (B) - (i), (C) - (iv), (D) - (iii)

37. (a)  $\text{L} \rightarrow \text{M}$  charge transfer spectra.  $\text{KMnO}_4$  is colored because it absorbs light in the visible range of electromagnetic radiation. The permanganate ion is the source of color, as a ligand to metal, ( $\text{L} \rightarrow \text{M}$ ) charge transfer takes place between oxygen's  $p$  orbitals and the empty  $d$ -orbitals on the metal. This charge transfer takes place when a photon of light is absorbed, which leads to the purple color of the compound.

38. (d) Out of all the four given metallic oxides  $\text{CrO}_2$  is attracted by magnetic field very strongly. The effect persists even when the magnetic field is removed. Thus  $\text{CrO}_2$  is metallic and ferromagnetic in nature

39. (d) Although  $\text{ZnO}$  is an amphoteric oxide but in given reaction.

