Chapter - 8

d - AND f - BLOCK ELEMENTS

VERY SHORT ANSWER TYPE QUESTIONS

(1 - MARK QUESTIONS)

- 1. Write the electronic configuration of Cr^{3+} ion (atomic number of Cr = 24)?
- 3. Explain CuSO₄. 5H₂O is blue while ZnSO₄ and CuSO₄ are colourless?
- 4. Why is the third ionisation energy of Manganese (Z = 25) is unexpectedly high?

[**Hint**: The third electron is to be removed from stable configuration Mn²⁺ (3d⁵). It requires higher energy.]

5. Which element among 3d- transition elements, exhibit the highest oxidation state?

[**Hint**: Mn (+7)]

- 6. Silver (Ag) has completely filled d-orbitals (4d¹⁰) in its ground state. How can you say that it is a transition element.
- 7. In 3d series (Sc \rightarrow Zn), the enthalpy of atomisation of Zn is low. Why? [**Hint**: Poor interatomic bonding in zinc.]
- 8. Out of the following elements, identify the element which does not exhibit variable oxidation state?

Cr, Co, Zn.

- 9. The +3 oxidation state of lanthanum (Z = 57), gadolinium (Z = 64) and lutetium (Z = 71) are especially stable. Why?
- 10. Mention one consequence of Lanthanoid Contraction?
- 11. The first ionization enthalpies of 5d- series elements is higher than those of 3d and 4d series elements why?

[Hint: Increasing value of effective nuclear charge due to lanthanoid contraction.]

12. Why Mn²⁺ compounds are more stable than Fe²⁺ compounds towards oxidation to their +3 state?

14. Calculate the magnetic moment of Cu^{2+} (Z = 29) on the basis of "spin-only" formula.

[**Hint** :
$$\mu = \sqrt{n (n + 2)}$$
 B.M.]

15. What is the shape of chromate ions?

[Hint: Tetrahedral]

16. Why does vanadium pentoxide act a catalyst?

[Hint: In V₂O₅, Vanadium shows variable oxidation sates.]

- 17. What are interstitial compounds?
- 18. The transition metals and their compounds are known for their catalytic activity. Give two specific reasons to justify the statement.
- 19. Write the chemical equation for the reaction of thiosulphate ions and alkaline potassium permanganate.

[Hint:
$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 8MnO_2 + 2OH^- + 6SO_4^{2-}].$$

20. Mention the name and formula of the ore from which potassium dichromate is prepared.

[Hint: FeCr₂O₄ (Chromite)].

- 21. Write the electronic configuration of Lu^{3+} (At. No. = 71).
- 22. What is the most common oxidation state of actinoids?
- 23. Write the names of the catalyst used in the :
 - (a) Manufacture of sulphuric acid by contact process.
 - (b) Manufacture of polythene.
- 24. Mention the name of the element among lanthanoids known to exhibit +4 oxidation state.
- 25. Name one ore each of manganese and chromium.
- 26. Why is Cd2+ ion white?
- *27. Draw the structure of dichromate anion.
- *28. Arrange the following monoxides of transition metals on the basis of decreasing basic character TiO, VO, CrO, FeO.[Hint: TiO > VO > CrO > FeO]

SHORT ANSWER TYPE QUESTIONS (2-MARK QUESTIONS)

- 1. Write the chemical equation, when the yellow colour of aqueous solution of Na₂CrO₄ changes to orange on passing CO₂ gas?
- 2. The stability of Cu²⁺ (aq) is more than that of Cu+ (aq). Why?
- 3. Indicate the steps in the preparation of
 - (a) $K_2Cr_2O_7$ from Chromite ore.
 - (b) KMnO₄ from Pyrolusite ore.
- 4. Give reason for : -
 - (a) In permanganate ions, all bonds formed between manganese and oxygen are covalent.
 - (b) Permanganate titrations in presence of hydrochloric acid are unsatisfactory.
- 5. Write complete chemical equations for
 - (a) oxidation of Fe²⁺ by Cr₂O₇²⁻ in acidic medium
 - (b) oxidation of Mn²⁺ by MnO₄⁻ in neutral or faintly alkaline medium.
- 6. (a) Why do transition metals show high melting points?
 - (b) Out of Fe and Cu, which one would exhibit higher melting point?

[**Hint.** (i) Strong interatomic bonding arising from the participation of ns and unpaired (n-1) d-electrons.

- (ii) Fe has higher melting point due to presence of more unpaired electrons 3*d*-orbitals.
- 7. Describe giving reason which one of the following pairs has the property indicated:
 - (a) Cr²⁺ or Fe²⁺ (stronger reducing agent).
 - (b) Co²⁺ or Ni²⁺ (lower magnetic moments).
- 8. Of the ions Co²⁺, Sc³⁺, Cr³⁺ which one will give colourless aqueous solution and how will each of them respond to magnetic field and why?

[Hint: Co^{2+} (3d⁷); Cr^{3+} (3d⁴); Sc^{3+} (3d°)]

- 9. Complete the following equations:
 - (a) $MnO_2 + KOH + O_2 \longrightarrow$ (b) $Na_2Cr_2O_7 + KCI \longrightarrow$

10. Transition metals show low oxidation states with carbon monoxide.

[Hind : CO is a π acceptor ligand capable of forming a π bond by accepting π electrons from the filled d-orbitals of transition metal and CO also form σ bond by donating σ electrons to transition metal orbital.

11. For the first row transition metals the enthalpy of atomisation value are :

	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn
$\Delta_{\rm a} {\rm H}^{\rm heta}/{\rm kJ \ mol^{-1}}$	326	473	515	397	281	416	425	430	339	26

Assign reason for the following:

- (a) Transition elements have higher values of enthalpies of atomisation.
- (b) The enthalpy of atomisation of zinc is the lowest in 3d series.
- 12. Account for the following:
 - (a) Copper shows its inability to liberate hydrogen gas from the dilute acids.
 - (b) Scandium (Z = 21) does not exhibit variable oxidation states.
- 13. Copper (I) compounds undergo disproportionation. Write the chemical equation for the reaction involved and give reason.
- 14. Iron (III) catalyses the reaction:

$$2I^{-} + S_2O_8^{2-} \xrightarrow{Fe^{3+}} I_2 + 2SO_4^{2-}$$

15. Complete the equations:

(a)
$$MnO_4^- + NO_2^- + H^+ \longrightarrow$$

(b) KMnO₄
$$\longrightarrow$$
 513 k

16. The following two reactions of MNO₃ with Zn are given.

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

(b)
$$Zn + dil.HNO_3 \longrightarrow Zn(NO_3)_2 + Y + H_2O$$

Identify X and Y and write balanced equations.

[Hint: X is NO_2 and Y is N_2O].

17. Titanium shows magnetic moment of 1.73 BM in its compound. What is the oxidation number of Ti in the compound?

[Hint: O.N. of Ti = +3].

- 18. Account for the following:
 - (a) Transition metals and majority of their compounds act as good catalysts.
 - (b) From element to element, actionoid contraction is greater than lanthanoid contraction
- 19. Calculate the number of electrons transferred in each case when ${\rm KMnO_4}$ acts as an oxidising agent to give
 - (i) $\mathrm{MnO_2}$ (ii) $\mathrm{Mn^{2+}}$ (iii) $\mathrm{Mn(OH)_3}$ (iv) $\mathrm{MnO_4}^{2-}$ respectively.

[Hint: 3, 5, 4, 1].]

20. Calculate the number of moles of KM_nO_4 that is needed to react completely with one mole of sulphite ion in acidic medium.

[Hint: 2/5 moles].

SHORT ANSWER TYPE QUESTIONS (3 - MARK QUESTIONS)

- 1. Account for the following:
 - (a) $La(OH)_3$ is more basic than $Lu(OH)_3$
 - (b) Zn²⁺ salts are white.
 - (c) Cu(I) compounds are unstable in aqueous solution and undergo disproportination.
- 2. Describe the oxidising action of potassium dichromate with following. Write ionic equations for its reaction with.
 - (a) Iodide ion
- (b) Iron (II)
- (c) H_2S .
- 3. (a) Deduce the number of 3d electrons in the following ions : Fe^{3+} , Cu^{2+} and Sc^{3+} .
 - (b) Why do transition metals form alloys.
 - (c) Write any two characteristics of interstitial compounds.
- *4. In the following reaction, Mn(VI) changes to Mn(VII) and Mn(IV) in acidic solution.

 $3\mathsf{Mn^{VI}O_4^{\,2-}} + 4\mathsf{H} + \longrightarrow \ 2\mathsf{Mn^{VII}O_4^{\,-}} + \ \mathsf{Mn^{IV}O_2} + 2\mathsf{H_2O}$

- (a) Explain why Mn(VI) changes to Mn(VII) and Mn(IV).
- (b) What special name is given to such type of reactions?
- 5. What happens when
 - (a) thiosulphate ions react with alkaline KMnO₄.
 - (b) ferrous oxalate reacts with acidified KMnO₄.
 - (c) sulphurous acid reacts with acidified KMnO₄

Write the chemical equations for the reactions involved.

- 7. Name the catalysts used in the
 - (a) manufacture of ammonia by Haber's Process
 - (b) oxidation of ethyne to ethanol
 - (c) photographic industry.
- *8. Among TiCl₄, VCl₃ and FeCl₂ which one will be drawn more strongly into a magnetic field and why?

[Hint: Among these halides the transition metal ion having maximum number of unpaired electrons will be drawn strongly into the magnetic field.

$$Ti^{4+}=3d^0$$
 no. of unpaired $e^-=0$ $\mu=0$

$$V^{3+} = 3d^2 \qquad \qquad \text{no. of unpaired } e^- = 2 \qquad \qquad \mu = 2.76 \text{ BM}$$

$$\label{eq:power_power} \text{Fe}^{2+} = 3\text{d}^6 \qquad \qquad \text{no. of unpaired } \text{e}^- = 4 \qquad \qquad \mu = 4.9 \text{ BM}]$$

- 9. Complete the following equations
 - (a) $Mn0_4^{2-} + H+ \longrightarrow \dots + \dots + \dots$

(b)
$$KMnO_4 \xrightarrow{Heat}$$

(c)
$$H^+ + MnO_4^- + Fe^{2+} + C_2O_4^{2-} \longrightarrow$$

- 10. How do you account for the following?
 - (a) With the same d-orbital configuration (d⁴), Cr²⁺ is a reducing agent while Mn³⁺ is an oxidiising agent.
 - (b) The actinoids exhibit a larger number of oxidation states than the corresponding members in the lanthanoid series.
 - (c) Most of transition metal ions exhibit characteristic colours in aqueous solutions.

LONG ANSWER TYPE QUESTIONS (5 - MARK QUESTIONS)

1. A green compound 'A' on fusion with NaOH in presence of air forms yellow compound 'B' which on acidification with dilute acid, gives orange solution of compound 'C'. The orange solution when reacted with equimolar ammonuim salt gives compound 'D' which when heated liberates nitrogen gas and compound 'A'. Identify compounds A to D and write the chemical equation of the reactions involved.

[Hint: 'A' =
$$CrO_3$$
; 'B' = Na_2CrO_4 ; 'C' = $Na_2Cr_2O_7$ 'D' = $(NH_4)_2 Cr_2O_7$

- 2. Assign reasons for the following:
 - (a) There is no regular trends in E° values of M^{2+}/M systems in 3d series.
 - (b) There is gradual decrease in the ionic radii of M²⁺ ion in 3d series.
 - (c) Majority of transition metals form complexes.
 - (d) Ce3+ can be easily oxidised to Ce4+
 - (e) Tantalum and palladium metals are used to electroplate coinage metals.
- 3. Account for the following:
 - (a) Actinoids display a variety of oxidation states.
 - (b) Yb2+ behaves as a good reductant.
 - (c) Cerium (iv) is a good analytical reagent.
 - (d) Transition metal fluorides are ionic in nature while chlorides and bromides are covalent in nature.
 - (e) Hydrochloric acid attacks all the actinoids.
- *4. Explain by giving suitable reason:
 - (a) Co(II) is stable in aqueous solution but in the presence of complexing agent it is readily oxidised.
 - (b) Eu^{2+} , Yb^{2+} are good reductants whereas Tb^{4+} is an oxidant.
 - (c) AgCl dissolves in ammonia solution
 - (d) Out of Cr2+ or Fe2+, which one is a stronger reducing agent?
 - (e) The highest oxidation state is exhibited in oxoanions of a transition metal.

5. When a white crystalline compound A is heated with K₂Cr₂O₇ and conc. H₂SO₄, a reddish brown gas B is evolved, which gives a yellow coloured solution C when passed through NaOH. On adding CH₃COOH and (CH₃COO)₂ Pb to solution C, a yellow coloured ppt. D is obtained. Also on heating A with NaOH and passing the evolved gas through K₂Hgl₄ solution, a reddish brown precipitate E is formed.

Identify A, B, C, D and E and write the chemical equations for the reactions involved.

[Hint : (A) NH_4CI , (B) CrO_2CI_2 (g), (C) Na_2CrO_4

(D) PbCrO
$$_4$$
, (E) NH $_2$ $\begin{bmatrix} HgO \\ HgI \end{bmatrix}$

- *6. (a) Describe the preparation of potassium dichromate $(K_2Cr_2O_7)$. Write the chemical equations of the reactions involved.
 - (b) "The chromates and dichromates are interconvertible by the change in pH of medium." Why? Give chemical equations in favour of your answer.
- 7. Explain giving reasons:
 - (a) Transition metals are less reactive than the alkali metals and alkaline earth metals.
 - (b) $E^{\varnothing}_{cu^{2+}/\!\!\!/cu}$ has positive value
 - (c) Elements in the middle of transition series have higher melting points.
 - (d) The decrease in atomic size of transition elements in a series is very small.
- 8. (a) Compare the chemistry of the actinoids with that of lanthanoids with reference to—
 - (i) electronic configuration
 - (ii) oxidation states
 - (iii) chemical reactivity.

- (b) How would you account for the following:
 - (i) of the d⁴ species, Cr²⁺ is strongly reducing while Mn³⁺ is strongly oxidising.
 - (ii) the lowest oxide of a transition metal is basic whereas highest is amphoteric or acidic.
- 9. (a) What is meant by disproportionation of an oxidation state. Give one example.
 - (b) Explain why europium (II) is more stable than Ce(II)?

[Hint: (a) When particular state becomes less stable relative to other oxidation states, one lower and one higher, it is said to undergo disproportionation, for example,

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

- (b) Eu (II)= [Xe] 4f⁷ 5d⁰ (4f subshell is half filled)
 - Ce (II)= [Xe] $4f^1$ $5d^0$ (5d Subshell is empty and 4f subshell has only one electron which can be easily lost.)]
- 10. (a) For M^{2+}/M and M^{3+}/M^{2+} systems, the E^{θ} values for some metals are as follows :

$$Cr^{2+}/Cr = -0.9V$$
 and $Cr^{3+}/Cr^{2+} = -0.4V$

$$Mn^{2+}/Mn = -1.2 \text{ V}$$
 and $Mn^{3+}/Mn^{2+} = +1.5 \text{ V}$

$$Fe^{2+}/Fe = -0.4V$$
 and $Fe^{3+}/Fe^{2+} = +0.8V$

Use this data to comment upon:

- (i) the stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} and Mn^{3+}
- (ii) the ease with which iron can be oxidised as compared to a similar process for either chromium or manganese.
- (b) How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples.