The d- and f- Block Elements Multiple Choice Questions (Type-I)

- 1. Electronic configuration of a transition element X in +3 oxidation state is $[Ar]3d^5$. What is its atomic number?
 - (i) 25
 - (ii) 26
 - (iii) 27
 - (iv) 24
- Ans. (ii)

Explanation: Electronic configuration of element $X = [Ar]3d^{5+}$ oxidation state = 18+5+3=26.

- 2. The electronic configuration of Cu(II) is $3d^9$ whereas that of Cu(I) is $3d^{10}$. Which of the following is correct?
 - (i) Cu(II) is more stable
 - (ii) Cu(II) is less stable
 - (iii) Cu(I) and Cu(II) are equally stable
 - (iv) Stability of Cu(I) and Cu(II) depends on nature of copper salts
- Ans. (i)

Explanation: The stability of $Cu^{2+}(aq)$ rather than $Cu^{+}(aq)$ is due to the much more negative Δ_{hyd} of $Cu^{2+}(aq)$ than Cu^{+} , which more than compensates for the second ionisation enthalpy of Cu.

3. Metallic radii of some transition elements are given below. Which of these elements will have highest density?

Elements Fe Co Ni Cu Metallic radii/pm 126 125 125 128

- (i) Fe
- (ii) Ni
- (iii) Co
- (iv) Cu
- Ans. (iv)

Explanation: On moving across the period in the periodic table the atomic radii of the element decreases towards right that is why density increases towards right in a period.

- 4. Generally transition elements form coloured salts due to the presence of unpaired electrons. Which of the following compounds will be coloured in solid state?
 - (i) Ag₂SO₄
 - (ii) CuF₂
 - (iii) ZnF₂
 - (iv) Cu₂Cl₂
- Ans. (ii)

Explanation: Here copper is in +2 states in which Cu contains one unpaired electron. Hence it produce colour in solid state.

- 5. On addition of small amount of KMnO₄ to concentrated H₂SO₄, a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following.
 - (i) Mn₂O₇
 - (ii) MnO₂
 - (iii) MnSO₄
 - (iv) Mn₂O₃

Ans. (i)

Explanation: KMnO₄ reacts with conc. H₂SO₄ as:

2 4 2 2 4 2 7 2

 Mn_2O_7 is highly explosive in nature.

- 6. The magnetic nature of elements depends on the presence of unpaired electrons. Identify the configuration of transition element, which shows highest magnetic moment.
 - (i) $3d^7$
 - (ii) $3d^5$
 - (iii) 3d8
 - (iv) $3d^2$

Ans. (ii)

Explanation: Greater the no. of unpaired electrons higher will be the magnetic moment. $\mu \sqrt{n \ n}$ where n is the number of unpaired electrons and is the magnetic moment in units of Bohr magneton (BM).

That is why 3d⁵ has maximum magnetic moment due to maximum no. of unpaired electrons.

- 7. Which of the following oxidation state is common for all lanthanoids?
 - (i) + 2
 - (ii) + 3
 - (iii) +4
 - (iv) + 5

Ans. (ii)

Explanation: In the lanthanoids, La(II) and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or filled subshell.

- 8. Which of the following reactions are disproportionation reactions?
 - (a) $Cu^+ \rightarrow Cu^{2+} + Cu$
 - (b) 3 $^{-}_{4} + 4 ^{+} \rightarrow 2 ^{-}_{4} + ^{-}_{2} + 2 ^{-}_{2}$
 - (c) 2

(d) $_{4} + _{2}$

 $_{1}$ + $_{2}$ + $_{2}$ \rightarrow $_{2}$

- (i) a, b
- (ii) a, b, c
- (iii) b, c, d
- (iv) a, d

Ans. (i)

Explanation: Copper (I) compounds are unstable in aqueous solution and undergo disproportionation:

 $2 \xrightarrow{+} \rightarrow \xrightarrow{2+} +$

In a disproportionation reaction, an element is simultaneously oxidized and reduced.

- 9. When KMnO₄ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because
 - (i) CO₂ is formed as the product.
 - (ii) Reaction is exothermic.
 - (iii) catalyses the reaction.
 - (iv) Mn²⁺ acts as autocatalyst.

Ans. (iv)

Explanation: Oxalate ion is oxidized to CO₂ by acidified KMnO₄.

2 $_{4} + 5 _{2} _{4} + 16 _{2} + 2 _{2} + 2 _{2} + 8 _{2}$

In acid, medium

$$(pink)$$
 $^{+}+8$ $^{+}+5$ $^{-}\rightarrow (colourless)$ $^{2+}+4$ $_{2}$

Mn²⁺ formed in the reaction act as autocatalyst.

- 10. There are 14 elements in actinoid series. Which of the following elements does not belong to this series?
 - (i) U
 - (ii) Np
 - (iii) Tm
 - (iv) Fm

Ans. (iii)

Explanation: Tm (thulium) atomic no. =69 belongs to Lanthanoids series.

- 11. KMnO₄ acts as an oxidising agent in acidic medium. The number of moles of KMnO₄ that will be needed to react with one mole of sulphide ions in acidic solution is
 - (i) -
 - (ii) -
 - (iii) —

(iv)
$$\frac{1}{5}$$

Ans. (i)

Explanation: Hydrogen sulphide is oxidised, sulphur being precipitated.

$$H_2S \rightarrow 2H^+ + S^{2-}$$

$$5S^{2-} + 2MnO^{-4} + 16H^{+} \rightarrow 2Mn^{2+} + 8H_{2}O + 5S$$

It is clear from the above reaction that 5 moles of sulphide ions needs 2 moles of permanganate ion therefore one mole of sulphide ion require $\frac{2}{5}$ moles of permanganate ion.

12. Which of the following is amphoteric oxide?

 Mn_2O_7 , CrO_3 , Cr_2O_3 , CrO, V_2O_5 , V_2O_4

- (i) V₂O₅, Cr₂O₃
- (ii) Mn₂O₇, CrO₃
- (iii) CrO, V₂O₅
- (iv) V_2O_5 , V_2O_4

Ans. (i)

Explanation: Since they react with acid as well as base.

13. Gadolinium belongs to 4f series. It's atomic number is 64. Which of the following is the correct electronic configuration of gadolinium?

- (i) [Xe] $4f^75d^16s^2$
- (ii) [Xe] $4f^65d^26s^2$
- (iii) [Xe] $4f^{8}6d^{2}$
- (iv) [Xe] $4f^95s^1$

Ans. (i)

Explanation: Gadolinium belongs to 4f series it has atomic no.= 64. It has extra stability due to half-filled 4f sub shell.

14. Interstitial compounds are formed when small atoms are trapped inside the crystal lattice of metals. Which of the following is not the characteristic property of interstitial compounds?

- (i) They have high melting points in comparison to pure metals.
- (ii) They are very hard.
- (iii) They retain metallic conductivity.
- (iv) They are chemically very reactive.

Ans. (iv)

Explanation: Following are the principal properties of interstitial compounds:

- (i) They have high melting points, higher than those of pure metals.
- (ii) They are very hard, some borides approach diamond in hardness.
- (iii) They retain metallic conductivity.
- (iv) They are chemically inert.

15 .	The magnetic moment is associated with its spin angular momentum and orbital
	angular momentum. Spin only magnetic moment value of Cr3+ ion is

- (i) 2.87 B.M.
- (ii) 3.87 B.M.
- (iii) 3.47 B.M.
- (iv) 3.57 B.M.

Ans. (ii)

Explanation: Paramagnetism arises from the presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. For these, the magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula.

The magnetic moment μ is given by the formula

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

For $Cr^{3+}=3d^{3}$ the magnetic moment $=\sqrt{3(3+2)}=\sqrt{15}=3.87\,$ BM.

16. KMnO₄ acts as an oxidising agent in alkaline medium. When alkaline KMnO₄ is treated with KI, iodide ion is oxidised to ______.

- (i) I₂
- (ii) IO-
- (iii) IO_3^-
- (iv) IO_4^-

Ans. (iii)

Explanation: Iodide ion neutral of faintly alkaline solutions converts iodide to iodate: $2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$

17. Which of the following statements is not correct?

- (i) Copper liberates hydrogen from acids.
- (ii) In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine.
- (iii) Mn^{3+} and Co^{3+} are oxidising agents in aqueous solution.
- (iv) Ti^{2+} and Cr^{2+} are reducing agents in aqueous solution.

Ans. (i)

Explanation: Cu, having a positive E^{Θ} =+1.34 V accounts for its inability to liberate H₂ from acids.

18. When acidified K₂Cr₂O₇ solution is added to Sn²⁺ salts then Sn²⁺ changes to

- (i) Sn
- (ii) Sn³⁺
- (iii) Sn⁴⁺
- (iv) Sn+

Ans. (iii)

Thus, Acidified potassium dichromate will oxidize tin(II) to tin(IV) **Explanation:** $Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \rightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

19. Highest oxidation state of manganese in fluoride is +4 (MnF₄) but highest oxidation state in oxides is +7 (Mn₂O₇) because ______.

- (i) fluorine is more electronegative than oxygen.
- (ii) fluorine does not possess *d*-orbitals.
- (iii) fluorine stabilises lower oxidation state.
- (iv) in covalent compounds fluorine, can form single bond only while oxygen forms double bond.

Ans. (iv)

Explanation: Manganese in fluorine is +4 (MnF₄) but higher oxidation state in oxides is +7 (Mn₂O₇) because in covalent compounds fluorine can form single bond only while oxygen forms double bond. Oxygen has ability to form multiple bonds.

20. Although Zirconium belongs to 4d transition series and Hafnium to 5d transition series even then they show similar physical and chemical properties

because_____.

- (i) both belong to *d*-block.
- (ii) both have same number of electrons.
- (iii) both have similar atomic radius.
- (iv) both belong to the same group of the periodic table.

Ans. (iii)

Explanation: The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction, account of their occurrence together in nature and for the similar physical and chemical properties.

21. Why is HCl not used to make the medium acidic in oxidation reactions of KMnO₄ in acidic medium?

- (i) Both HCl and KMnO₄ act as oxidising agents.
- (ii) KMnO₄ oxidises HCl into Cl₂ which is also an oxidising agent.
- (iii) KMnO₄ is a weaker oxidising agent than HCl.
- (iv) KMnO₄ acts as a reducing agent in the presence of HCl.

Ans. (ii)

Explanation: Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.

The d- and f- Block Elements Multiple Choice Questions (Type-II)

Note: In the following questions two or more options may be correct.

- 22. Generally, transition elements and their salts are coloured due to the presence of unpaired electrons in metal ions. Which of the following compounds are coloured?
 - (i) KMnO₄
 - (ii) Ce(SO₄)₂
 - (iii) TiCl₄
 - (iv) Cu₂Cl₂
- Ans. (i) and (ii)

Explanation: It is due to charge transfer. In MnO_4^- an electron is momentarily transferred from 0 to the metal, thus momentarily O^{2-} is changed to O^- and reducing the oxidation state of the metal from Mn (VII) to Mn (VI).

- 23. Transition elements show magnetic moment due to spin and orbital motion of electrons. Which of the following metallic ions have almost same spin only magnetic moment?
 - (i) Co^{2+}
 - (ii) Cr²⁺
 - (iii) Mn²⁺
 - (iv) Cr3+
- Ans. (i) and (iv)

Explanation:

 $Co^{2+}=[Ar]3d^7$ no. of unpaired electrons=3

 $Cr^{2+}=[Ar]3d^4$ no. of unpaired electrons=4

 $Mn^{2+}=[Ar]3d^5$ no. of unpaired electrons=5

 $Cr^{3+}=[Ar]d^3$ no. of unpaired electrons=3

We can see that Co²⁺ and Cr³⁺ have same no. of unpaired electrons i.e.=3

- 24. In the form of dichromate, Cr (VI) is a strong oxidising agent in acidic medium but Mo (VI) in MoO₃ and W (VI) in WO₃ are not because _____.
 - (i) Cr (VI) is more stable than Mo(VI) and W(VI).
 - (ii) Mo(VI) and W(VI) are more stable than Cr(VI).
 - (iii) Higher oxidation states of heavier members of group-6 of transition series are more stable.
 - (iv) Lower oxidation states of heavier members of group-6 of transition series are more stable.
- Ans. (ii) and (iii)

Explanation: In the groups of d-block element higher oxidation states are favourable by heavier element. For example, in group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas MoO₃ and WO₃ are not.

25. Which of the following actinoids show oxidation states upto +7?

- (i) Am
- (ii) Pu
- (iii) U
- (iv) Np

Ans. (ii) and (iv)

Explanation: Oxidation states of the actinoids are as follows:

(i) Americium (Z=95)

Electronic configuration= $[R_n]^5 f^7 6d^o 7s^2$

Oxidation states=+3, +4, +5, +6

(ii) Plutonium (Z=94)

Electronic configuration = $[R_n]5f^66d^07s^2$

Oxidation states=+3, +4, +5, +6, +7

(iii) Uranium (Z=92)

Electronic configuration= $[R_n]5f^36d^17s^2$

Oxidation states=+3, +4, +5, +6, +7

(iv) Neptunium (Z=93)

Electronic configuration= $[R_n]5f^46d^17s^2$

Oxidation states=+3, +4, +5, +6, +7

26. General electronic configuration of actionoids is $(n-2)f^{1-14}(n-1)d^{0-2}ns^2$. Which of the following actinoids have one electron in 6d orbital?

- (i) U (Atomic no. 92)
- (ii) Np (Atomic no. 93)
- (iii) Pu (Atomic no. 94)
- (iv) Am (Atomic no. 95)

Ans. (i) and (ii)

Explanation:

$$U \rightarrow 5f^36d^17s^2$$

$$Np \rightarrow 5 f^4 6d^1 7s^2$$

27. Which of the following lanthanoids show +2 oxidation state besides the characteristic oxidation state +3 of lanthanoids?

- (i) Ce
- (ii) Eu
- (iii) Yb
- (iv) Ho

Ans. (ii) and (iii)

Explanation:

(i) Cerium (Z=57)

E.C.=[Xe]4f⁵5d⁰6s²

Oxidation states of Ce=+3, +4

- (ii)Europium (Z=63)
- E.C.=[Xe]4f⁷5d⁰6s²

Oxidation states of Eu=+2, +3

- (iii) Ytterbium (Z=70)
- E.C.=[Xe]4f¹⁴5d⁰6s²
- (iv) Holmium (Z=67)
- E.C.=[Xe]4 $f^{11}5d^{0}6s^{2}$

Oxidation state of Ho=+3

28. Which of the following ions show higher spin only magnetic moment value?

- (i) Ti^{3+}
- (ii) Mn²⁺
- (iii) Fe2+
- (iv) Co3+

Ans. (ii) and (iii)

Explanation:

- (ii) $Mn^{2+} = [Ar]3d^5 \cdot [t_{2g}^3 e_g^2]$
- (iii) $Fe^{2+} = [Ar]3d^{6}[t_{2g}^{4}e_{2g}^{2}]$

According CFT, electron pair up in t_{2g} and fe^{2+} and Mn^{2+} will show higher spin magnetic value.

29. Transition elements form binary compounds with halogens. Which of the following elements will form MF₃ type compounds?

- (i) Cr
- (ii) Co
- (iii) Cu
- (iv) Ni

Ans. (i) and (ii)

Explanation: Only Co and Cr can form halides like MF₃ beyond Mn no metal has a trihalide except FeX₃, and CoF₃.

30. Which of the following will not act as oxidising agents?

- (i) CrO₃
- (ii) MoO_3
- (iii) WO₃
- (iv) CrO_4^{2-}

Ans. (ii) and (iii)

Explanation: Higher oxidation states of W and Mo are more stable that is why they will not act as oxidizing agent.

31. Although +3 is the characteristic oxidation state for lanthanoids but cerium also shows +4 oxidation state because _____.

- (i) it has variable ionisation enthalpy
- (ii) it has a tendency to attain noble gas configuration
- (iii) it has a tendency to attain f^0 configuration
- (iv) it resembles Pb4+

Ans. (ii) and (iii)

Explanation: This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or completely filled f subshell. Thus, the formation of Ce(IV) is favoured by its noble gas configuration.

The d- and f- Block Elements <u>Matching Type</u>

Note: Match the items of Column I and Column II in the following questions.

52. Match the catalysts given in Column I with the processes given in Column II.

Column I	Column II
(i) Ni in the presence of hydrogen	(a) Zieglar Natta catalyst
(ii) Cu ₂ Cl ₂	(b) Contact process
(iii) V ₂ O ₅	(c) Vegetable oil to ghee
(iv) Finely divided iron	(e) Sandmeyer reaction
(v) TiCl ₄ +Al(CH ₃) ₃	(d) Haber's Process
	(f) Decomposition of KClO ₃

Ans. (i)-(c)

(ii)- (d)

(iii)- (b)

(iv)- (e)

(v)-(a)

Explanation: Catalyst \rightarrow Process

- (i) Ni in presence of $H_2 \rightarrow \mbox{Vegetable}$ oil to ghee
- (ii) $Cu_2Cl_2 \rightarrow Sandmayer reaction$
- (iii)- $V_2O_5 \rightarrow Contact process$
- (iv)Finely divided iron \rightarrow Haber's process
- (v) $TiCl_4+Al(CH_3)_3 \rightarrow Zieglar Natta catalyst$

53. Match the compounds/elements given in Column I with uses given in Column II.

Column I (Compound/element)	Column II (Use)
(i) Lanthanoid oxide	(a) Production of iron alloy
(ii) Lanthanoid	(b) Television screen
(iii) Misch metal	(c) Petroleum cracking
(iv) Magnesium based alloy is	(d) Lanthanoid metal + iron
constituent of	
(v) Mixed oxides of lanthanoids	(e) Bullets
are employed	
	(f) In X-ray screen

Ans. (i)- (b)

(ii)- (a)

(iii)- (d)

(iv)-(e)

(v)-(c)

Explanation: Compound/ element- use

- (i) Lanthanoid oxide /television screen
- (ii) Lanthanoid production of iron alloy
- (iii) Misch metal-Lanthanoid metal + iron

- (iv) Magnesium based alloy-bullets
- (v) Mixed oxide of lanthanoids are employed petroleum cracking.

54. Match the properties given in Column I with the metals given in Column II.

Column I (Property)	Column II (Metal)
(i) An element which can show +8	(a) Mn
oxidation state	
(ii) 3d block element that can show	(b) Cr
upto +7 oxidation state	
(iii) 3 <i>d</i> block element with highest	(c) 0s
melting point	
	(d) Fe

Ans. (i)- (c)

(ii)- (a)

(iii)- (b)

Explanation:

- (i) An element can show +8 oxidation states-Os
- (ii) 3d block element that can show upto +7 oxidation states-Mn
- (iii) 3d block element with highest melting point-Cr

55. Match the statements given in Column I with the oxidation states given in Column

Column I	Column II
(i) Oxidation state of Mn in MnO ₂ is	(a) + 2
(ii) Most stable oxidation state of	(b) + 3
Mn is	
(iii) Most stable oxidation state of	(c) + 4
Mn in oxides is	
(iv) Characteristic oxidation state of	(d) + 5
lanthanoids is	
	(e) + 7

Ans. (i)-(c)

(ii)- (a)

(iii)-(e)

(iv)-(b)

Explanation:

- (i) Oxidation state of Mn in MnO₂-+4
- (ii) Most stable oxidation state of Mn- +2
- (iii) Most stable oxidation state of Mn in oxides is -+7
- (iv) Characteristic oxidation state of lanthanoid- +3

56. Match the solutions given in Column I and the colours given in Column II.

Column I	Column II
(Aqueous solution of salt)	(Colour)

(i) FeSO ₄ .7H ₂ O	(a) Green
(ii) NiCl ₂ .4H ₂ O	(b) Light pink
(iii) MnCl ₂ .4H ₂ O	(c) Blue
(iv) CoCl ₂ .6H ₂ O	(d) Pale green
(v) Cu ₂ Cl ₂	(e) Pink
	(f) Colourless

Ans. (i)- (d)

(ii)- (a)

(iii)- (b)

(iv)-(e)

(v)-(f)

Explanation:

- (i) FeSO₄.7H₂O Pale green
- (ii) NiCl₂.4H₂O- Green
- (iii) MnCl₂.4H₂O-Light Pink
- (iv) CoCl₂.6H₂O- Pink
- (v) Cu₂Cl₂ Colourless

57. Match the property given in Column I with the element given in Column II)

Column I	Column II
(Property)	(Elements)
(i) Lanthanoid which shows +4 oxidation state	(a) Pm
(ii) Lanthanoid which can show +2 oxidation state	(b) Ce
(iii) Radioactive lanthanoid	(c) Lu
(iv) Lanthanoid which has 4f ⁷ electronic	(d) Eu
configuration in +3 oxidation state	
(v) Lanthanoid which has $4f^{14}$ electronic	(e) Gd
configuration in +3 oxidation state	
	(f) Dy

Ans. (i)- (b)

(ii)- (d)

(iii)-(a)

(iv)-(e)

(v)-(c)

Explanation:

- (i) Lanthanoid shows +4 oxidation state- Cerium (Ce)
- (ii) Lanthanoid shows +2 oxidation state- Europium (Eu)
- (iii) Radioactive lanthanoid Promethium (Pm)
- (iv) Lanthanoid having 4f⁷ configuration in +3 states Gadolinium (Gd)
- (v) Lanthanoid having 4f¹⁴ configuration in +3 states Lutetium (Lu)

58. Match the properties given in Column I with the metals given in Column II. Column I (Property) Column II (Metal)

(i) Element with highest second ionisation enthalpy	(a) Co
(ii) Element with highest third ionisation Enthalpy	(b) Cr
(iii) M in M (CO) ₆ is	(c) Cu
(iv) Element with highest heat of atomisation	(d) Zn
	(e) Ni

Ans.

- (i)-(c)
- (ii)- (d)
- (iii)- (b)
- (iv)-(a)

Explanation:

- (i) Element with highest second ionization enthalpy –Cu
- (ii) Element with highest third ionization enthalpy- Zn
- (iii) Metal carbonyl with formula M(CO)₆- Cr as it forms Cr(CO)₆
- (iv) Highest heat of atomisation -Co

The d- and f- Block Elements Assertion and Reason Type

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (i) Both assertion and reason are true, and reason is the correct explanation of the assertion.
- (ii) Both assertion and reason are true but reason is not the correct explanation of assertion.
- (iii) Assertion is not true but reason is true.
- (iv) Both assertion and reason are false.
- **59. Assertion:** Cu^{2+} iodide is not known.

Reason: Cu²⁺ oxidises I⁻ to iodine.

Ans. (i

Explanation: All Cu(II) halides are known except the iodide. In this case, Cu²⁺ oxidises I- to I₂:

60. Assertion: Separation of Zr and Hf is difficult.

Reason: Because Zr and Hf lie in the same group of the periodic table.

Ans. (ii)

Explanation: The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

- **61. Assertion:** Actinoids form relatively less stable complexes as compared to lanthanoids. **Reason:** Actinoids can utilise their 5*f* orbitals along with 6*d* orbitals in bonding but lanthanoids do not use their 4*f* orbital for bonding.
- Ans. (iii)

Explanation: The actinoids are highly reactive metals this is because the 5f electrons, will therefore be more effectively shielded from the nuclear charge than the 4f electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

62. Assertion: Cu cannot liberate hydrogen from acids.

Reason: Because it has positive electrode potential.

Ans. (i)

Explanation: Cu having a positive E^{Θ} accounts for its inability to liberate H₂ from acids. Only oxidising acids (nitric and hot concentrated sulphuric acid) react with Cu, as the acids being reduced. The high energy to transform Cu(s) to Cu²⁺(aq) is not balanced by its hydration enthalpy.

63. Assertion: The highest oxidation state of osmium is +8.

Reason: Osmium is a 5*d*-block element.

Ans. (ii)

Explanation: By using all the electrons from 6s and 5d with expanded octet osmium can show maximum +8 oxidation states.

The d- and f- Block Elements <u>Short Answer Type</u>

32. Why does copper not replace hydrogen from acids?

Ans. The unique behavior of Cu, having a positive E^{Θ} =+0.34 V accounts for its inability to liberate H₂ from acids.

33. Why E^{Θ} values for Mn, Ni and Zn are more negative than expected?

Ans. The stability of the half-filled d sub-shell in Mn²⁺ and the completely filled d¹⁰ configuration in Zn²⁺ are related to their E^{Θ} values, whereas for Ni is related to the highest negative Δ_{hwl} H.

34. Why first ionisation enthalpy of Cr is lower than that of Zn?

Ans. Ionisation enthalpy of Cr is lower due to stability of *d* ⁵ and the value for Zn is higher because its electron comes out from 4*s* orbital.

35. Transition elements show high melting points. Why?

Ans. The high melting points of these metals are attributed to the involvement of greater number of electrons from (n-1)d in addition to the ns electrons in the interatomic metallic bonding.

36. When Cu²⁺ ion is treated with KI, a white precipitate is formed. Explain the reaction with the help of chemical equation.

Ans. $2C^{2+} + 4I^{-} \rightarrow Cu_{2}I_{2}(s) + I_{2}$ When Cu^{2+} reacts with potassium iodide white precipitate of $Cu_{2}I_{2}$ is formed.

37. Out of Cu₂Cl₂ and CuCl₂, which is more stable and why?

Ans. CuCl₂ is more stable than Cu₂Cl₂. The stability of Cu²⁺(aq) rather than Cu⁺(aq) is due to the much more negative $\Delta_{hyd}H^{\Theta}$ of Cu²⁺(aq) than Cu⁺, which is more than to compensate for the second ionisation enthalpy of Cu.

38. When a brown compound of manganese (A) is treated with HCl it gives a gas (B). The gas taken in excess, reacts with NH₃ to give an explosive compound (C). Identify compounds A, B and C.

Ans.
$$A = MnO_2$$
 $B = Cl_2$ $C = NCl_3$
 $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$
 (A) (B) $($

39. Although fluorine is more electronegative than oxygen, but the ability of oxygen to stabilise higher oxidation states exceeds that of fluorine. Why?

Ans. The Ability of oxygen to stabilize high oxidation states exceeds that of fluorine because oxygen has the ability to form multiple bond with the metal.

- 40. Although Cr³⁺ and Co²⁺ ions have same number of unpaired electrons but the magnetic moment of Cr³⁺ is 3.87 B.M. and that of Co²⁺ is 4.87 B.M. Why?
- **Ans.** Magnetic moment is associated with its spin angular momentum and orbital angular momentum however due to symmetrical electronic configuration there is no orbital motion in Cr^{3+} . In Co^{2+} appreciable orbital contribution takes place.
- 41. Ionisation enthalpies of Ce, Pr and Nd are higher than Th, Pa and U. Why?
- Ans. All the actinoids are believed to have the electronic configuration of 7s² and variable occupancy of the 5f and 6d subshells. The fourteen electrons are formally added to 5f, though not in thorium (Z=90) but from Pa onwards the 5f orbitals are complete at element 103. Although the 5f orbitals resemble the 4f orbitals (lanthanoids) in their angular part of the wave-function, they are not as buried as 4f orbitals and hence 5f electrons can participate in bonding to a far greater extent that is why ionization enthalpy of lanthanoids Ce, Pr and Nd are higher than Th, Pa and U.
- 42. Although Zr belongs to 4*d* and Hf belongs to 5*d* transition series but it is quite difficult to separate them. Why?
- **Ans.** The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.
- 43. Although +3 oxidation states is the characteristic oxidation state of lanthanoids but cerium shows +4 oxidation state also. Why?
- **Ans.** This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or completely filled f subshell. Thus, the formation of Ce(IV) is favoured by its noble gas configuration.
- 44. Explain why does colour of KMnO₄ disappear when oxalic acid is added to its solution in acidic medium.
- **Ans.** In acidic medium

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

(pink) (colourless)

Oxalate ion is oxidized CO_2 by acidified $KMnO_4$ and itself changes to Mn^{2+} ion which is colourless.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 2CO_2 + 8H_2O$$

- 45. When orange solution containing $Cr_2O_7^{2-}$ ion is treated with an alkali, a yellow solution is formed and when H+ ions are added to yellow solution, an orange solution is obtained. Explain why does this happen?
- **Ans.** Chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution.

Acidification of Na₂CrO₄:

$$2Na_{2}CrO_{4} + H_{2}SO_{4} \rightarrow Na_{2}Cr_{2}O_{7} + Na_{2}SO_{4} + H_{2}O$$

$$^{(Orange)}$$

Or

$$2CrO_4^{2-} + 2H^+ \xrightarrow{Low pH} Cr_2O_7^{2-} + H_2O$$

$$(yellow) \qquad (orange)$$

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

- 46. A solution of KMnO₄ on reduction yields either a colourless solution or a brown precipitate or a green solution depending on pH of the solution. What different stages of the reduction do these represent and how are they carried out?
- **Ans.** Oxidising behaviour of KMnO₄ depends on pH of the solution.

In acidic medium (pH < 7)

$$MnO_4^- + 8H^+ + 5e^- \to Mn^{2+} + 4H_2O$$

In alkaline medium (pH>7)

$$MnO_4^- + e^- \rightarrow MnO_4^{2-}$$
(Green)

In neutral medium(pH=7)

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$
(Brown precipitate)

- 47. The second and third rows of transition elements resemble each other much more than they resemble the first row. Explain why?
- **Ans.** Due to lanthanoid contraction, the atomic radii of the second and third row transition elements is almost same. So, they resemble each other much more as compared to first row elements.
- 48. E^{Θ} of Cu is + 0.34 V while that of Zn is 0.76 V. Explain.
- **Ans.** The high energy to transform Cu(s) to $Cu^{2+}(aq)$ is not balanced by its hydration enthalpy. E^{Θ} for Mn, Ni and Zn are more negative than expected from the trend. The completely filled d^{10} configuration in Zn^{2+} are related to their E^{Θ} values.
- 49. The halides of transition elements become more covalent with increasing oxidation state of the metal. Why?
- **Ans.** As the oxidation state increases, size of the ion of transition element decreases. As per Fajan's rule, as the size of metal ion decreases, covalent character of the bond formed increases.
- 50. While filling up of electrons in the atomic orbitals, the 4s orbital is filled before the 3d orbital but reverse happens during the ionisation of the atom. Explain why?

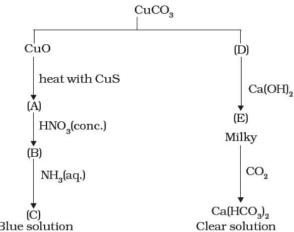
Ans.
$$n + 1$$
 rule: For $3d = n + 1 = 5$
 $4s = n + 1 = 4$

Ionisation enthalpy is responsible for the ionisation of atom. 4*s* electrons are loosely held by the nucleus. So, electrons are removed from 4*s* orbital prior to 3*d*.

51. Ans.	Reactivity of transition elements decreases almost regularly from Sc to Cu. Explain. From Sc to Cu ionization enthalpy increases that is why reactivity decreases regularly from Sc to Cu.

The d- and f- Block Elements Long Answer Type

64. Identify A to E and also explain the reactions involved.



Ans. A= Cu B= Cu(NO₃)₂ C= [Cu(NH₃)₄] D=CO₂
E= CaCO₃ F= Cu₂[Fe(CN)₆] G= Ca(HCO₃)₂

$$CuCO_3 \rightarrow CuO + CO_2$$

 $CuO + CuS \rightarrow Cu + SO_2$
 $Cu + 4HNO_3(Conc.) \rightarrow [Cu(NO_3)_2 + 2NO + 2H_2O$
 $Cu_{(B)}^{2+} + NH_3 \rightarrow [Cu(NH_3)_4]$
 $Cu_{(B)}^{2+} + CO_2 \rightarrow CaCO_3 + H_2O$
 $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$
 $CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$

65. When a chromite ore (A) is fused with sodium carbonate in free excess of air and the product is dissolved in water, a yellow solution of compound (B) is obtained. After treatment of this yellow solution with sulphuric acid, compound (C) can be crystallised from the solution. When compound (C) is treated with KCl, orange crystals of compound (D) crystallise out. Identify A to D and also explain the reactions.

Ans. A= FeCr₂O₄ B= Na₂Cr₀4 C=Na₂Cr₂O₇.2H₂O D=K₂Cr₂O₇
$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

$$2NaCrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

$$(C)$$

66. When an oxide of manganese (A) is fused with KOH in the presence of an oxidising agent and dissolved in water, it gives a dark green solution of compound (B).

Compound (B) disproportionates in neutral or acidic solution to give purple compound (C). An alkaline solution of compound (C) oxidises potassium iodide solution to a compound (D) and compound (A) is also formed. Identify compounds A to D and also explain the reactions involved.

Ans. A= MnO₂ B=k₂MnO₄ C=KMnO₄ D=KIO₃
$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$
$$3MnO_4^{2-} + 4H^4 \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$
$$(C)$$
$$3MnO_4^{2-} + H_2O + KI \rightarrow 2MnO_2 + 2OH^- + KIO_3$$

67. On the basis of Lanthanoid contraction, explain the following:

- (i) Nature of bonding in La₂O₃ and Lu₂O₃.
- (ii) Trends in the stability of oxo salts of lanthanoids from La to Lu.
- (iii) Stability of the complexes of lanthanoids.
- (iv) Radii of 4d and 5d block elements.
- (v) Trends in acidic character of lanthanoid oxides.

Ans. Explanation:

- (i) As the size decreases covalent character increases. Therefore, La₂O₃ is more ionic and Lu₂O₃ is more covalent.
- (ii) As the size decreases from La to Lu, stability of oxo salts also decreases.
- (iii) Stability of complexes increases as the size of lanthanoids decreases.
- (iv) Radii of 4d and 5d block elements will be almost same.
- (v) Acidic character of oxides increases from La to Lu.

68. (a) Answer the following questions:

- (i) Which element of the first transition series has highest second ionisation enthalpy?
- (ii) Which element of the first transition series has highest third ionisation enthalpy?
- $(iii) \ Which \ element \ of \ the \ first \ transition \ series \ has \ lowest \ enthalpy \ of \ atomisation?$
- **(b)** Identify the metal and justify your answer.
- (i) Carbonyl M (CO)₅
- (ii) MO₃F
- **Ans.** (a)(i) Exchange the second ionization enthalpy shows unusually high values for Cr and Cu first transition series where the d⁵ and d¹⁰ configuration of the M⁺ ions are disrupted, with considerable loss of energy.
 - (ii) The trend in the third ionisation enthalpies is not complicated by the 4s orbital factor and shows the greater difficulty of removing an electron from the d^5 (Mn²⁺) and d^{10} (Zn²⁺) ions.
 - (iii) because of the completely filled 3d sub shell no unpaired electron is left for metallic bonding.
 - **(b)** (i) It is Fe(CO)₅ by EAN rule

 $EAN=x+2\times5=36$ (Kr is the nearest inert gas)

x=26 (atomic no. of the metal) so the metal is iron.

(ii) MO₃F is MnO₃F

In MO₃F let us assume M=x

$$x+3 \times (-2) + (-1) = 0$$

$$x = +7$$

M is in +7 oxidation state so that the given compound is MnO₃F

- 69. Mention the type of compounds formed when small atoms like H, C and N get trapped inside the crystal lattice of transition metals. Also, give physical and chemical characteristics of these compounds.
- **Ans.** Interstitial compounds are formed when small atoms like H, C or N are trapped inside the crystal lattices of metal. They are usually non-stoichiometric and are neither typically ionic nor covalent.

The principal physical and chemical characteristics of these compounds are as follows:

- (i) They have high melting points, higher than those of pure metals.
- (ii) They are very hard, some borides approach diamond in hardness.
- (iii) They retain metallic conductivity.
- (iv) They are chemically inert.
- 70. (a) Transition metals can act as catalysts because these can change their oxidation state. How does Fe(III) catalyse the reaction between iodide and persulphate ions?
- **Ans.** The reaction between iodide and persulphate ions.

$$2I^{-} + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

An explanation of this catalytic action can be given as:

$$2Fe^{3+} + 2I^{-} \rightarrow 2Fe^{2+} + I_{2}$$

$$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$$

(b) Mention any three processes where transition metals act as catalysts.

Ans.
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

In the above reaction, Fe is used as catalyst.

$$2KClO_3 \xrightarrow{Heat} 2KCl + 3O_2$$

$$2SO_2 + O_2 \xrightarrow{V_2O_3} 2SO_3$$

71. A violet compound of manganese (A) decomposes on heating to liberate oxygen and compounds (B) and (C) of manganese are formed. Compound (C) reacts with KOH in the presence of potassium nitrate to give compound (B). On heating compound (C) with conc. H₂SO₄ and NaCl, chlorine gas is liberated and a compound (D) of manganese along with other products is formed. Identify compounds A to D and also explain the reactions involved.

$$\textbf{Ans.} \quad A=KMnO_4 \qquad B=K_2MnO_4 \qquad C=MnO_2 \qquad \quad D=MnCl_2$$

$$K\!M\!nO_4 \xrightarrow{\quad \Delta \quad} K_2M\!nO_4 + M\!nO_2 + O_2$$

$$MnO_2 + KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$MnO_2 + 4NaCl + 4H_2SO_4 \rightarrow MnCl_2 + 2NaHSO_4 + 2H_2O + Cl_2$$

														_
Since, mangai	compound nese dioxid	(C) on le (MnO ₂	heating 2).	with	conc.	H ₂ SO ₄	and	NaCl	gives	Cl ₂	gas.	So,	it	is