

**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

**Q1. Answer all of the following :**

**5×10=50**

- (a)  $\text{Fe}_3\text{O}_4$  adopts inverse spinel structure while  $\text{Co}_3\text{O}_4$  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)  ${}_{53}\text{I}^{133}$  is a beta emitter, while  ${}_{53}\text{I}^{121}$  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  $\text{CaCl}_2$  and  $\text{AgBr}$  ? 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  $[\text{Ni}(\text{CN})_4]^{2-}$  ion. Comment on the magnetic behaviour of the complex. 10
- (c) Explain the intense purple colour of  $\text{KMnO}_4$ . 5

## SECTION C

Attempt any *one* question :

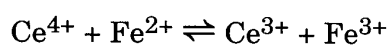
- Q4.** (a) Electronic spectrum of  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  shows unsymmetric broad band. Justify. 15
- (b) Assign the absorption bands observed at 10750, 17500 and 28200  $\text{cm}^{-1}$  in the electronic spectrum of  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ . Calculate ligand field parameters,  $10Dq$ ,  $B'$ ,  $\beta$ ,  $\beta^0\%$  and LFSE. Give significance of these parameters. The value of  $B$  for free gaseous nickel metal ion is 1060  $\text{cm}^{-1}$ . 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  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  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 :

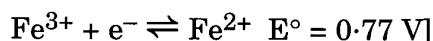
- Q6.** (a) Distinguish between solubility and solubility product citing suitable example. 10
- (b) What do you mean by co-precipitation and post-precipitation ? Explain giving suitable example in each case. 10
- (c) What is Zimmermann-Reinhardt solution ? Explain its role in the titration of  $\text{Fe}^{2+}$  ion with  $\text{KMnO}_4$  in  $\text{HCl}$  medium. 10

- Q7.** (a) Consider the redox titration of  $\text{Fe}^{2+}$  ion by  $\text{Ce}^{4+}$  ion in dilute  $\text{H}_2\text{SO}_4$  medium at 298 K.



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 :  $\text{Ce}^{4+} + \text{e}^- \rightleftharpoons \text{Ce}^{3+}$   $E^\circ = 1.44 \text{ V}$



- (b) The standard reduction potentials of the  $\text{Ni}^{2+}/\text{Ni}$  and  $\text{Co}^{2+}/\text{Co}$  couples are  $-0.25 \text{ V}$  and  $-0.277 \text{ V}$  respectively. Comment on the feasibility of the following reaction at 298 K.



## 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 metalochromic 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  $[\text{RhCl}(\text{PPh}_3)_3]$ . 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,  $^{40}_{18}\text{Ar}$ . 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.

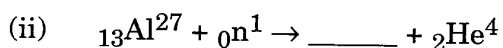
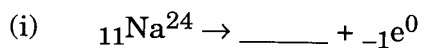
isotopic mass of Ar = 39.962384 a.m.u.

1 a.m.u. = 931.5 MeV]

- (b) Calculate magnetic moment of  $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  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



- 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  $\text{NiCl}_4^{2-}$ ,  $\text{PdCl}_4^{2-}$  and  $\text{PtCl}_4^{2-}$  with respect to structure and magnetic properties. 5

- (d)  $\text{AmO}_2^{2+}$  is oxidizing while  $\text{Bk}^{3+}$  is reducing in nature. Explain. 5

