CHEMISTRY
Paper – I

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

Q1. Answer all of the following :   *5×10=50*

(a) Fe_3O_4 adopts inverse spinel structure while Co_3O_4 adopts normal spinel
       structure. Explain.   *5*

(b)   Explain Trans effect with suitable example.   *5*

(c)   How is boric acid titrated using NaOH solution ?   *5*

(d)   What is oxine ? Draw the structure of aluminium oxinate complex.   *5*

(e)   Distinguish between iodometry and iodimetry.   *5*

(f)   Small amount of magnesium chloride is added during the estimation of
       calcium by EDTA and solochrome black indicator. Justify.   *5*

(g)   Write the structure of triiron dodecarbonyl. Mention the number of
       M – M bonds.   *5*

(h)   Explain masking and demasking with reference to the complexometric
       titration.   *5*

(i) $_{53}I^{133}$ is a beta emitter, while $_{53}I^{121}$ is a positron emitter. Explain.   *5*

(j)   Define transition elements. Is CuCl a transition metal compound ?
       Justify your answer.   *5*

SECTION B

Attempt any *one* question :

Q2. (a) Describe preparation, structure and properties of tetrasulphur tetranitride. *15*

(b) What types of defects are shown by $CaCl_2$ and $AgBr$? Explain. *10*

(c) Why are non-stoichiometric defects shown by the transition metal compounds ? Give examples. *5*

Q3. (a) Explain the factors affecting the stability of a metal complex in solution. *15*

(b) Sketch the splitting of d-orbitals in $[Ni(CN)_4]^{2-}$ ion. Comment on the magnetic behaviour of the complex. *10*

(c) Explain the intense purple colour of $KMnO_4$. *5*

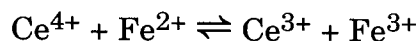## SECTION C

Attempt any _one_ question :

Q4. (a) Electronic spectrum of $[Cu(H_2O)_6]^{2+}$ shows unsymmetric broad band. Justify. *15*

(b) Assign the absorption bands observed at 10750, 17500 and 28200 cm^{-1} in the electronic spectrum of $[Ni(NH_3)_6]^{2+}$. Calculate ligand field parameters, 10Dq, B′, β, β⁰% and LFSE. Give significance of these parameters. The value of B for free gaseous nickel metal ion is 1060 cm^{-1}. *15*

Q5. (a) Which indicator is employed in the titration of hydrochloric acid versus ammonium hydroxide ? Explain with suitable neutralization curve. *10*

(b) Outline the principle as used in determination of $NaHCO_3$ and Na_2CO_3 in a mixture. *10*

(c) Mention the underlying principle for the gravimetric determination of nickel using dimethylglyoxime. Draw the structure of the complex. *10*
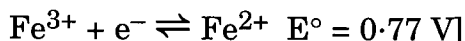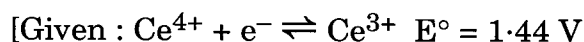
SECTION D

Attempt any *one* question :

Q6. (a) Distinguish between solubility and solubility product citing suitable example. *10*

(b) What do you mean by co-precipitation and post-precipitation ? Explain giving suitable example in each case. *10*

(c) What is Zimmermann-Reinhardt solution ? Explain its role in the titration of Fe^{2+} ion with $KMnO_4$ in HCl medium. *10*

Q7. (a) Consider the redox titration of Fe^{2+} ion by Ce^{4+} ion in dilute H_2SO_4 medium at 298 K.

$$Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+}$$

Calculate the equilibrium constant of the above reaction. Comment on the feasibility of the above titration. Draw the titration curve and suggest a suitable indicator to detect the equivalence point of the titration. *15*

[Given : $Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$ $E° = 1·44$ V

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E° = 0·77$ V]

(b) The standard reduction potentials of the Ni^{2+}/Ni and Co^{2+}/Co couples are $- 0·25$ V and $- 0·277$ V respectively. Comment on the feasibility of the following reaction at 298 K.

$$Ni^{2+} + Co \rightleftharpoons Ni + Co^{2+}$$ *15*

SECTION E

Attempt any *one* question :

Q8. (a) Explain the three different types of EDTA titrations. *15*

(b) Define hardness of water. Give the outline of the procedure for the determination of total hardness of water using EDTA. *15*

Q9. (a) Define metallochromic indicators. Explain the mechanism of colour change in the complexometric titration with suitable example. *15*

(b) Write the catalytic cycle for the hydrogenation of propene by $[RhCl(PPh_3)_3]$. Write the drawback of this catalyst. *15*

SECTION F

Attempt any *one* question :

Q10. (a) Calculate the packing fraction, mass defect and energy released in the formation of Argon atom, $_{18}^{40}Ar$. Mention the significance of the packing fraction so calculated. *15*

[Given : mass of proton = 1·007825 a.m.u.

mass of neutron = 1·008665 a.m.u.

isotopic mass of Ar = 39·962384 a.m.u.

1 a.m.u. = 931·5 MeV]

(b) Calculate magnetic moment of $Pr_2(SO_4)_3 \cdot 8H_2O$ and compare it with spin-only value. Justify the observed deviation. *10*

(Atomic number of Pr is 59)

(c) Complete the following nuclear reactions : *5*

(i) $_{11}Na^{24} \rightarrow \underline{\hspace{1cm}} + _{-1}e^0$

(ii) $_{13}Al^{27} + _0n^1 \rightarrow \underline{\hspace{1cm}} + _2He^4$

Q11. (a) Why do the transition metals show a large number of oxidation states ? Write all the oxidation states of chromium and manganese and mention the most stable state. *10*

(b) How do ionic radii vary in the lanthanide series ? Describe separation of lanthanide ions by ion exchange method. *10*

(c) Compare $NiCl_4^{2-}$, $PdCl_4^{2-}$ and $PtCl_4^{2-}$ with respect to structure and magnetic properties. *5*

(d) AmO_2^{2+} is oxidizing while Bk^{3+} is reducing in nature. Explain. *5*