CHEMISTRY
Paper – I

Time Allowed : **Three** Hours

Maximum Marks : **200**

Question Paper Specific Instructions

Please read each of the following instructions carefully before attempting questions :

*There are **ELEVEN** questions divided under **SIX** sections.*

*Candidate has to attempt **SIX** questions in all.*

*The **ONLY** question in Section **A** is **compulsory**.*

*Out of the remaining **TEN** questions, the candidate has to attempt **FIVE,** choosing **ONE** from each of the other Sections **B, C, D, E** and **F**.*

The number of marks carried by a question / part is indicated against it.

Neat sketches are to be drawn to illustrate answers, wherever required. These shall be drawn in the space provided for answering the question itself.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Assume suitable data, if necessary, and indicate the same clearly.

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly.

Any page or portion of the page left blank in the Question-cum-Answer Booklet must be clearly struck off.

*Answers must be written in **ENGLISH** only.*

SECTION A

Answer all of the following :   *5×10=50*

Q1. (a) Explain why aluminophosphate forms quartz-like structure.   5

(b) The stepwise formation constants for the complexes of NH_3 with $\left[Cu(OH_2)_6\right]^{2+}_{(aq)}$ are $\log K_{f_1} = 4 \cdot 15$, $\log K_{f_2} = 3 \cdot 50$, $\log K_{f_3} = 2 \cdot 89$, $\log K_{f_4} = 2 \cdot 13$, and $\log K_{f_5} = -0 \cdot 52$. Why is K_{f_5} so different ?   5

(c) Both H^- and $P(C_6H_5)_3$ are ligands of similar field strength, high in spectrochemical series. Discuss the orbital factors that account for the field strength of each ligand.   5

(d) Why is methyl orange not a suitable indicator for titration of a strong base against a weak acid ?   5

(e) Explain how post-precipitation differs from co-precipitation.   5

(f) Explain the role of $HgCl_2$ in the volumetric determination of iron using potassium dichromate.   5

(g) Explain the role of chelating agents in complexometric titrations.   5

(h) Arrange the following metal carbonyls in the increasing order of their increasing $C - O$ bond strength giving reason :   5

     $[Cr(CO)_6]$

     $[Mn(CO)_6]^+$

     $[V(CO)_6]^-$

(i) Complete the following nuclear reactions by giving the value of X :   5

     (i) $^{14}_{7}N + ^{4}_{2}He \longrightarrow X + ^{1}_{1}H$

     (ii) $X + ^{4}_{2}He \longrightarrow ^{30}_{15}P + ^{1}_{0}n$

     (iii) $^{23}_{11}Na + X \longrightarrow ^{23}_{12}Mg + ^{1}_{0}n$

     (iv) $^{113}_{48}Cd + X \longrightarrow ^{114}_{48}Cd + energy$

     (v) $X \longrightarrow ^{0}_{-1}e + ^{232}_{91}Pa$

(j) Why does the μ_{eff} value for transition metal ions with ground state term S agree well with $\mu_{s.o.}$ value while it differs with metal ions having ground state term as D or F ? Explain with reason.   5

SECTION B

Attempt any *one* question :

Q2. (a) Sketch the unit cell of ReO_3 and determine (i) the coordination number of Re and O, and (ii) the identity of the structure type that would be generated if a cation is inserted in the centre of each ReO_3 unit cell. *10*

(b) Would gallium arsenide be a suitable compound for a semiconductor ? How could n- and p-type semiconductors be designed from it ? *10*

(c) (i) The compound Fe_xO generally has x < 1. Describe the probable metal ion defect that leads to x being less than 1. *5*

(ii) Identify the product of the following : *5*

(I) $BaCO_3 \text{ (s)} + TiO_2 \text{ (s)} \xrightarrow{\text{1000°C}}$

(II) $ZrO_2 \text{ (s)} + 2H_3PO_4 \text{ (}l\text{)} \longrightarrow$

(III) $3KF \text{ (aq)} + MnBr_2 \text{ (aq)} \longrightarrow$

Q3. (a) Explain the magnetic properties of the following coordination compounds using Crystal Field Theory : *5*

(i) $[Co(NH_3)_6]^{3+}$

(ii) $[Co(en)_3]^{3+}$

(iii) $[Co(NO_2)_6]^{3-}$

(iv) $[CoF_6]^{3-}$

(v) $[Co(H_2O)_3F_3]^{3-}$

(b) Why are the chemical properties of d-block elements seemingly erratic and irregular as compared to homogeneous chemical properties of lanthanides ? *10*

(c) Why are the electronic spectra of lanthanides sharper as compared to transition metal complexes ? Explain by giving suitable reason(s). *15*

SECTION C

Attempt any *one* question :

Q4. (a) An approximately 'octahedral' complex of Co(III) with ammine and chlorido ligands gives two bands with ε_{max} between 60 and 80 dm^3 mol^{-1} cm^{-1}, one weak peak with $\varepsilon_{max} = 2$ dm^3 mol^{-1} cm^{-1} and a strong band at higher energy with $\varepsilon_{max} = 2 \times 10^4$ dm^3 mol^{-1} cm^{-1}. What do you suggest for the origin of these transitions ?   *15*

    (b) (i) Given that only the split between the top two energy levels of a square planar field can give rise to high and low-spin states, what number of d electrons, d^n, would have both possibilities ? Explain your answer.   *10*

       (ii) Consider the following cyanide complexes :

        $[Ni(CN)_4]^{2-}$, $[Mn(CN)_6]^{3-}$, $[Cr(CN)_6]^{3-}$

       Write the order of their lability. Justify your answer.   *5*

Q5. (a) Bearing in mind the Jahn-Teller effect, predict the structure of $[Cr(H_2O)_6]^{2+}$.   *10*

    (b) Predict the product and explain its formation in the following reactions :   *10*

       (i) $[Pt(PR_3)_4]^{2+} + 2Cl^- \longrightarrow$

       (ii) $[PtCl_4]^{2-} + 2PR_3 \longrightarrow$

       (iii) $cis - [Pt(NH_3)_2(py)_2]^{2+} + 2Cl^- \longrightarrow$

    (c) The equilibrium constants for the successive reactions of 1,2-diaminoethane with Co^{2+}, Ni^{2+} and Cu^{2+} are as follows :

       $[M(OH_2)_6]^{2+} + en \rightleftharpoons [M(en)(OH_2)_4]^{2+} + 2H_2O$ K_1

       $[M(en)(OH_2)_4]^{2+} + en \rightleftharpoons [M(en)_2(OH_2)_2]^{2+} + 2H_2O$ K_2

       $[M(en)_2(OH_2)_2]^{2+} + en \rightleftharpoons [M(en)_3]^{2+} + 2H_2O$ K_3

Ion	$\log K_1$	$\log K_2$	$\log K_3$
Co^{2+}	5·89	4·83	3·10
Ni^{2+}	7·52	6·28	4·26
Cu^{2+}	10·72	9·31	– 1·0

       (i) What does the above data inform about successive formation constants ?

       (ii) How do you account for very low value of K_3 for Cu^{2+} ?   *10*

SECTION D

Attempt any *one* question :

Q6. (a) Find out the volume in mL of 0·1 N HCl solution required to react completely with 1·0 g of a mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of two components.   *10*

(b) Methyl red has $K_a = 10^{-5}$. The acid form HIn is red and its conjugate base, $In^{\ominus}$ is yellow. Complete the following table :   *10*

pH	3	5	7
$[In^{\ominus}]\,/\,[HIn]$	–	–	–
Colour	–	–	–

(c) Sketch the general appearance of the curve for the titration of a weak diprotic base with strong acid. Explain different regions of the curve.   *10*

Q7. (a) What are redox titrations ? Explain the various types of redox titrations with examples.   *15*

(b) Give reasons for the following :   *15*

    (i) Starch solution is added near the end point in iodometry titrations.

    (ii) Why is hot solution titrated against $KMnO_4$ solution ?

    (iii) Potassium iodide is added in iodometric titration.

SECTION E

Attempt any *one* question :

Q8. (a) Explain the complexometric titration curve for the titration of EDTA vs. M^{n+} ion solution. *15*

(b) Explain the principle in the determination of Mn-Mg-Zn mixture using complexometric titration. *15*

Q9. (a) (i) What peculiarities does the Wilkinson's catalyst have that it behaves as a catalyst ? *5*

(ii) Explain the mechanism for hydrogenation of alkene by Wilkinson's catalyst. *10*

(b) How would you account for metal-metal bonding in $[Re_2Cl_8]^{2-}$ with the help of MO approach ? *15*

SECTION F

Attempt any *one* question :

Q10. (a)   What are the common possible nuclear fission reactions in case of $^{235}_{92}U$ when a slow neutron enters the uranium nucleus ?   *5*

(b)   What is radioactive displacement law ? Illustrate the radioactive displacements by referring to the four radioactive decay series.   *15*

(c)   What do you understand by Alpha Decay ? Explain by giving suitable examples.   *10*

Q11. (a)   Explain the general methods to avoid the supersaturation during precipitation in gravimetric estimation.   *10*

(b)   Explain the term peptisation with suitable example.   *10*

(c)   A very large excess of the precipitating agent is avoided in quantitative analysis. Justify.   *5*

(d)   Explain the effect of temperature on the solubility of a precipitate in gravimetric estimation.   *5*