

The d- and f-Block Elements



TOPIC 1 Characteristics of d-Block Elements



- The incorrect statement(s) among (1) - (3) is (are) :
[Sep. 04, 2020 (II)]
 - W(VI) is more stable than Cr(VI).
 - in the presence of HCl, permanganate titrations provide satisfactory results.
 - some lanthanoid oxides can be used as phosphorus.
 - (2) and (3) only
 - (1) and (2) only
 - (2) only
 - (1) only
- The third ionization enthalpy is minimum for:
[Jan. 08, 2020 (I)]
 - Co
 - Fe
 - Ni
 - Mn
- For the following Assertion and Reason, the correct option is:
Assertion: For hydrogenation reactions, the catalytic activity increases from Group 5 to Group 11 metals with maximum activity shown by Group 7-9 elements.
Reason: The reactants are most strongly adsorbed on group 7-9 elements. [Jan. 08, 2020 (II)]
 - The assertion is true, but the reason is false.
 - Both assertion and reason are false.
 - Both assertion and reason are true and the reason is the correct explanation for the assertion.
 - Both assertion and reason are true but the reason is not the correct explanation for the assertion.
- The atomic radius of Ag is closest to: [Jan. 07, 2020 (I)]
 - Au
 - Ni
 - Cu
 - Hg
- The pair that has similar atomic radii is :
[April 12, 2019 (II)]
 - Mn and Re
 - Ti and Hf
 - Sc and Ni
 - Mo and W
- Consider the hydrated ions of Ti^{2+} , V^{2+} , Ti^{3+} , and Sc^{3+} . The correct order of their spin-only magnetic moments is:
[April 10, 2019 (I)]
 - $V^{2+} < Ti^{2+} < Ti^{3+} < Sc^{3+}$
 - $Sc^{3+} < Ti^{3+} < Ti^{2+} < V^{2+}$
 - $Ti^{3+} < Ti^{2+} < Sc^{3+} < V^{2+}$
 - $Sc^{3+} < Ti^{3+} < V^{2+} < Ti^{2+}$
- The correct order of the first ionization enthalpies is :
[April 10, 2019 (II)]
 - $Ti < Mn < Zn < Ni$
 - $Ti < Mn < Ni < Zn$
 - $Mn < Ti < Zn < Ni$
 - $Zn < Ni < Mn < Ti$
- The INCORRECT statement is : [April 10, 2019 (II)]
 - the gemstone, ruby, has Cr^{3+} ions occupying the octahedral sites of beryl.
 - the spin-only magnetic moment of $[Ni(NH_3)_4(H_2O)_2]^{2+}$ is 2.83 BM.
 - the color of $[CoCl(NH_3)_5]^{2+}$ is violet as it absorbs the yellow light.
 - the spin-only magnetic moments of $[Fe(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$ are nearly similar.
- Match the catalysts (Column I) with products (Column II).
[April 9, 2019 (I)]

Column I Catalyst	Column II Product
(A) V_2O_5	(i) Polyethylene
(B) $TiCl_4/Al(Me)_3$	(ii) ethanol
(C) $PdCl_2$	(iii) H_2SO_4
(D) Iron Oxide	(iv) NH_3

 - (A)-(iii); (B)-(iv); (C)-(i); (D)-(ii)
 - (A)-(ii); (B)-(iii); (C)-(i); (D)-(iv)
 - (A)-(iii); (B)-(i); (C)-(ii); (D)-(iv)
 - (A)-(iv); (B)-(iii); (C)-(ii); (D)-(i)
- The statement that is INCORRECT about the interstitial compounds is :
[April 8, 2019 (II)]
 - they are chemically reactive.
 - they are very hard.
 - they have metallic conductivity.
 - they have high melting points.
- The pair of metal ions that can give a spin only magnetic moment of 3.9 BM for the complex $[M(H_2O)_6]Cl_2$, is:
[Jan. 12, 2019 (I)]
 - V^{2+} and Co^{2+}
 - V^{2+} and Fe^{2+}
 - Co^{2+} and Fe^{2+}
 - Cr^{2+} and Mn^{2+}
- The element that usually does NOT show variable oxidation states is:
[Jan. 11, 2019 (I)]
 - Cu
 - Ti
 - Sc
 - V
- The highest value of the calculated spin only magnetic moment (in BM) among all the transition metal complexes is :
[Jan. 9, 2019 (I)]
 - 5.92
 - 6.93
 - 3.87
 - 4.90

14. The transition element that has lowest enthalpy of atomisation is: [Jan. 9, 2019 (II)]
 (a) Fe (b) Cu (c) V (d) Zn
15. Which of the following ions does **not** liberate hydrogen gas on reaction with dilute acids? [Online April 9, 2017]
 (a) Ti^{2+} (b) V^{2+} (c) Cr^{2+} (d) Mn^{2+}
16. The reaction of zinc with dilute and concentrated nitric acid, respectively, produces: [2016]
 (a) NO and N_2O (b) NO_2 and N_2O
 (c) N_2O and NO_2 (d) NO_2 and NO
17. Which one of the following species is stable in aqueous solution? [Online April 9, 2016]
 (a) Cr^{2+} (b) MnO_4^{2-} (c) MnO_4^{3-} (d) Cu^+
18. The transition metal ions responsible for colour in ruby and emerald are, respectively: [Online April 10, 2016]
 (a) Co^{3+} and Cr^{3+} (b) Co^{3+} and Co^{3+}
 (c) Cr^{3+} and Cr^{3+} (d) Cr^{3+} and Co^{3+}
19. Chloro compound of Vanadium has only spin magnetic moment of 1.73 BM. This Vanadium chloride has the formula: [Online April 9, 2014]
 (a) VCl_2 (b) VCl_4
 (c) VCl_3 (d) VCl_5
20. Which one of the following exhibits the large number of oxidation states? [Online April 12, 2014]
 (a) Ti (22) (b) V (23)
 (c) Cr (24) (d) Mn (25)
21. 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
22. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E_{M^{3+}/M^{2+}}^0$ value? [2013]
 (a) Cr (Z=24) (b) Mn (Z=25)
 (c) Fe (Z=26) (d) Co (Z=27)
23. The element with which of the following outer electron configuration may exhibit the largest number of oxidation states in its compounds: [Online April 9, 2013]
 (a) $3d^2 4s^2$ (b) $3d^8 4s^2$
 (c) $3d^7 4s^2$ (d) $3d^6 4s^2$
24. Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is incorrect? [2012]
 (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.
25. Which pair of elements with the given atomic numbers is expected to have similar properties? [Online May 19, 2012]
 (a) 40, 72 (b) 20, 36 (c) 10, 28 (d) 11, 12
26. The correct order of $E_{M^{2+}/M}^0$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is [2010]
 (a) $Mn > Cr > Fe > Co$ (b) $Cr < Fe > Mn > Co$
 (c) $Fe > Mn > Cr > Co$ (d) $Cr > Mn > Fe > Co$
27. The "spin-only" magnetic moment [in units of Bohr magneton, (μ_B)] of Ni^{2+} in aqueous solution would be (At. No. Ni = 28) [2006]
 (a) 6 (b) 1.73 (c) 2.82 (d) 4.90
28. 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
29. 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)
30. 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 the $4f$ electrons by another in the subshell
 (d) Poor shielding of one of the $4f$ electrons by another in the subshell
31. The lanthanide contraction is responsible for the fact that
 (a) Zr and Zn have the same oxidation state [2005]
 (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
32. 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) $(n-1)d^6 ns^2$ (d) $(n-1)d^6 ns^2$
33. The correct order of magnetic moments (spin only values in B.M.) among the following 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)



34. Which of the following ions has the maximum magnetic moment? [2002]
 (a) Mn^{+2} (b) Fe^{+2} (c) Ti^{+2} (d) Cr^{+2}
35. The most stable ion is [2002]
 (a) $[Fe(OH)_3]^{3-}$ (b) $[FeCl_6]^{3-}$
 (c) $[Fe(CN)_6]^{3-}$ (d) $[Fe(H_2O)_6]^{3+}$

TOPIC 2 Compounds of Transition Metals



36. The incorrect statement is: [Sep. 03, 2020 (II)]
 (a) Manganate and permanganate ions are tetrahedral
 (b) In manganate and permanganate ions, the π -bonding takes place by overlap of p -orbitals of oxygen and d -orbitals of manganese
 (c) Manganate and permanganate ions are paramagnetic
 (d) Manganate ion is green in colour and permanganate ion is purple in colour
37. The sum of the total number of bonds between chromium and oxygen atoms in chromate and dichromate ions is _____. [NV, Jan. 09, 2020 (II)]
38. Consider the following reactions:
 $NaCl + K_2Cr_2O_7 + H_2SO_4$ (Conc.) \rightarrow (A) + Side products
 $(A) + NaOH \rightarrow$ (B) + Side products
 $(B) + H_2SO_4$ (dilute) + $H_2O_2 \rightarrow$ (C) + Side products
 The sum of the total number of atoms in one molecule each of (A), (B) and (C) is _____. [NV, Jan. 07, 2020 (II)]
39. Thermal decomposition of a Mn compound (X) at 513 K results in compound Y, MnO_2 and a gaseous product. MnO_2 reacts with NaCl and concentrated H_2SO_4 to give a pungent gas Z. X, Y, and Z, respectively, are: [April 12, 2019 (II)]
 (a) $KMnO_4$, K_2MnO_4 and Cl_2
 (b) K_2MnO_4 , $KMnO_4$ and SO_2
 (c) K_3MnO_4 , K_2MnO_4 and Cl_2
 (d) K_2MnO_4 , $KMnO_4$ and Cl_2
40. $A \xrightarrow[Green]{4KOH, O_2} 2B + 2H_2O$
 $B \xrightarrow[Purple]{4HCl} 2C + MnO_2 + 2H_2O$
 $2C \xrightarrow{H_2O, KI} 2A + KOH + D$
 In the above sequence of reactions, A and D, respectively, are: [Jan. 11, 2019 (II)]
 (a) KI and $KMnO_4$ (b) MnO_2 and KIO_3
 (c) KIO_3 and MnO_2 (d) KI and K_2MnO_4
41. When XO_2 is fused with an alkali metal hydroxide in presence of an oxidizing agent such as KNO_3 , a dark green product is formed which disproportionates in acidic solution to afford a dark purple solution. X is: [Online April 16, 2018]
 (a) Mn (b) Cr (c) V (d) Ti
42. In the following reactions, ZnO is respectively acting as a/an: [2017]
 (i) $ZnO + Na_2O \rightarrow Na_2ZnO_2$
 (ii) $ZnO + CO_2 \rightarrow ZnCO_3$
 (a) base and acid (b) base and base
 (c) acid and acid (d) acid and base
43. Which of the following compounds is metallic and ferromagnetic? [2016]
 (a) VO_2 (b) MnO_2 (c) TiO_2 (d) CrO_2
44. When concentrated HCl is added to an aqueous solution of $CoCl_2$, its colour changes from reddish pink to deep blue. Which complex ion gives blue colour in this reaction? [Online April 11, 2015]
 (a) $[CoCl_4]^{2-}$ (b) $[CoCl_6]^{3-}$
 (c) $[CoCl_6]^{4-}$ (d) $[Co(H_2O)_6]^{2+}$
45. Which of the following statements is false? [Online April 11, 2015]
 (a) $Na_2Cr_2O_7$ is less soluble than $K_2Cr_2O_7$
 (b) $Na_2Cr_2O_7$ is primary standard in volumetry
 (c) CrO_4^{2-} is tetrahedral in shape
 (d) CrO_7^{2-} has a Cr–O–Cr bond
46. The equation which is balanced and represents the correct product(s) is: [2014]
 (a) $Li_2O + 2KCl \rightarrow 2LiCl + K_2O$
 (b) $[CoCl(NH_3)_5]^{+} + 5H^{+} \rightarrow Co^{2+} + 5NH_4^{+} + Cl^{-}$
 (c) $[Mg(H_2O)_6]^{2+} + (EDTA)^{4-} \xrightarrow{\text{excess NaOH}} [Mg(EDTA)]^{2-} + 6H_2O$
 (d) $CuSO_4 + 4KCN \rightarrow K_2[Cu(CN)_4] + K_2SO_4$
47. 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) $Fe \xrightarrow{O_2, \text{heat}} Fe_3O_4 \xrightarrow{CO, 600^\circ C} FeO \xrightarrow{CO, 700^\circ C} Fe$
48. Which of the following is not formed when H_2S reacts with acidic $K_2Cr_2O_7$ solution? [Online April 9, 2014]
 (a) $CrSO_4$ (b) $Cr_2(SO_4)_3$
 (c) K_2SO_4 (d) S



49. Potassium dichromate when heated with concentrated sulphuric acid and a soluble chloride, gives brown-red vapours of : **[Online April 9, 2013]**
 (a) CrO_3 (b) CrCl_3 (c) CrO_2Cl_2 (d) Cr_2O_3
50. When a small amount of KMnO_4 is added to concentrated H_2SO_4 , a green oily compound is obtained which is highly explosive in nature. Compound may be : **[Online April 23, 2013]**
 (a) MnSO_4 (b) Mn_2O_7 (c) MnO_2 (d) Mn_2O_3
51. Identify incorrect statement : **[Online April 23, 2013]**
 (a) Cu_2O is colourless.
 (b) Copper (I) compounds are colourless except when colour results from charge transfer.
 (c) Copper (I) compounds are diamagnetic.
 (d) Cu_2S is black.
52. Amount of oxalic acid present in a solution can be determined by its titration with KMnO_4 solution in the presence of H_2SO_4 . The titration gives unsatisfactory result when carried out in the presence of HCl , because HCl **[2008]**
 (a) gets oxidised by oxalic acid to chlorine
 (b) furnishes H^+ ions in addition to those from oxalic acid
 (c) reduces permanganate to Mn^{2+}
 (d) oxidises oxalic acid to carbon dioxide and water
53. Heating mixture of Cu_2O and Cu_2S will give **[2005]**
 (a) Cu_2SO_3 (b) $\text{CuO} + \text{CuS}$
 (c) $\text{Cu} + \text{SO}_3$ (d) $\text{Cu} + \text{SO}_2$
54. Calomel (Hg_2Cl_2) on reaction with ammonium hydroxide gives **[2005]**
 (a) HgO (b) Hg_2O
 (c) $\text{NH}_2 - \text{Hg} - \text{Hg} - \text{Cl}$ (d) HgNH_2Cl
55. 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]**
 (a) In acidic solutions, protons coordinate with ammonia molecules forming NH_4^+ ions and thus NH_3 molecules are not available
 (b) In alkaline solutions insoluble $\text{Cu}(\text{OH})_2$ is precipitated which is soluble in excess of any alkali
 (c) Copper hydroxide is an amphoteric substance
 (d) In acidic solutions hydration protects copper ions
56. 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]**
 (a) HgI_2 (b) HgO
 (c) Pb_3O_4 (d) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
57. What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid? **[2003]**
 (a) $\text{Cr}_2\text{O}_7^{2-}$ and H_2O are formed
 (b) CrO_4^{2-} is reduced to +3 state of Cr
 (c) CrO_4^{2-} is oxidized to +7 state of Cr
 (d) Cr^{3+} and $\text{Cr}_2\text{O}_7^{2-}$ are formed
58. Which one of the following nitrates will leave behind a metal on strong heating ? **[2003]**
 (a) Copper nitrate (b) Manganese nitrate
 (c) Silver nitrate (d) Ferric nitrate
59. When KMnO_4 acts as an oxidising agent and ultimately forms $[\text{MnO}_4]^{-2}$, MnO_2 , Mn_2O_3 , Mn^{+2} then the number of electrons transferred in each case respectively is **[2002]**
 (a) 4, 3, 1, 5 (b) 1, 5, 3, 7
 (c) 1, 3, 4, 5 (d) 3, 5, 7, 1.

TOPIC 3 Lanthanoids and Actinoids



60. The lanthanoid that does NOT show +4 oxidation state is: **[Sep. 06, 2020 (I)]**
 (a) Dy (b) Ce
 (c) Eu (d) Tb
61. Mischmetal is an alloy consisting mainly of: **[Sep. 06, 2020 (II)]**
 (a) lanthanoid metals
 (b) actinoid and transition metals
 (c) lanthanoid and actinoid metals
 (d) actinoid metals
62. The correct electronic configuration and spin-only magnetic moment (BM) of Gd^{3+} ($Z = 64$), respectively, are: **[Sep. 05, 2020 (I)]**
 (a) $[\text{Xe}] 4f^7$ and 8.9 (b) $[\text{Xe}] 4f^7$ and 7.9
 (c) $[\text{Xe}] 5f^7$ and 8.9 (d) $[\text{Xe}] 5f^7$ and 7.9
63. The electronic configurations of bivalent europium and trivalent cerium are: **[Jan. 09, 2020 (I)]**
 (atomic number : Xe = 54, Ce = 58, Eu = 63)
 (a) $[\text{Xe}] 4f^2$ and $[\text{Xe}] 4f^7$
 (b) $[\text{Xe}] 4f^7$ and $[\text{Xe}] 4f^1$
 (c) $[\text{Xe}] 4f^7 6s^2$ and $[\text{Xe}] 4f^2 6s^2$
 (d) $[\text{Xe}] 4f^4$ and $[\text{Xe}] 4f^9$
64. The highest possible oxidation states of uranium and plutonium, respectively, are : **[April 10, 2019 (II)]**
 (a) 6 and 7 (b) 6 and 4
 (c) 7 and 6 (d) 4 and 6

65. The maximum number of possible oxidation states of actinoids are shown by: **[April 9, 2019 (II)]**
 (a) Nobelium (No) and lawrencium (Lr)
 (b) Actinium (Ac) and thorium (Th)
 (c) Berkelium (Bk) and californium (Cf)
 (d) Neptunium (Np) and plutonium (Pu)
66. The lanthanide ion that would show colour is : **[April 8, 2019 (I)]**
 (a) Gd^{3+} (b) Sm^{3+}
 (c) La^{3+} (d) Lu^{3+}
67. The correct order of atomic radii is : **[Jan. 12, 2019 (II)]**
 (a) $N > Ce > Eu > Ho$ (b) $Ho > N > Eu > Ce$
 (c) $Ce > Eu > Ho > N$ (d) $Eu > Ce > Ho > N$
68. The effect of lanthanoid contraction in the lanthanoid series of elements by and large means: **[Jan. 10, 2019 (I)]**
 (a) increase in both atomic and ionic radii
 (b) decrease in atomic radii and increase in ionic radii
 (c) decrease in both atomic and ionic radii
 (d) increase in atomic radii and decrease in ionic radii
69. Which is not the correct statement? **[Online May 7, 2012]**
 (At. nos. Ce = 58, Lu = 71, La = 57, Yb = 70)
 (a) Colour of Yb^{3+} ion is pink.
 (b) La^{3+} is diamagnetic.
 (c) Ce^{4+} has f^0 configuration.
 (d) Lu^{3+} had f^{14} configuration.
70. Magnetic moment of Gd^{3+} ion ($Z = 64$) is **[Online May 12, 2012]**
 (a) 3.62 BM (b) 9.72 BM
 (c) 7.9 BM (d) 10.60 BM
71. Which of the following forms stable +4 oxidation state? **[Online May 26, 2012]**
 (a) La ($Z = 57$) (b) Eu ($Z = 63$)
 (c) Ce ($Z = 58$) (d) Gd ($Z = 64$)
72. The number of unpaired electrons in Gadolinium [$Z = 64$] is **[Online May 26, 2012]**
 (a) 3 (b) 8 (c) 6 (d) 2
73. Knowing that the chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements is incorrect? **[2009]**
 (a) The ionic size 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 predominantly ionic in character.
74. Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being **[2008]**
 (a) $4f$ orbitals more diffused than the $5f$ orbitals
 (b) lesser energy difference between $5f$ and $6d$ than between $4f$ and $5d$ orbitals
 (c) more energy difference between $5f$ and $6d$ than between $4f$ and $5d$ orbitals
 (d) more reactive nature of the actinoids than the lanthanoids
75. Identify the incorrect statement among the following: **[2007]**
 (a) $4f$ and $5f$ 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.
76. The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because **[2007]**
 (a) the $5f$ 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.
77. Lanthanoid contraction is caused due to **[2006]**
 (a) the same effective nuclear charge from Ce to Lu
 (b) the imperfect shielding on outer electrons by $4f$ electrons from the nuclear charge
 (c) the appreciable shielding on outer electrons by $4f$ electrons from the nuclear charge
 (d) the appreciable shielding on outer electrons by $5d$ electrons from the nuclear charge
78. 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
79. 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)? **[2003]**
 (a) 1.40 Å (b) 1.06 Å (c) 0.85 Å (d) 1.60 Å
80. A reduction in atomic size with increase in atomic number is a characteristic of elements of **[2003]**
 (a) d -block (b) f -block
 (c) radioactive series (d) high atomic masses
81. Most common oxidation states of Ce (cerium) are **[2002]**
 (a) +2, +3 (b) +2, +4 (c) +3, +4 (d) +3, +5.
82. Arrange Ce^{+3} , La^{+3} , Pm^{+3} and Yb^{+3} in increasing order of their ionic radii. **[2002]**
 (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) $Pm^{+3} < La^{+3} < Ce^{+3} < Yb^{+3}$.





Hints & Solutions



1. (c) (i) W(VI) is more stable than Cr(VI) due to smaller size of atoms and also due to lanthanide contraction.
 (ii) Permanganate titrations in presence of HCl are unsatisfactory as HCl is oxidised to Cl_2 .
 (iii) Lanthanoid oxides are used as phosphors.

2. (b) ${}_{26}\text{Fe} = [\text{Ar}] 3d^6 4s^2$. Third ionisation results into stable d^5 configuration.

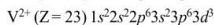
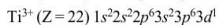
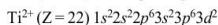
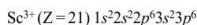
3. (a) Reactant should not be adsorbed strongly which might result into immobilisation that inhibit further adsorption on the catalyst's surface.

4. (a) Atomic size of elements of 4d and 5d transition series are nearly same due to lanthanide contraction.

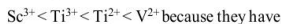
5. (d) Mo and W belong to group-6 and period 5 (4d series) and 6 (5d series) respectively.

Due to lanthanoid contraction, radius of Mo and W are almost same i.e. 0.140 nm and 0.141 nm respectively.

6. (b) Electronic configuration of the given transition metal ions are:



Since, magnetic moment is directly proportional to the number of unpaired electrons. The correct increasing order of magnetic moment is



0, 1, 2 and 3 unpaired electrons respectively.

7. (b) I.E. increases on moving left to right in a period.

$\therefore \text{Ti} < \text{Mn} < \text{Ni} < \text{Zn}$

8. (a) Ruby is aluminium oxide (Al_2O_3) containing about 0.5 – 1% Cr^{3+} ions, which are randomly distributed in place of Al^{3+} ions.

9. (c) (A) $\text{V}_2\text{O}_5 \rightarrow$ Preparation of H_2SO_4 in contact process
 (B) $\text{TiCl}_4 + \text{Al}(\text{Me})_3 \rightarrow$ Polyethylene

(Ziegler-Natta catalyst)

(C) $\text{PdCl}_2 \rightarrow$ Ethanol (Wacker's process)

(D) Iron oxide $\rightarrow \text{NH}_3$ in (Haber's process)

10. (a) Interstitial compounds are inert, i.e., they are chemically non-reactive.

11. (a) Given $\mu = 3.9 \text{ BM}$

$$\mu = \sqrt{n(n+2)} \text{ B.M.}; 3.9 = \sqrt{n(n+2)}; n = 3$$

So, the central metal ion has 3 unpaired electrons.

\therefore Configuration is either d^3 or d^7

As H_2O is a weak field ligand, V^{2+} and Co^{2+} will have 3 unpaired electrons.

V^{2+} has d^3 configuration; Co^{2+} has d^7 configuration.

12. (c) Sc shows oxidation state of +3 only.

13. (a) Magnetic moment, $\mu = \sqrt{n(n+2)} \text{ BM}$ (where, $n = \text{no. of unpaired electrons}$)

As transition metal atom/ion in a complex may have unpaired electrons ranging from zero to 5. So, maximum number of unpaired electrons that may be present in a complex is 5.

\therefore Maximum value of magnetic moment among all the transition metal complexes is

$$\sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ BM}$$

14. (d) As zinc has no unpaired of electrons to take part in the bond, it has least enthalpy of atomisation amongst the given transition elements.

15. (d) Ions $E^0(\text{V})$

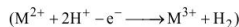
Ti^{2+} -0.37

V^{2+} -0.26

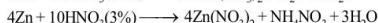
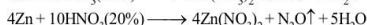
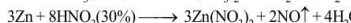
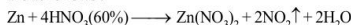
Cr^{2+} -0.41

Mn^{2+} +1.57

Negative value of E^0 means these metals liberate hydrogen from dilute acid.



16. (c) Reaction of Zn with different concentration of HNO_3 are as follows:

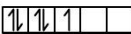
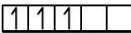
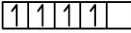
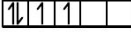

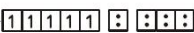
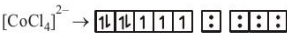


Hence option (c) is correct.

17. (b) In MnO_4^{2-} manganese is in +6 oxidation state which is having highest stability.

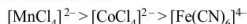
18. (c) A ruby is a crystal of alumina, aluminum oxide (Al_2O_3) containing a trace of chromium (III) ions replacing some of the aluminum ions. In ruby, each Al^{3+} ion and Cr^{3+} ion is surrounded by six oxide ions in an octahedral arrangement. The origin of the color of

emeralds is similar to that of the color of rubies. However, the bulk of an emerald crystal is composed of beryl, beryllium aluminum silicate ($\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$) instead of the alumina which forms rubies. The color is produced by chromium (III) ions, which replace some of the aluminum ions in the crystal. In emeralds, the Cr^{3+} is surrounded by six silicate ions, rather than the six oxide ions in ruby. Therefore, the color (green) of emeralds is different from that of ruby.

19. (a) $\mu = \sqrt{n(n+2)}$
 $1.73 = \sqrt{n(n+2)}$
 On calculating the value of n we find $m = 1$
 No. of unpaired electrons = 1
 hence its configuration will be
 $\text{V}(23) = [\text{Ar}] 3d^3 4s^2$
 $\text{V}^{2+} = [\text{Ar}] 3d^3 4s^2$
 \therefore Its chloride has the formula VCl_2
20. (d) Manganese exhibits the large number of oxidation states. The most common oxidation states of Mn are +2, +3, +4, +6 and +7.
21. (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
 $\text{Mn}^{2+} > \text{Fe}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$
 (c) Larger size, least hydrated more stable in aqueous solution. As we move across the period ($\text{Sc}^{3+} \rightarrow \text{Cr}^{3+} \rightarrow \text{Fe}^{3+} \rightarrow \text{Co}^{3+}$), the ionic size usually decreases. Sc^{3+} with the large size as least hydrated and hence more stable.
 (d) $\text{Sc} - (+2), (+3)$
 $\text{Ti} - (+2), (+3), (+4)$
 $\text{Cr} - (+2), (+3), (+4), (+5), (+6)$
 $\text{Mn} - (+2), (+3), (+4), (+5), (+6), (+7)$
 i.e. $\text{Sc} < \text{Ti} < \text{Cr} < \text{Mn}$
22. (d) $E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}} = -0.41 \text{ V}$,
 $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.77 \text{ V}$
 $E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}} = +1.57 \text{ V}$, $E^\circ_{\text{Co}^{3+}/\text{Co}^{2+}} = +1.97 \text{ V}$
23. (a) The element with outer electron configuration $3d^5 4s^2$ is Mn which exhibits oxidation states from +2 to +7.
24. (d) Fe^{3+} is easily hydrolysed than Fe^{2+} due to more positive charge.
25. (a) Zr (40), Hf (72) have similar properties as they belong to same group and have same valence shell electronic configuration.
26. (a) Across the first transition series, the negative values for standard electrode potential decrease except for Mn due to the stable d^5 configuration.
 Thus, correct order is
 $\text{Mn}^{2+} > \text{Cr}^{2+} > \text{Fe}^{2+} > \text{Co}^{2+}$.
27. (c) The number of unpaired electrons in $\text{Ni}^{2+}(\text{aq}) = 2$. Water is a weak ligand, hence no pairing will take place
 \therefore spin magnetic moment
 $= \sqrt{n(n+2)} = \sqrt{2(2+2)} = \sqrt{8} = 2.82$
28. (a) $\text{Cr}_2\text{O}_7^{2-} + 6\text{I}^- + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{I}_2$
29. (d) d^5 — strong ligand field

 $\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM}$
 d^3 — in weak as well as in strong field

 $\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ B.M.}$
 d^4 — in weak ligand field

 $\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.89$
 d^4 — in strong ligand field

 $\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.82$
30. (d) Lanthanide contraction is associated with the intervention of the $4f$ orbitals which must be filled before the $5d$ series of elements begin. The filling of $7f$ before $5d$ orbitals results in a regular decrease in atomic radii called lanthanoid contraction which essentially compensates for the expected increase in atomic size with increasing atomic number. The factor responsible for the lanthanoid contraction is the imperfect shielding of one electron by another in the same set of orbitals.
31. (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.
32. (d) $(n-1)d^5 ns^2$ attains the maximum O.S. of +7
33. (c) $[\text{Fe}(\text{CN})_6]^{4-} \rightarrow$ 
 No of unpaired electron = 0
 $[\text{MnCl}_4]^{2-} \rightarrow$ 
 No of unpaired electrons = 5
 $[\text{CoCl}_4]^{2-} \rightarrow$ 
 No of unpaired electrons = 3



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

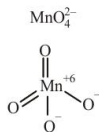


34. (a) Mn^{2+} - 5 unpaired electrons
 Fe^{2+} - 4 unpaired electrons
 Ti^{2+} - 2 unpaired electrons
 Cr^{2+} - 4 unpaired electrons

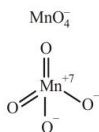
Note : Magnetic moment \propto Number of unpaired electrons

35. (c) The cyano and hydroxo complexes are far more stable than those formed by halide ion. This is due to the fact that CN^- and OH^- are strong Lewis bases (nucleophiles). Further $[\text{Fe}(\text{OH})_5]^{3-}$ is not formed. hence most stable ion is $[\text{Fe}(\text{CN})_6]^{3-}$

36. (c) **Manganate** **Permanganate**



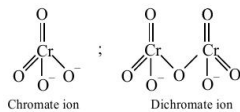
Paramagnetic, green in colour, Tetrahedral & contains $p\pi-d\pi$ bond



Diamagnetic, purple in colour, Tetrahedral & contains $p\pi-d\pi$ bond

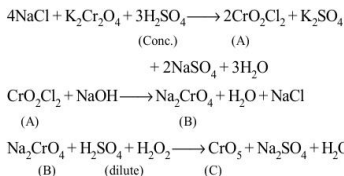
Manganate ion is paramagnetic while permanganate ion is diamagnetic.

37. (12.00)

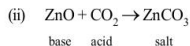
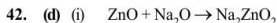
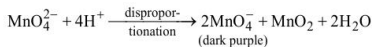
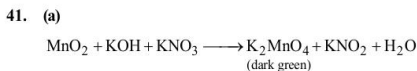
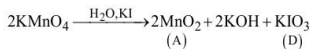
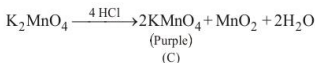
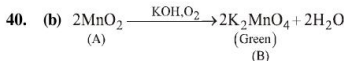
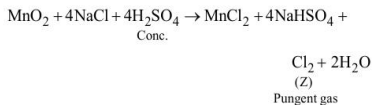
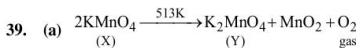


\Rightarrow Total number of Cr and O bonds is 12.

38. (18.00)



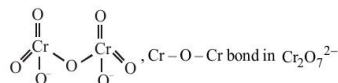
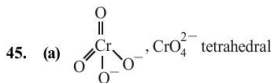
The sum of total no. of atoms in one molecules each of A, B & C = 5 + 7 + 6 = 18.0



43. (d) Out of all the four given metallic oxides, CrO_2 is attracted by magnetic field very strongly. The effect persists even when the magnetic field is removed. Thus CrO_2 is metallic and ferromagnetic in nature.

44. (a) Aqueous solution of CoCl_2 contains $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ which is pinkish in colour so option (d) is incorrect.

Reduction potential of $\text{Co}^{3+} \longrightarrow \text{Co}^{2+}$ is high so option (b) is incorrect. Co^{2+} does not oxidises easily to Co^{3+} . It is general case that symmetrical substituted octahedral complexes are less deeper in colour than tetrahedral complexes. So $[\text{CoCl}_4]^{2-}$ is deep blue in colour.



$\text{Na}_2\text{Cr}_2\text{O}_7$ is used as a primary standard in volumetry.

- Hydration energy of Na^{\oplus} is greater than K^{\oplus} . Because of smaller size of Na^{\oplus} , $\text{Na}_2\text{Cr}_2\text{O}_7$ is more soluble than $\text{K}_2\text{Cr}_2\text{O}_7$.
46. (b) The equation in option (b) is correct since both charges as well as atoms are balanced. For the rest,
 (a) Given reaction is unfavourable in the forward direction (K_2O is unstable, while Li_2O is stable)
 (c) Given reaction is not balanced w.r.t. charge.
 (d) Given reaction will give $\text{K}_3[\text{Cu}(\text{CN})_4]$ as product instead of $\text{K}_2[\text{Cu}(\text{CN})_4]$.
47. (d) In equation (a) $\text{Fe}_2(\text{SO}_4)_3$, and in equation (b) FeSO_4 , on decomposition will form oxide instead of Fe. In equation (c) FeCl_3 cannot be reduced when heated in air. Hence equation (d) is correct.
48. (a) $\text{K}_2\text{Cr}_2\text{O}_7 + 4\text{H}_2\text{SO}_4 + 3\text{H}_2\text{S} \longrightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O} + 3\text{S}$
49. (c) Solid potassium dichromate when heated with concentrated sulphuric acid and a soluble chloride gives orange red vapours of a volatile oily liquid CrO_2Cl_2
 $\text{K}_2\text{Cr}_2\text{O}_7 + 4\text{NaCl} + 6\text{H}_2\text{SO}_4 \longrightarrow 2\text{KHSO}_4 + 4\text{NaHSO}_4 + 2\text{CrO}_2\text{Cl}_2$
 chromyl chloride
50. (b) KMnO_4 reacts with H_2SO_4 to form Mn_2O_7 which is highly explosive substance.
 $2\text{KMnO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \text{Mn}_2\text{O}_7 + \text{H}_2\text{O}$
51. (a) Cu_2O is yellow in colour.
52. (c) The titration of oxalic acid with KMnO_4 in presence of HCl gives unsatisfactory result because of the fact that KMnO_4 can also oxidise HCl along with oxalic acid. HCl on oxidation gives Cl_2 and HCl reduces KMnO_4 to Mn^{2+} , thus the correct answer is (c).
53. (d) $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2$
 self reduction.
54. (d) $\text{Hg}_2\text{Cl}_2 + 2\text{NH}_4\text{OH} \longrightarrow \text{Hg} + \text{HgNH}_2\text{Cl} + \text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$
55. (a) $\ddot{\text{N}}\text{H}_3 + \text{H}^+ \text{ (acid medium)} \rightleftharpoons \overset{+}{\text{N}}\text{H}_4$
56. (a) $\text{Cr}_2\text{O}_7^{2-} + 6\text{I}^- + 14\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{I}_2$
57. (a) $2\text{K}_2\text{CrO}_4 + 2\text{HNO}_3 \longrightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{KNO}_3 + \text{H}_2\text{O}$
58. (c) AgNO_3 on heating till red hot decomposes as follows:
 $\text{AgNO}_3 \rightarrow \text{Ag} + \text{NO}_2 + \frac{1}{2}\text{O}_2$
59. (c) $\overset{+3}{\text{Mn}}_2\text{O}_3 \xleftarrow{-4e^-} [\overset{+7}{\text{KMnO}_4}] \xrightarrow{-e^-} [\overset{+6}{\text{MnO}_4}]^{2-}$
 $\swarrow -5e^- \quad \searrow -3e^-$
 $\text{Mn}^{2+} \quad \text{MnO}_2$
60. (c) Europium (Eu)
 Atomic No. - 63
 Electronic configuration - $[\text{Xe}]4f^7 6s^2$
 It shows only +2 and +3 oxidation state.
61. (a) Mischmetal is an alloy consisting mainly of lanthanoid metals.
 Alloy \Rightarrow
 Lan. metal $\Rightarrow \approx 95\%$
 Iron $\Rightarrow \approx 5\%$
 S, C, Ca, Al \Rightarrow traces
62. (b) Electronic configuration of
 ${}_{64}\text{Gd} = [\text{Xe}] 4f^7 5d^1 6s^2$
 ${}_{64}\text{Gd}^{3+} = [\text{Xe}] 4f^7$
 No. of unpaired electron = 7
 $\mu = \sqrt{n(n+2)} \text{ BM} = \sqrt{63} = 7.93 \text{ BM}$
63. (b) $\text{Eu}^{2+} : [\text{Xe}]4f^7 ; \text{Ce}^{3+} : [\text{Xe}]4f^1$
64. (a) Maximum oxidation state shown by uranium is +6 and plutonium is 7.
65. (d) Actinoids Oxidation state shown
 Th +3, +4
 Ac +3
 Pu +3, +4, +5, +6, +7
 Np +3, +4, +5, +6, +7
 Bk +3, +4
 Cm +3, +4, +5
 Lr +3
 \therefore Maximum oxidation state is shown by Np and Pu.
66. (b) $\text{Sm} = 4f^6 6s^2$
 $\text{Sm}^{3+} = 4f^5$ = Partially filled f-orbital
 $\therefore \text{Sm}^{3+}$ will be coloured
 $\text{Lu}^{3+} = 4f^{14}$ = colourless.
67. (d) Atomic radii follows the order
 Eu > Ce > Ho > N
 185 pm 182 pm 177 pm 71 pm
68. (c) Due to lanthanoid contraction, size of atoms as well as ions of lanthanoid decreases.
69. (a) Option (a) is incorrect as Yb^{3+} is colorless.
70. (c) $\text{Gd} (64) = [\text{Xe}] 4f^7 5d^1 6s^2$
 $\text{Gd}^{3+} = [\text{Xe}] 4f^7 5d^0 6s^0$
 i.e. no. of unpaired electrons = 7
 $\mu = \sqrt{n(n+2)} = \sqrt{7(7+2)}$
 $= \sqrt{63} = 7.93 \text{ BM}$
71. (c) Only Ce (Z = 58) shows stable (+4) oxidation state.
72. (b) $\text{Gd} (64) = [\text{Xe}]4f^7 5d^1 6s^2$
 \therefore No. of unpaired electrons = 8



73. (b) Most of the Ln^{3+} compounds except La^{3+} and Lu^{3+} are coloured due to the presence of unpaired f -electrons.
74. (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 well as from $6d$ and due to this actinoids exhibit larger number of oxidation state than lanthanoids.
75. (a) $4f$ Orbital is nearer to nucleus as compared to $5f$ orbital therefore, shielding of $4f$ is more than $5f$.
76. (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.
77. (b) The configuration of lanthanides shows 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 of which atomic and ionic radii decrease gradually from La to Lu.

78. (a) The +4 oxidation state of cerium is also known in solution.
79. (c) Ionic radii $\propto \frac{1}{z}$

$$\text{Thus, } \frac{z_2}{z_1} = \frac{71}{57} = \frac{1.06}{(\text{Ionic radii of } \text{Lu}^{3+})}$$

$$\therefore \text{Ionic radii of } \text{Lu}^{3+} = 0.85 \text{ \AA}$$

80. (b) f -Block elements show a regular decrease in atomic size due to lanthanide/actinide contraction.
81. (c) Common oxidation states of Ce (cerium) are +3 and +4.
82. (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 decrease from La to Lu. Thus the correct order is.

