CHAPTER



d-and f-Block Elements

The colour of KMnO₄ is due to

(a) $L \to M$ charge transfer transition

1. When XO_2 is fused with an alkali metal hydroxide in presence of an oxidizing agent such as KNO3, a dark green product is formed which disproportionates in acidic solution to afford a dark purple solution. X is (d) Mn (a) Ti (b) Cr (c) V

2. In the following reactions, ZnO is respectively acting as a/an

(A) $ZnO + Na_2O \rightarrow Na_2ZnO_2$

- (B) $ZnO + CO_2 \rightarrow ZnCO_3$
- (a) acid and acid (b) acid and base
- (c) base and acid (d) base and base.

(2017)

(Online 2017)

8.

The pair of compounds having metals in their highest 3. oxidation state is

(a) $[Fe(CN)_6]^{3-}$ and $[Cu(CN)_4]^{2-}$

- (b) $[FeCl_4]^-$ and Co_2O_3
- (c) $[NiCl_4]^{2-}$ and $[CoCl_4]^{2-}$
- (d) MnO_2 and CrO_2Cl_2
- Which of the following ions does not liberate hydrogen 4. gas on reaction with dilute acids?

(a)
$$Mn^{2+}$$
 (b) Ti^{2+} (c) V^{2+} (d) Cr^{2+} (Online 2017)

Which one of the following species is stable in aqueous 5. solution?

(a)
$$Cr^{2+}$$
 (b) MnO_4^{2-} (c) MnO_4^{3-} (d) Cu^+
(Online 2016)

Match the catalysts to the correct processes. 6.

Catalyst Process

(A) TiCl₄ (i) Wacker process

- (B) PdCl, (ii) Ziegler-Natta polymerization
- (C) CuCl₂ (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)
$$(A) - (ii), (B) - (i), (C) - (iv), (D) - (iii)$$
 (2015)

(b) $\sigma \rightarrow \sigma^*$ transition (c) $M \rightarrow L$ charge transfer transition (d) d - d transition. (2015)Which of the following statements is false? (a) $\operatorname{CrO}_4^{2-}$ is tetrahedral in shape. (b) $\operatorname{Cr}_2^{O_7^{2-}}$ has a $\operatorname{Cr} - O - \operatorname{Cr}$ bond. (c) $Na_2Cr_2O_7$ is a primary standard in volumetry. (d) $Na_{2}Cr_{2}O_{7}$ is less soluble than $K_{2}Cr_{2}O_{7}$. (Online 2015) A pink coloured salt turns blue on heating. The presence

9. of which cation is most likely? (a) $7n^{2+}$ (1) C_{2}^{2+} (a) Cu^{2+} (b) Fe^{2+}

$$(0) ZII^2 \qquad (0) CO^2$$

$$(Online 2015)$$

- 10. The equation which is balanced and represents the correct product(s) is
 - (a) $CuSO_4 + 4KCN \rightarrow K_2[Cu(CN)_4] + K_2SO_4$
 - (b) $Li_2O + 2KCl \rightarrow 2LiCl + K_2O$
 - (c) $[CoCl(NH_3)_5]^+ + 5H^+ \rightarrow Co^{2+} + 5NH_4^+ + Cl^-$
 - (d) $[Mg(H_2O)_6]^{2+} + (EDTA)^{4-} \xrightarrow{excess NaOH}$

$$[Mg(EDTA)]^{2-} + 6H_2O$$
 (2014)

- 11. Which of the following arrangements does not represent the correct order of the property stated against it?
 - (a) Sc < Ti < Cr < Mn: number of oxidation states
 - (b) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behaviour (c) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size

 - (d) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution. (2013)
- 12. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E^{\circ}_{M^{3+}/M^{2+}}$ value?

(a) Co
$$(Z = 27)$$
 (b) Cr $(Z = 24)$

(c) Mn (
$$Z = 25$$
) (d) Fe ($Z = 26$) (2013)

- 13. Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is incorrect?
 - (a) Ferrous compounds are relatively more ionic than the corresponding ferric compounds.
 - (b) Ferrous compounds are less volatile than the corresponding ferric compounds.
 - Ferrous compounds are more easily hydrolysed than (c) the corresponding ferric compounds.
 - (d) Ferrous oxide is more basic in nature than the ferric oxide. (2012)

- 14. The outer electronic configuration of Gd (Atomic No : 64) is
 - (a) $4f^{3}5d^{5}6s^{2}$ (b) $4f^{8}5d^{0}6s^{2}$
 - (c) $4f^45d^46s^2$ (d) $4f^75d^16s^2$ (2011)
- **15.** In context of the lanthanoids, which of the following statement is not correct?
 - (a) There is a gradual decrease in the radii of the members with increasing atomic number in the series.
 - (b) All the members 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.
 (2011)
- 16. The correct order of $E^{\circ}_{M^{2+}/M}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is
 - (a) Cr > Mn > Fe > Co (b) Mn > Cr > Fe > Co
 - (c) Cr > Fe > Mn > Co (d) Fe > Mn > Cr > Co

(2010)

- 17. In context with the transition elements, which of the following statements is incorrect?
 - (a) In addition to the normal oxidation states, the zero oxidation state is also shown by these elements in complexes.
 - (b) In the highest oxidation states, the transition metals show basic character and form cationic complexes.
 - (c) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding.
 - (d) Once the d^5 configuration is exceeded, the tendency to involve all the 3*d* electrons in bonding decreases. (2009)
- **18.** Knowing that the chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements is incorrect?
 - (a) Because of the large size of the Ln(III) ions the bonding in its compounds is predominantly ionic in character.
 - (b) The ionic sizes of Ln(III) decrease in general with increasing atomic number.
 - (c) Ln(III) compounds are generally colourless.
 - (d) Ln(III) hydroxides are mainly basic in character.

(2009)

- 19. In which of the following octahedral complexes of Co (At. no. 27), will the magnitude of Δ_{oct} be the highest?
 - (a) $[Co(NH_3)_6]^{3+}$ (b) $[Co(CN)_6]^{3-}$
 - (c) $[Co(C_2O_4)_3]^{3-}$ (d) $[Co(H_2O)_6]^{3+}$ (2008)
- **20.** Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being
 - (a) more reactive nature of the actinoids than the lanthanoids
 - (b) 4f orbitals more diffused than the 5f orbitals
 - (c) lesser energy difference between 5f and 6d than between 4f and 5d orbitals
 - (d) more energy difference between 5f and 6d than between 4f and 5d-orbitals. (2008)

- 21. The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because
 - (a) the 5*f* orbitals extend further from the nucleus than the 4f orbitals
 - (b) the 5f orbitals are more buried than the 4f orbitals
 - (c) there is a similarity between 4f and 5f orbitals in their angular part of the wave function
 - (d) the actinoids are more reactive than the lanthanoids. (2007)
- 22. Identify the incorrect statement among the following:
 - (a) 4*f*-and 5*f*-orbitals are equally shielded.
 - (b) *d*-Block elements show irregular and erratic chemical properties among themselves.
 - (c) La and Lu have partially filled *d*-orbitals and no other partially filled orbitals.
 - (d) The chemistry of various lanthanoids is very similar. (2007)
- 23. The "spin-only" magnetic moment [in units of Bohr magneton, (μ_B)] of Ni²⁺ in aqueous solution would be (atomic number of Ni = 28)

- 24. Nickel (Z = 28) combines with a uninegative monodentate ligand X⁻ to form a paramagnetic complex $[NiX_4]^{2-}$. The number of unpaired electron(s) in the nickel and geometry of this complex ion are, respectively
 - (a) one, tetrahedral (b) two, tetrahedral
 - (c) one, square planar (d) two, square planar.

(2006)

- **25.** Which of the following factors may be regarded as the main cause of lanthanide contraction?
 - (a) Poor shielding of one of 4*f*-electron by another in the subshell.
 - (b) Effective shielding of one of 4*f*-electrons by another in the subshell.
 - (c) Poorer shielding of 5d electrons by 4f-electrons.

(d) Greater shielding of 5d electrons by 4f-electrons.

(2006)

- 26. The lanthanide contraction is responsible for the fact that
 - (a) Zr and Y have about the same radius
 - (b) Zr and Nb have similar oxidation state
 - (c) Zr and Hf have about the same radius
 - (d) Zr and Zn have the same oxidation state. (2005)
- 28. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is
 (a) +4
 (b) +6
 (c) +2
 (d) +3

(b)
$$+6$$
 (c) $+2$ (d) $+3$ (2005)

29. Heating mixture of Cu₂O and Cu₂S will give

(a) Cu + SO₂
(b) Cu + SO₃
(c) CuO + CuS
(d) Cu₂SO₃

- **30.** The correct order of magnetic moments (spin only values in B.M.) among is
 - (a) $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [Fe(CN)_6]^{4-}$
 - (b) $[MnCl_4]^{2-} > [Fe(CN)_6]^{4-} > [CoCl_4]^{2-}$
 - (c) $[Fe(CN)_6]^{4-} > [MnCl_4]^{2-} > [CoCl_4]^{2-}$
 - (d) $[Fe(CN)_6]^{4-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$.
 - (Atomic nos.: Mn = 25, Fe = 26, Co = 27) (2004)
- **31.** Cerium (Z = 58) is an important member of the lanthanoids. Which of the following statements about cerium is incorrect?
 - (a) The common oxidation states of cerium are +3 and +4.
 - (b) The +3 oxidation state of cerium is more stable than +4oxidation state
 - The +4 oxidation state of cerium is not known in (c) solutions.
 - (d) Cerium (IV) acts as an oxidising agent. (2004)
- 32. Excess of KI reacts with CuSO₄ solution and then Na₂S₂O₃ solution is added to it. Which of the statements is incorrect for this reaction?
 - (b) CuI₂ is formed. (a) Cu_2I_2 is formed.
 - (c) $Na_2S_2O_3$ is oxidised. (d) Evolved I_2 is reduced.
 - (2004)
- **33.** Of the following outer electronic configurations of atoms, the highest oxidation state is achieved by which one of them?
 - (a) $(n-1)d^8ns^2$ (b) $(n-1)d^5ns^1$ (c) $(n-1)d^3ns^2$ (d) $(n-1)d^5ns^2$. (2004)
- 34. For making good quality mirrors, plates of float glass are used. These are obtained by floating molten glass over a liquid metal which does not solidify before glass. The metal used can be
 - (a) mercury (b) tin
 - (c) sodium (d) magnesium. (2003)
- 35. Which one of the following nitrates will leave behind a metal on strong heating?
 - (a) Ferric nitrate (b) Copper nitrate (c) Manganese nitrate (d) Silver nitrate (2003)
- **36.** The radius of La^{3+} (Atomic number of La = 57) is 1.06 Å. Which one of the following given values will be closest to the radius of Lu^{3+} (Atomic number of Lu = 71)? (a) 1.60 Å (b) 1.40 Å
 - (c) 1.06 Å (d) 0.85 Å (2003)
- 37. What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid?
 - (a) Cr^{3+} and $Cr_2O_7^{2-}$ are formed.
 - (b) $Cr_2O_7^{2-}$ and H_2O are formed.

(c) CrO_4^{2-} is reduced to +3 state of Cr.

(d) CrO_4^{2-} is oxidised to +7 state of Cr. (2003)

- **38.** The number of *d*-electrons retained in Fe^{2+} (At. no. Fe = 26) ions is
 - (a) 3 (b) 4 (c) 5 (d) 6
- **39.** The atomic numbers of vanadium (V), chromium (Cr), manganese (Mn) and iron (Fe) are respectively 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionisation enthalpy? (c) M (b) Cr (a) V

(2003)

(2003)

- **40.** A reduction in atomic size with increase in atomic number is a characteristic of elements of
 - (a) high atomic masses (b) d-block
 - (c) f-block (d) radioactive series.

(2003)

- 41. 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
 - (a) $(NH_4)_2Cr_2O_7$ (b) HgI₂ (d) Pb₃O₄. (2003)(c) HgO

42. How do we differentiate between Fe^{3+} and Cr^{3+} in group III? (a) By taking excess of NH₄OH solution.

- (b) By increasing NH_4^+ ion concentration.
- (c) By decreasing OH⁻ ion concentration.
- (d) Both (b) and (c). (2002)
- 43. The most stable ion is
 - (a) $[Fe(OH)_3]^{3-1}$ (b) [Fe(Cl)₆]³⁻ (c) $[Fe(CN)_6]^{3-}$ (d) $[Fe(H_2O)_6]^{3+}$ (2002)
- 44. Arrange Ce³⁺, La³⁺, Pm³⁺ and Yb³⁺ in increasing order of their ionic radii.
 - (a) $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$
 - (b) $Ce^{3+} < Yb^{3+} < Pm^{3+} < La^{3+}$
 - (c) $Yb^{3+} < Pm^{3+} < La^{3+} < Ce^{3+}$
 - (d) $Pm^{3+} < La^{3+} < Ce^{3+} < Yb^{3+}$ (2002)
- 45. Most common oxidation states of Ce (cerium) are (a) +2, +3 (b) +2, +4 (c) +3, +4 (d) +3, +5(2002)

46. Which of the following ions has the maximum magnetic moment? (a) Mn²⁺

(b)
$$Fe^{2+}$$
 (c) Ti^{2+} (d) Cr^{2+} (2002)

ANSWER KEY													
1.	(d)	2. (b)	3. (None) 4. (a)	5. (b)	6. (d)	7. (a)	8. (c,d)	9. (d)	10. (c)	11. (b)	12. (a)		
13.	(c)	14. (d)	15. (d) 16. (b)	17. (b)	18. (c)	19. (b)	20. (c)	21. (a)	22. (a)	23. (a)	24. (b)		
25.	(a)	26. (c)	27. (a) 28. (d)	29. (a)	30. (a)	31. (c)	32. (b)	33. (b)	34. (a)	35. (d)	36. (d)		
37.	(b)	38. (d)	39. (b) 40. (c)	41. (b)	42. (d)	43. (b)	44. (a)	45. (c)	46. (a)				

Explanations

1. (d): X is Mn. MnO₂ reacts with alkali metal hydroxide in presence of an oxidising agent, KNO₃ to give potassium manganate, K₂MnO₄.

 $\begin{array}{l} MnO_2+2KOH+KNO_3 \longrightarrow K_2MnO_4+KNO_2+H_2O\\ In \ acidic \ solution, \ K_2MnO_4 \ changes \ to \ KMnO_4 \ \ (dark \ purple \ solution) \end{array}$

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

2. (b): ZnO is an amphoteric oxide. So, it can act either as an acid or as a base.

 $ZnO + Na_2O \longrightarrow Na_2ZnO_2$ Acid Base Salt

ZnO acts as an acidic oxide.

 $ZnO + CO_2 \longrightarrow ZnCO_3$ Base Acid Salt

ZnO acts as a basic oxide.

3. (None) : (a) $[Fe(CN)_6]^{3-} \Rightarrow x + (6 \times -1) = -3 \Rightarrow x = +3$ $[Cu(CN)_4]^{2-} \Rightarrow x + (4 \times -1) = -2 \Rightarrow x = +2$

The possible highest oxidation state of Fe is +6 while that of Cu is +2.

(b) $[\operatorname{FeCl}_4]^- \Rightarrow x + (4 \times -1) = -1 \Rightarrow x = +3$ $\operatorname{Co}_2 O_3 \Rightarrow 2x + (3 \times -2) = 0 \Rightarrow x = +3$ The possible highest oxidation state of Co is +4. (c) $[\operatorname{NiCl}_4]^{2-} = x + (4 \times -1) = -2 \Rightarrow x = +2$ $[\operatorname{CoCl}_4]^{2-} = x + (4 \times -1) = -2 \Rightarrow x = +2$ The possible highest oxidation state of Ni is +4. (d) $\operatorname{MnO}_2 = x + (2 \times -2) = 0 \Rightarrow x = +4$ $\operatorname{CrO}_2 \operatorname{Cl}_2 = x + (2 \times -2) + (2 \times -1) = 0 \Rightarrow x = +6$

The possible highest oxidation state of Mn is +7 while that of Cr is +6.

4. (a) : The third ionisation energy of Mn is too high due to stable half filled 3*d*-orbital. Hence, it cannot further get oxidised to liberate hydrogen.

5. (b): $Cr^{2+}(d^4)$ is unstable and is oxidised to $Cr^{3+}(d^3 i.e., t^3_{2g})$ which is more stable.

 Cu^+ is unstable and is oxidised to Cu^{2+} which has more negative enthalpy of hydration.

Similarly $Mn^{3+}(d^4)$ in MnO_4^{3-} is unstable and is reduced to $Mn^{2+}(d^5)$. MnO_4^{2-} ion is far more likely to exist in a very high pH solution and is stable for a few hours in alkalies.

6. (d)

7. (a) : The deep purple colour of KMnO_4 is not due to *d-d* transitions but due to charge transfer from O to Mn (*i.e*; $L \rightarrow M$), which reduces the oxidation state of Mn from +7 to +6 momentarily. (c,d): Na₂Cr₂O₇ is not used as primary standard in volumetry as it is deliquescent. Na₂Cr₂O₇ is more soluble than K₂Cr₂O₇.
 (d): In aqueous solution, Co²⁺ ion exists as [Co(H₂O)₆]²⁺

ion and has pink colour. When heated, it turns blue due to dehydration.

10. (c) : (a) $2CuSO_4 + 10KCN \longrightarrow 2K_3[Cu(CN)_4]$

Pot. cuprocyanide + $2K_2SO_4 + (CN)_2$

(b) Reaction is unfavourable in the forward direction, as K_2O is unstable while Li_2O is stable.

(c) Complex $[CoCl(NH_3)_5]^+$ decomposes to NH_4^+ salt under acidic medium.

(d)
$$[Mg(H_2O)_6]^{2+}_{(aq)} + (EDTA)^{4-}_{(aq)} \xrightarrow{excess NaOH}$$

 $[Mg(EDTA)]^{2-}_{(aq)} + 6H_2O_{(l)}$

Reaction is unbalanced w.r.t. charge.

11. (b) : Number of unpaired electrons in Fe^{2+} is less than Mn^{2+} , so Fe^{2+} is less paramagnetic than Mn^{2+} .

12. (a)

13. (c) : Ferrous oxide is more basic, more ionic, less volatile and less easily hydrolysed than ferric oxide.

14. (d) : The electronic configuration of ${}_{64}$ Gd = [Xe]⁵⁴ 4f⁷ 5d¹ 6s²

15. (d): Availability of 4f electrons does not result in the formation of compounds in +4 state for all the members of the series.

16. (b): $E^{\circ}_{Mn^{2+}/Mn} = -1.18 \text{ V}$ $E^{\circ}_{Cr^{2+}/Cr} = -0.91 \text{ V}$ $E^{\circ}_{Fe^{2+}/Fe} = -0.44 \text{ V}$ $E^{\circ}_{Co^{2+}/Co} = -0.28 \text{ V}$

17. (b): When the transition metals are in their highest oxidation state, they no longer have tendency to give away electrons, thus they are not basic but show acidic character and form anionic complexes.

18. (c) : Ln^{3+} compounds are generally coloured in the solid state as well as in aqueous solution. Colour appears due to presence of unpaired *f*-electrons which undergo *f*-*f* transition.

19. (b) : Strong field ligand such as CN^- , usually produce low spin complexes and large crystal field splittings. H₂O is a weaker field ligand than NH₃ and C₂O₄²⁻ therefore

 $\Delta_{oct} [Co(H_2O)_6]^{3+} \le \Delta_{oct} [Co(C_2O_4)]^{3-} \le [Co(NH_3)_6]^{3+}$

Common ligands in order of increasing crystal field strength are given below :

 $I^- < Br^- < Cl^- < F^- < OH^- < C_2O_4^{-2-} < H_2O < NH_3 < en < NO_2^{-2-} < CN^{-1}$

20. (c) : Actinoids show different oxidation states such as +2, +3, +4, +5, +6 and +7. However +3 oxidation state is most common among all the actinoids.

The wide range of oxidation states of actinoids is attributed to the fact that the 5*f*, 6*d* and 7*s* energy levels are of comparable energies. Therefore all these three subshells can participate. **21.** (a) : As the distance between the nucleus and 5*f* orbitals (actinides) is more than the distance between the nucleus and 4*f* orbitals (lanthanides) hence the hold of nucleus on valence electron decreases in actinides. For this reason the actinoides exhibit more number of oxidation states in general.

22. (a) : The decrease in the force of attraction exerted by the nucleus on the valency electrons due to presence of electrons in the inner shells is called shielding effect. An 4*f* orbital is nearer to the nucleus than 5*f* orbitals. Hence shielding of 4*f* is more than 5*f*.

Number of unpaired electrons = 2

Geometry = tetrahedral.

25. (a) : As we proceed from one element to the next element in the lanthanide series, the nuclear charge, *i.e.* atomic number increases by one unit and the addition of one electron occurs at the same time in 4f-energy shell. On account of the very diffused shapes of f-orbitals, the 4f-electrons shield each other quite poorly from the nuclear charge. Thus, the effect of nuclear charge increase is somewhat more than the changed shielding effect. This brings the valence shell nearer to the nucleus and hence the size of atom or ion goes on decreasing as we move in the series. The sum of the successive reactions is equal to the total lanthanide contraction.

26. (c) : In each vertical column of transition elements, the elements of second and third transition series resemble each other more closely than the elements of first and second transition series on account of lanthanide contraction. The pairs of elements such as Zr-Hf, Mo-W, Nb-Ta, etc; possess almost the same properties.

27. (a) : Calomel on reaction with ammonium hydroxide turns black. The black substance is a mixture of mercury and mercuric amino chloride.

$$Hg_{2}Cl_{2} + 2NH_{4}OH \rightarrow \underbrace{Hg \swarrow _{Cl}^{NH_{2}} + Hg + NH_{4}Cl + 2H_{2}O}_{Black}$$

28. (d):
$$\operatorname{Cr}_2 \operatorname{O}_7^{2-} + 14\operatorname{H}^+ + 6\operatorname{I}^- \longrightarrow 2\operatorname{Cr}^{3+} + 7\operatorname{H}_2 \operatorname{O} + 3\operatorname{I}_2$$

29. (a) : $Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$ This is an example of auto-reduction. **30.** (a) :

$$[\operatorname{MnCl}_{4}]^{2-} \rightarrow \overbrace{\uparrow \uparrow \uparrow \uparrow \uparrow}^{3d} \overbrace{\vdots}^{4s} \overbrace{\downarrow}^{4p} \overbrace{\vdots}^{4p} \overbrace{\vdots}^{sp^{3}}$$
Number of unpaired electrons = 5
$$[\operatorname{CoCl}_{4}]^{2-} \rightarrow \overbrace{1l}^{1l} 11111 \overbrace{\vdots}^{1l} \overbrace{\vdots}^{sp^{3}} \overbrace{\vdots}^{sp^{3}}$$

Number of unpaired electrons = 3

Number of unpaired electrons = 0

Magnetic moment = $n\sqrt{n+2}$

where n = number of unpaired electrons.

i.e. greater the number of unpaired electrons, greater will be the paramagnetic character.

31. (c) : +4 oxidation state of cerium is also known in solutions.

32. (b):
$$4KI + 2CuSO_4 \longrightarrow \overset{0}{I_2} + Cu_2I_2 + 2K_2SO_4$$

 $\overset{0}{I_2} + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$
33. (b): $1 1 1 1 1 1 1 1$

 $(n-1)d^5 ns^2$ can achieve the maximum oxidation state of +7.

34. (a) : Mercury is such a metal which exists as liquid at room temperature.

35. (d) : When heated at red heat, $AgNO_3$ decomposes to metallic silver.

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

36. (d) : Due to lanthanide contraction, the ionic radii of Ln^{3+} (lanthanide ions) decreases from La^{3+} to Lu^{3+} . Thus the lowest value (here 0.85 Å) is the ionic radius of Lu^{3+} .

37. (b) : Dilute nitric acid converts chromate into dichromate and H_2O .

 $2K_2CrO_4 + 2HNO_3 \rightarrow K_2Cr_2O_7 + 2KNO_3 + H_2O_3$

or,
$$2 \operatorname{CrO}_{4}^{2-} \xrightarrow{\operatorname{H}^{+}} \operatorname{Cr}_{2}\operatorname{O}_{7}^{2-} + \operatorname{H}_{2}\operatorname{O}$$

Yellow Orange

38. (d): ${}_{26}Fe = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ Fe²⁺ = $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

The number of d -electrons retained in $Fe^{2+} = 6$.

39. (b) : The second ionisation potential values of Cu and Cr are sufficiently higher than those of neighbouring elements. This is because of the electronic configuration of Cu⁺ which is $3d^{10}$ (completely filled) and of Cr⁺ which is $3d^5$ (half-filled), *i.e.*, for the second ionisation potentials, the electron is to be removed from very stable configurations.

40. (c) : With increase in atomic number *i.e.* in moving down a group, the number of the principal shell increases and therefore, the size of the atom increases. But in case of f-block elements there is a steady decrease in atomic size with increase in atomic number due to lanthanide contraction.

As we move through the lanthanide series, 4f electrons are being added one at each step. The mutual shielding effect of f electrons is very little. This is due to the shape of the f-orbitals. The nuclear charge, however increases by one at each step. Hence, the inward pull experienced by the 4f electrons increases. This causes a reduction in the size of the entire $4f^n$ shell. **41. (b) :** The precipitate of mercuric iodide dissolves in excess of potassium iodide forming a complex, K_2HgI_4 .

 $HgI_2 + 2KI \rightarrow K_2HgI_4$

 HgI_2 on heating liberates I_2 gas.

 $HgI_2 \longrightarrow Hg + I_2$ Violet vapours

42. (d) : NH_4^+ ions are increased to suppress release of OH^- ions, hence solubility product of $Fe(OH)_3$ is attained. Colour of precipitate is different.

43. (b) : A more basic ligand forms stable bond with metal ion, Cl^{-} is most basic amongst all.

44. (a) : According to their positions in the periods, these values are in the order:

	Yb ³⁺ <	$Pm^{3+} <$	Ce^{3+}	$< La^{3+}$
At. Nos.	70	61	58	57
Ionic radii (pm)	86	98	103	106

Ionic size decreases from La^{3+} to Lu^{3+} due to lanthanide contraction.

45. (c) : The common stable oxidation state of all the lanthanides is +3. The oxidation states of +2 and +4 are also exhibited and these oxidation states are only stable in those cases where stable $4f^0$, $4f^7$ or $4f^{14}$ configurations are achieved. Ce⁴⁺ is stable due to $4f^0$ configuration.

46. (a) : $Mn^{2+} (3s^23p^63d^5)$ has the maximum number of unpaired electrons (5) and therefore has maximum moment.

