UNIT 7

THE d- AND f-BLOCK ELEMENTS

1. Introduction

d-block elements are present from fourth period onwards. There are mainly three series of the transition metals – 3d series (Sc to Zn), 4d series (Y to Cd) and 5d series (La to Hg, omitting Ce to Lu).

d-block elements are known as transition elements because their position in the periodic table is between the s-block and p-block elements. Electronic configuration of the d-block elements is $(n-1)d^{1-10}ns^{o-2}$ but Cu⁺, Zn, Cd, Hg etc. $[(n-1)d^{10}]$ are d-block elements, but not transition metals because these have completely filled d-orbitals.

3rd group ns ²	4th group d ¹ ns ² d ²	5th group ns ² d ³	6th group ns ² d ⁵	7th group ns ² d ⁵	8th group ns ² d ⁶	9th group ns ² d ⁷	10th group ns ² d ⁸	11th group ns ² d ¹⁰	12th group ns^2d^{10}
(n-1)	(n - 1)	(n – 1)	(n-1)	(n-1)	(n – 1)	(n - 1)	(n – 1)	(n – 1)	(n - 1)
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Transition Metals of d-block Elements

2. General Properties of the Transition Elements

(i) Atomic and Ionic Radii

In transition metals, left to right net nuclear charge increases due to poor shielding effect. Due to this, the atomic and ionic radii for transition elements for a given series show a decreasing trend for first five elements and then becomes almost constant for next five elements of the series.

(ii) Enthalpies of Atomisation

Transition elements exhibit higher enthalpies of atomization because of large number of unpaired electrons in their atoms. They have stronger interatomic interaction and hence, stronger bond.

(iii) Ionisation Enthalpies

• In a series from left to right, ionization enthalpy increases due to increase in nuclear charge.

• The irregular trend in the first ionization enthalpy of the 3d metals, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4s and 3d orbitals.

(iv) Oxidation States

• Transition metals shows variable oxidation state due to two incomplete outermost shells. Only stable oxidation states of the first row transition metals are

- The transition elements in their lower oxidation states (+2 and +3) usually forms ionic compounds. In higher oxidation state compounds are normally covalent.
 - Only Os and Ru show + 8 oxidation states in their compounds.
 - Ni and Fe in Ni(CO)₄ and Fe(CO)₅ show zero oxidation state.

(v) Trends in the Standard Electrode Potentials

- \bullet Transformation of the solid metal atoms to M^{2+} ions in solution and their standard electrode potentials.
- If sum of the first and second ionization enthalpies is greater than hydration enthalpy standard potential $(E^o_{M^{2+}/M})$ will be positive and reactivity will be lower and vice-versa.

(vi) Trends in Stability of Higher Oxidation States

The higher oxidation numbers are achieved in TiX_4 , VF_5 and CrF_6 . The + 7 state for Mn is not represented in simple halides but MnO_3F is known and beyond Mn no metal has a trihalide except FeX_3 and CoF_3 and increasing order of oxidizing power in the series $VO_2^+ < Cr_2O_7^{-2-} < MnO_4^-$.

(vii) Magnetic Properties

- When a magnetic field is applied to substances, mainly two types of magnetic behavior are observed: diamagnetism and paramagnetism. Paramagnetism due to presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum.
 - The magnetic moment is determined by the number of unpaired electrons.

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

where, n = number of unpaired electrons.

If all electrons are paired, substance will be diamagnetic and magnetic moment will be zero.

(viii) Formation of Coloured Ions

- The d-orbitals are non-degenerated in presence of ligands. When an electron from a lower energy d-orbital is excited to a higher energy d-orbital, the energy of required wavelength is absorbed and rest light is transmitted out. Therefore, the colour observed corresponds to the complementary colour of the light absorbed.
- In V_2O_5 , V is in + 5 oxidation state. It is coloured due to defects in crystal lattice.

(ix) Formation of Complex Compounds

- Transition metals have small size high nuclear charge which facilitates the acceptance of lone pair of electron from ligands.
- They have vacant *d*-orbitals of appropriate energy in order to accommodate the lone pair of electrons.

(x) Catalytic Properties

- Transition metals have two outermost shells incomplete and ability to adopt multiple oxidation states and to form complexes, therefore used as a catalyst.
- Transition metals also provide larger surface area for the reactant to be adsorbed.

(xi)Formation of Interstitial Compounds

- Small size of non-metals (H, C, N) fit into the voids of crystalline solid of transition metals and form interstitial compounds.
- 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.

(xii) Alloy Formation

Alloy is the homogeneous mixture of two or more metals. Transition metals have approximate same size therefore, in molten form they can fit to each other crystalline structure and form homogeneous mixture and form the alloy.

E.g., Brass (copper-zinc) and bronze (copper-tin) etc.

3. Some Important Compounds of Transition Elements

Potassium Dichromate $(K_2Cr_2O_7)$

(i) Ore

Ferrochrome or chromate (FeO.Cr₂O₃) or (FeCr₂O₄)

(ii) Preparation

$$4\text{FeO.Cr}_2\text{O}_3 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$$
(yellow)

$$2\mathrm{Na_2CrO_4} + 2\mathrm{H^+} \rightarrow \mathrm{Na_2Cr_2O_7} + 2\mathrm{Na^+} + \mathrm{H_2O}$$
 (orange)

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

Sodium dichromate is more soluble than potassium dichromate.

• Chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solutions.

(iii) Properties

Sodium and potassium dichromates are strong oxidizing agents, thus, acidified $K_2Cr_2O_7$ will oxidise iodides to iodine, sulphides to sulphur, tin (II) to tin (IV) and iron (II) salts to iron (III).

$$\begin{split} & \text{Cr}_2\text{O}_7^{\,2-} + 14\text{H}^+ + 6\text{I}^- \to 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{I}_2 \\ & \text{Cr}_2\text{O}_7^{\,2-} + 3\text{H}_2\text{S} + 8\text{H}^+ \to 2\text{Cr}^{3+} + 3\text{S} + 7\text{H}_2\text{O} \\ & \text{Cr}_2\text{O}_7^{\,2-} + 14\text{H}^+ + 3\text{Sn}^{2+} \to 3\text{Sn}^{4+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \end{split}$$

(iv) Uses

- (a) K₂Cr₂O₇ is used as oxidizing agent in volumetric analysis.
- (b) It is used in mordant dyes, leather industry, photography (for hardening of film).
 - (c) It is used in chromyl chloride test.
 - (d) It is used in cleaning glassware.

Potassium Permanganate (KMnO₄)

(i) Ore

Pyrolusite (MnO₂)

(ii) Preparation

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$
(green)

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^{-} + MnO_2 + 2H_2O_4^{-}$$

(iii) Commercial preparation

$$\begin{array}{ccc} \operatorname{MnO}_2 & \xrightarrow{\operatorname{Fused with KOH oxidised}} & \operatorname{MnO}_4^{\ 2^-} \\ & \operatorname{with air or KNO}_3 & \xrightarrow{\operatorname{MnO}_4^{\ 2^-}} \\ \operatorname{Manganate ion} & & \operatorname{MnO}_4^{\ 2^-} & \xrightarrow{\operatorname{Electrolytic oxidation}} & \operatorname{MnO}_4^{\ 2^-} & \xrightarrow{\operatorname{Permanganate ion}} & & & & & & \\ \operatorname{MnO}_4^{\ 2^-} & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ \end{array}$$

(iv) Properties

KMnO₄ acts as strong oxidizing agent.

(a) In presence of dilute H₂SO₄, KMnO₄ is reduced to manganous salt.

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

Acidic KMnO₄ solution oxidizes oxalates to CO₂, iron (II) and iron (III), nitrites to nitrates and iodides to iodine. The half reactions of reductants are

$$C_2O_4^{2-} \rightarrow CO_2 + 2e^-$$

 $Fe^{2+} \rightarrow Fe^{3+} + e^-$
 $NO_2^- \rightarrow NO_3^- + 2e^-$
 $2I^- \rightarrow I_2 + 2e^-$

To acidify KMnO₄, only H₂SO₄ is used and not HCl or HNO₃ because HCl reacts with KMnO₄ and produce Cl₂ while HNO₃, itself acts as oxidizing agent.

(b) In alkaline medium, KMnO₄ is reduced to insoluble MnO₂.

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

Alkaline or neutral $KMnO_4$ solution oxidizes I^- to IO_3^- , $S_2O_3^{\ 2-}$ to $SO_4^{\ 2-}$, Mn^{2+} to MnO_2 etc.

(v) Uses

- (a) In laboratory preparation of Cl₂.
- (b) KMnO₄ is used as an oxidizing agent, disinfectant.
- (c) In making Baeyer's reagent.

4. The Inner Transition Elements (f-Block)

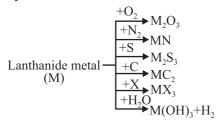
The *f*-block consists of the two series, lanthanoids and actinoids. Lanthanoids are known as rare earth metals and actinoids are known as radioactive elements (Th to Lr).

Lanthanoids

General characteristics

- General configuration [Xe] $4f^{1-14}$, $5d^{0-1}$, $6s^2$.
- Atomic and ionic size from left to right, decreases due to increase in nuclear charge. This is known as lanthanoid contraction.

- All the lanthanoids are silvery white soft metals and tarnish rapidly in air.
- Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Neither La³⁺ nor Lu³⁺ ion shows any colour but the rest do so.
- The lanthanoid ions other than the f^0 type (La³+ and Ce⁴+) and the f^{14} type (Yb²+ and Lu³+) are all paramagnetic. The paramagnetism arises to maximum in neodymium.
- Oxidation states \rightarrow Ce⁴⁺; (Some elements) is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common + 3 state. The E^o_{value} for Ce⁴⁺/Ce³⁺ is + 1.74 V, the reaction rate is very slow and hence, Ce(IV) is a good analytical reagent. Pr, Nd, Tb and Dy also exhibit + 4 state but only in oxides. Eu²⁺ is formed by losing the two s-electrons and its f^{7} configuration accounts for the formation of this ion. However, Eu2+ is a strong reducing agent changing to the common + 3 state. Similarly, Yb²⁺ which has f^{14} configuration is a reductant, Tb⁴⁺ has half-filled f-orbitals and is an oxidant.
 - Lanthanoid are very reactive metals like alkaline earth metals.



• Misch metals, contain lanthanoids about 90-95% (Ce 40-5%, Lanthanum and neodymium 44%) iron 4.5%, calcium, carbon and silicon, used in cigarette and gas lighters, toys, tank and tracer bullets.

Actinoids

- Genral configuration [Rn] $5f^{1-14}$, $6d^{0-2}$, $7s^2$.
- Actinoids exhibit a range of oxidation states due to comparable energies of 5f, 6d and 7s orbitals. The genral oxidation state of actinoids is +3.
 - All the actinoids are strong reducing agents and very reactive.
- Actinoids also react with oxygen, halogen, hydrogen and sulphur, etc. like lanthanoids.
- Actinoids are radioactive in nature and therefore, it is difficult to study their chemical nature.

(c) Providing empty *d*-orbitals(d) Having small charge/size ratio

(a) Having unpaired electron in *d*-subshell(b) Having paired electrons in *d*-subshells

1. One of the characteristics of transition metals to form the complex ion is:

2.	The correct electronic configuratio	n of copper atom is:					
	(a) $3d^{10}4s^1$	(b) $3d^{10}4s^2$					
	(c) $3d^94s^2$	(d) $3d^54s^24p^4$					
3.	The equivalent wight of $K_2Cr_2O_7$ in acid medium is equal to						
	(a) molecule weight	(b) 1/2 molecular weight					
	(c) 1/6 molecular weight	(d) 1/5 molecular weight					
4.	Manganese exhibits maximum oxid	lation state in:					
	(a) K ₂ MnO ₄	(b) KMnO ₄					
	(c) MnO ₂	(d) Mn_3O4					
5.	The equivalent weight of \mathbf{KMnO}_4 (oxidant in neural medium is	formula weight M) when it is used as an					
	(a) M	(b) M/2					
	(c) M/3	(d) M/5					
6.	Number of moles of $K_2Cr_2O_7$ reduce	ed by one mole of Sn ²⁺ ions is					
	(a) 1/3	(b) 3					
	(c) 1/6	(d) 6					
7.	${\rm CrO_3}$ dissolves in aqueous NaOH to	give:					
	(a) CrO ₄ ²⁻	(b) $Cr(OH)_3$					
	(c) $Cr_2O_7^{2-}$	(d) $Cr(OH)_2$					
8.	The electronic configuration of gad	olinium (At. No 64) is:					
	(a) [Xe] $4f^8 5d^0 6s^2$	(b) [Xe] $4f^7 5d^2 6s^2$					
	(c) [Xe] $4f^3 5d^5 6s^2$	(d) [Xe] $4f^6 5d^2 6s^2$					
9.	Electronic configuration of a transfiguration of a	ition element in + 3 oxidation state is [Al]					
	(a) 25	(b) 26					
	(c) 27	(d) 24					
10.		KMnO ₄ to concentrated H ₂ SO ₄ , a green s highly explosive in nature. Identify the					

18. Which of the following actionoids show oxidation states upto + 7?

(a) Am (b) Pu (c) U (d) Np

- 19. Which of the following ions show higher spin only magnetic moment value?
 - (a) Ti³⁺

(b) Mn^{2+}

(c) Fe^{2+}

- (d) Co3+
- 20. Which of the following will not act as oxidising agents?
 - (a) CrO₂

(b) MnO₂

(c) WO₂

- (d) CrO₄²
- 21. Match the components/elements given in column I with uses given in column

Column 1

- (A) Lanthanoid oxide
- (B) Lanthanoid
- (C) Misch metal
- (D) Magnesium based alloy
- (E) Mixed oxides of lanthanoids are employed
- (a) A-4, B-3, C-1, D-2
- (c) A-4, B-1, C-2, D-3

- Column 2
- (1) Production of iron alloy
- (2) Television screen
- (3) Petroleum cracking
- (4) Lanthanoid metal + iron
- (5) bullets
- (6) In X-ray screen
- (b) A-3, B-4, C-1, D-2
- (d) A-2, B-1, C-3, D-4
- 22. Match the solutions given in Column 1 and the colours given in column II.

Column 1

(i) FeSO₄.7H₂O

- (ii) NiCl₂.4H₂O
- (iii) MnCl₂.4H₂O
- (iv) COCl₂.6H₂O
- (v) Cu₂Cl₂

Column 2

- (a) green
- (b) light pink
- (c) Blue
- (d) Pale green
- (e) pink
- (f) colourless

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 choice.

- (a) Both assertion and reason are True, and reason is the correct explanation of the assertion.
- (b) Both assertion and reason are True, but reason is not the correct explanation of the assertion.
- (c) Assertion is not True, but reason is True.
- (d) Both assertion and reason are False.
- 23. Assertion: Cu²⁺ iodide is not known.

Reason: Cu²⁺ oxidises I⁻ to iodine.

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

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

25. The magnetic moment of a transition metal ion is found to be 4.90 BM. The number of unpaired electrons present in the ion is

		r	1		
3	4	5	6	5.5	2

ANSWERS

- 1. (d) 2. (b) 3. (c) 4. (a) 5. (d) 6. (c) 7. (a) 8. (b) 9. (b) 10. (a)
- **11.** (b) **12.** (d) **13.** (a) **14.** (a) **15.** (b)
- **16.** (a, b)
- **17.** (a, d)

- **18.** (b, d)
- **19.** (b, c)
- **20.** (b, c)
- **21.** (i)—(b), (ii)—(a), (iii)—(d), (iv)—(e), (v)—(c)
- 22. (i)—(d), (ii)—(a), (iii)—(b), (iv)—(e), (v)—(f) 23. (a) 24. (b) 25.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

- Q. 1. Explain CuSO₄.5H₂O is blue while CuSO₄ is colourless?
- **Ans.** Because water molecules act as ligands and results in crystal field splitting of d-orbitals of Cu^{2+} ion.
- Q. 2. Which element among 3d series exhibit highest oxidation state?
- Ans. Mn
- Q. 3. In 3d series (Sc to Zn), the enthalpy of atomization of Zn is low. Why?
- **Ans.** Due to absence of unpaired electrons.
- Q. 4. Which element among 3d series exhibit only one oxidation state?
- Ans. SC
- Q. 5. Why is the 3rd ionization energy of Mn (Z = 25) is unexpectedly high?
- **Ans.** Due to half-filled electronic configuration.
- Q. 6. Define alloy.
- **Ans.** Alloys are homogeneous solid solutions of two or more metals.
- Q. 7. Transition metals show zero oxidation state with ligands like CO. Explain.
- **Ans.** Co form synergic bonding with metal ion.
- Q. 8. Why can't HCl acid be used to acidify KMnO₄ solution?
- **Ans.** Because KMnO₄ oxidize HCl into Cl₂.
- O. 9. Name one ore of Mn and Cr.
- **Ans.** Mn: MnO $_{2}$

 $\operatorname{Cr}:\operatorname{FeCr_2O_4}$

Q. 10. Why Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their + 3 state ?

Ans. Mn⁺² has half-filled electronic configuration.

Q. 11. Why do transition metal (elements) show variable oxidation states?

Ans. Due to presence of vacant *d*-orbitals.

Q. 12. Write any uses of pyrophoric alloy.

Ans. Making bullets, shells and ligher flints.

Q. 13. Which is more basic – La(OH), or Lu(OH), ? Why?

Ans. La(OH)₃, due to lanthanide contraction, lower size, more covalent character, least basic.

Q. 14. Find out number of Cr - O - Cr bond/bonds in $Cr_2O_7^{2-}$ ion.

Ans.

Q. 15. What is effect of increasing pH on $K_2Cr_2O_7$ solution?

Ans. It changes into K₂CrO₄ solution/orange colour change into yellow colour.

O. 16. Why is Ce⁴⁺ in aqueous solution a good oxidizing agent?

Ans. Because Ce⁴⁺ is most stable in Ce⁺³ state in aqueous solution.

Q. 17. Why do Zr and Hf exhibit similar properties?

Ans. Due to lanthanide contraction.

Q. 18. What is lanthanoid contraction?

Ans. The regular slow decrease in the atomic or ionic radii of lanthanoids with increasing atomic number.

Q. 19. Why is Cu(Z = 29) considered a transition metal?

Ans. Due to its partially filled d-orbital in Cu^{2+} state.

Q. 20. Arrange the given in increasing order of acidic character:

Ans. $CrO < Cr_2O_3 < CrO_3$

Q. 21. Why $KMnO_4$ or MnO_4^- ion is coloured ?

Ans. Due to charge transfer complex formation.

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Chromium is typical hard metal while mercury is a liquid. Explain why?

Ans. Cr has five unpaired *d*-electrons. Hence metallic bonds are strong. In Hg, there is absence of unpaired electrons and size is larger.

- Q. 2. Why KMnO₄ is used in cleaning surgical instruments in hospitals?
- **Ans.** This is because KMnO₄ has a germicidal action.
- Q. 3. Most of the transition metals do not displace hydrogen from dilute acids, why?
- **Ans.** Due to their –ve reduction potential.
- Q. 4. Explain why Cu⁺ is not stable in aqueous solution?
- Ans. Due to less –ve $\Delta_{hyd}H^{\theta}$ of Cu^{+}/it cannot compensate 2nd ionization potential of Cu.
- Q. 5. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?
- **Ans.** Oxygen and fluoride have small size and high electronegativity. They can oxidise the metal.
- Q. 6. Write electronic configuration of Cu⁺² and Co⁺².

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

 $Co^{+2} = [Ar] 3d^7$

- Q. 7. Balance the following equations:
 - (a) $MnO_4^- + Fe^{2+} + H^+ \rightarrow$
 - (b) $Cr_2O_7^{2-} + Sn^{2+} + H^+ \rightarrow$
- **Ans.** (a) $MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{+2} + Fe^{+3}$
 - (b) $\operatorname{Cr_2O_7^{2-}} + \operatorname{Sn^{2+}} + \operatorname{H^+} \to \operatorname{Cr^{+3}} + \operatorname{Sn^{+4}}$
- Q. 8. Briefly explain why electronic configuration of lanthanoids are not known with certainty?
- **Ans.** 4f/5d subshells are very close in energy. +ve electrons can jump from 4f to 5d or vice-versa.
- Q. 9. Why Zn, Cd, Hg are soft and have low melting point?
- **Ans.** Due to weak interatomic attraction/absence of unpaired electrons.
- Q. 10. What is the effect of pH on the solution of K₂Cr₂O₄ solution?
- **Ans.** $K_2Cr_2O_4$ solution changes into $K_2Cr_2O_7$ /yellow colour changes into orange colour.
- Q. 11. Which of the following is/are transition element and why? Zn, Cd, Ag, Fe, Ni
- Ans. Fe, Ni, Ag

Q. 12. What are interstitial compounds? Give example.

Ans. When small atoms like C, H, B and N occupy interstitial site in their lattice. Example, TiC, Fe₃H,

Q. 13. Why are Zn, Cd, Hg volatile metals? Explain.

Ans. Due to weak interatomic attraction/low boiling point.

- Q. 14. Why is first ionization energy of 5d elements higher than those of 3d and 4d elements?
- Q. 15. Explain 'Misch metal' and write its use.

Ans. It is an alloy of 95% lanthanoid and 5% iron and traces of S, C, Ca and Al. Used in lighter flint, bullet tips etc.

Q. 16. The following two reactions of HNO3 with Zn are given:

(a)
$$Zn + conc. HNO_3 \rightarrow Zn(NO_3)_2 + X + H_2O$$

$$\textbf{(b)} \quad \textbf{Zn} + \textbf{dil.} \ \textbf{HNO}_3 \rightarrow \textbf{Zn(NO}_3)_2 + \textbf{Y} + \textbf{H}_2\textbf{O}$$

Identify X and Y.

Ans.
$$X = NO_2$$

 $Y = N_2O$

Q. 17. Complete the equations:

(a)
$$KMnO_4 \xrightarrow{\Delta}$$

(b)
$$3K_2MnO_4 \xrightarrow{\text{on standing } \\ \text{for long time } \\ \text{acidic medium}}$$

Ans. (a)
$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

(b)
$$3K_2MnO_4 \rightarrow MnO_4^- + MnO_2 + 2H_2O$$

Q. 18. Out of Fe and Cu, which one would exhibit higher melting point?

Ans. Fe, due to large number of unpaired d-electrons/more interatomic attraction.

Q. 19. Sc, the first member of first transition series does not exhibit variable oxidation state. Why?

Ans. Due to noble gas electronic configuration in + 3 oxidation state no other oxidation state is stable.

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. (a) Deduce the number of 3d electrons in the following ions:

- (b) Why do transition metals form alloy?
- (c) Why Zn⁺² salts are white?

Ans. (a) Cu^{+2} : 9 electrons

Sc⁺³: 0 electron

- (b) Transition metals have similar atomic radii.
- (c) Absence of unpaired electron.
- Q. 2. Complete and balance the following equations:
 - (a) $MnO_4^{2-} + H^+ \rightarrow$
 - (b) $KMnO_4 \xrightarrow{heat}$
 - (c) $MnO_4^- + FeC_2O_4 \xrightarrow{H^+}$

Ans. (a) $3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^{-} + \text{MnO}_2 + 2\text{H}_2\text{O}$

- (b) $2KMnO_4 \xrightarrow{heat} K_2MnO_4 + MnO_2 + O_2$
- (c) $MnO_4^- + FeC_2O_4 + H^+ \rightarrow Mn^{+2} + Fe^{+3} + CO_2$
- Q. 3. Describe the oxidizing action of $K_2Cr_2O_7$ with the following. Write ionic equations for its reaction (acidic medium) with :
 - (a) I-
- (b) Iron(II)
- (c) H,S

Ans. (a) It liberates I₂ form I⁻.

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{+3} + 7H_2O + 3I_2$$

(b) It oxidizes Fe⁺² to Fe⁺³.

$$Cr_2O_7^{2-} + 6Fe^{+2} + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O + 6Fe^{+3}$$

(b) It oxidizes H_2S to sulphur.

$$Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow 2Cr^{+3} + 7H_2O + 3S$$

Q. 4. Write any four differences between lanthanoids and actinoids.

Ans. Lanthanoids

Actinoids

(a) They are generally

They are radioactive.

non-radioactive.

- (b) Most of their ions are colourless.
- Coloured ions.
- (c) Show +3, +4 and +2 oxidation state.
- Beside + 3, show higher

oxidation state.

- (d) Less tendency of complex formation. Higher tendency.
- Q. 5. (a) Why is separation of lanthanoid elements difficult?
 - (b) Transition metal exhibit higher enthalpies of atomization. Explain why?
 - (c) Why have the transition metal high enthalpy of hydration?

- **Ans.** (a) Due to lanthanide contraction, the size of these elements is nearly same.
 - (b) Transition metal contain large number of unpaired electrons, and they have strong interatomic attractions.
 - (c) Due to their small size and large nuclear charge.
- Q. 6. (a) Use Hund's rule to derive the electronic configuration of Ce⁺³ ions and calculate its magnitude moment.
 - (b) Is lanthanum a f-block element?
- Ans. (a) $_{58}\text{Ce} = [\text{Xe}] 4f^1 5d^1 6s^2$ $\text{Ce}^{+3} = 4f^1 \text{ one unpaired electron}$ $= \sqrt{n(n+2)} = 1.73 \text{ BM}$
 - (b) No, it is a *d*-block element.
- Q. 7. Account for the following:
 - (a) Silver chloride dissolves in excess of NH₃.
 - (b) Cuprous chloride is diamagnetic while cupric chloride is paramagnetic.
 - (c) In CrO₄²⁻ ion, all the Cr O bond length are equal.
- **Ans.** (a) AgCl forms a soluble complex with NH₃.

$$AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$$

- (b) $Cu^+: 3d^{10} 4s^0$ All electrons are paired. $Cu^{+2}: 3d^9$ – Here, one unpaired electron is present.
- (c) Due to resonance.
- Q. 8. The E^{o} values in respect of electrodes of Cr, Mn and iron are :

$$Cr^{+3}/Cr^{+2} = -0.4 \text{ V}$$

 $Mn^{+3}/Mn^{+2} = +1.5 \text{ V}$

$$Fe^{+3}/Fe^{+2} = + 0.8 V$$

Compare the feasibilities of further oxidation of these ions.

Ans. Cr^{+3} is more stable than Cr^{2+} .

 Mn^{+2} is more stable than Mn^{+3} .

 Fe^{3+} is more stable than Fe^{2+} .

Order of feasibility of +2 oxidation state is :

$$Mn^{+2} > Fe^{+2} > Cr^{+2}$$

- Q. 9. Write any three properties of interstitial compounds.
- Ans. (a) They are chemically inert.
 - (b) They retain metallic conductivity.

- (c) They have high melting point than their pure metals.
- (d) These are harder and more corrosion resistant.
- Q. 10. Account for the following:
 - (a) All Scandium salts are white.
 - (b) The 1st ionization energy of the 5d series are higher than 3d and 4d transition elements in respective groups.
 - (c) Ce^{+3} can be easily oxidized to Ce^{+4} .
- **Ans.** (a) Sc has only + 3 oxidation state, there is no unpaired electron.
 - (b) Due to lanthanide contraction, effective nuclear charge increase.
 - (c) Due to gain noble gas electron configuration.
- Q. 11. A green chromium compound (A) on fusion with alkali gives a yellow compound (B) which on acidification gives a orange coloured compound (C). Identify A, B, C. Write equations for reactions.

Ans. A:
$$FeCr_2O_4$$
 B: Na_2CrO_4 C. $Na_2Cr_2O_7$

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$
(A) (B)
$$Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$
(C)

Q. 12. When an oxide of Mn (A) is fused with KOH in the presence of an oxidizing agent and dissolved in water, it gives a dark solution of compound (B). Compound (B) disproportionate in neutral or acidic solution to give purple compound (C). Identify A, B, C.

Ans.
$$A: MnO_2$$
 $B: K_2MnO_4$ $C: KMnO_4$

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. A violet compound of manganes (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 KNO₃ to give compound (B). On heating compound (C) with conc. H₂SO₄ and NaCl, Cl₂ gas is liberated and compound (D) of manganese is formed. Identify A, B, C, D alongwith reactions involved.

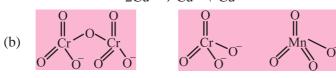
Ans. A:
$$KMnO_4$$
 B: K_2MnO_4 C: MnO_2 D: $MnCl_2$
$$KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$$
 (A) (B)
$$MnO_2 + KOH + KNO_3 \rightarrow K_2MnO_4$$

(C) (B)

$$MnO_2 + NaCl + conc. H_2SO_4 \rightarrow MnCl_2$$

(C) (D)

- (a) What is meant by disproportionation of an oxidation state? Give one Q. 2. example.
 - Draw the structures of $Cr_2O_7^{2-}$, CrO_4^{-2} , MnO_4^{-} .
 - (c) What is the effect of lanthoids contraction beyond lanthanoid?
- (a) When any atom or ion undergo oxidation and reduction simultaneously it Ans. is called disproportionation.



Size of respective 4d and 5d series elements becomes comparable from fourth group onwards (e.g., Zr and Hf).