

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.

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

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

Neat sketches are to be drawn to illustrate answers, wherever required.

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

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

SECTION 'A'

1. Answer *all* of the following : 5×10=50
- 1.(a) Complete the following reaction and balance it by ion-electron method :
 $\text{MnO}_4^- + \text{Fe}^{2+} + \text{H}^+ \longrightarrow$
- 1.(b) Carbon-14 is radioactive and beta-emitter while carbon-12 is not radioactive. Justify.
- 1.(c) Illustrate diagonal relationship with an appropriate example.
- 1.(d) Although H_3PO_4 is viscous it exhibits large electrical conductivity. Why ?
- 1.(e) Fe^{2+} is more easily oxidized to Fe^{3+} while Mn^{2+} to Mn^{3+} is not. Why ?
- 1.(f) Br_2 melts at 7.2°C whereas ICl melts at 272°C . Explain.
- 1.(g) The dipole moment of CO is merely 0.12 D although electronegativity difference between C and O is large. Why ?
- 1.(h) The strength of HF would increase with concentration. Explain.
- 1.(i) The electrical conductance of semiconductor increases with temperature unlike those of metals. Why ?
- 1.(j) Identify the product(s) in the following reaction :
- $$\text{B}_2\text{H}_6 + \text{NH}_3(\text{excess}) \xrightarrow{\text{low temperature}}$$

SECTION 'B'

(Attempt any *one* question)

- 2.(a) Which indicator is employed in the titration of acetic acid with sodium hydroxide ? Explain with suitable neutralization curve(s). 10
- 2.(b) Calculate the equilibrium constant of the following reaction at 298 K.
 $\text{Zn(s)} + \text{Cu}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Cu(s)}$
Given : $\text{Cu}^{2+} + 2\text{e} \rightleftharpoons \text{Cu} \quad E^\circ = 0.337 \text{ V}$
 $\text{Zn}^{2+} + 2\text{e} \rightleftharpoons \text{Zn} \quad E^\circ = -0.763 \text{ V}$
Comment on the feasibility of the above redox reaction. 10
- 2.(c) Define Lewis acid and Lewis base. Arrange BF_3 , BCl_3 and BBr_3 in the increasing order of their acid strength. 5
- 2.(d) How the concept of radius ratio governs the coordination number of the ions in a compound ? Illustrate with suitable examples. 5
- 3.(a) Draw the molecular structures of H_3PO_4 , H_3PO_3 and H_3PO_2 . Arrange them in accordance with their pK_a values. 10
- 3.(b) What is borazine ? Why it is called 'inorganic benzene' ? Write down the resonance structure of borazine. Why it is more reactive than benzene ? 10
- 3.(c) If a copper wire is dipped into an aqueous silver nitrate solution what will happen ?
Given : $\text{Cu}^{2+} + 2\text{e} \rightleftharpoons \text{Cu} \quad E^\circ = 0.337 \text{ V}$
 $\text{Ag}^+ + \text{e} \rightleftharpoons \text{Ag} \quad E^\circ = 0.799 \text{ V}$ 5

- 3.(d) Standard electrode potentials (E°) of M^{3+}/M of Al, Ga, In and Tl in aqueous solution are -1.66 , -0.56 , -0.34 and $+1.26$ V, respectively. What would you infer on the stabilities of their +3 oxidation state? 5

SECTION 'C'

(Attempt any *one* question)

- 4.(a) What are inner sphere and outer sphere complexes in the framework of Valence Bond Theory? Why $[\text{CoF}_6]^{3-}$ is labile whereas $[\text{Co}(\text{NH}_3)_6]^{3+}$ is stable? 10
- 4.(b) Predict the structure and magnetic behaviour of $[\text{NiX}_4]^{2-}$ ($X = \text{Cl}, \text{CN}$) complexes on the basis of Valence Bond Theory. 10
- 4.(c) Why nickel tetracarbonyl is stable? 10
- 5.(a) What are high spin and low spin complexes? Give an example of each. Why high spin tetrahedral complexes are relatively uncommon? 10
- 5.(b) Define Crystal Field Stabilization Energy (CFSE) in tetrahedral and octahedral ligand field environments. Calculate CFSE for
 (i) d^5 system in weak and strong ligand fields
 (ii) d^5 system in tetrahedral environments. 10
- 5.(c) The crystal structure of CuF_2 revealed that the Cu^{2+} ion is six coordinated wherein four Cu-F bond distances are of 1.93\AA and the remaining two being 2.27\AA . Explain. 10

SECTION 'D'

(Attempt any *one* question)

- 6.(a) Using IUPAC nomenclature state the formulae of
 (i) Tetrakis(trifluorophosphine) nickel(0)
 (ii) Diamidotetra ammine cobalt(III) bromide
 (iii) Ammonium trioxalatocobaltate(III)
 (iv) Hexammine chromium(III) hexafluorocobaltate(III) 10
- 6.(b) What are geometrical isomers? Draw all possible isomers of
 (i) $[\text{Pt}(\text{NH}_3)(\text{Py})\text{Cl}\cdot\text{Br}]$
 (ii) $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ 10
- 6.(c) What is Zeise's salt? Illustrate its structural features. 10
- 7.(a) Calculate the lattice energy of calcium chloride.
 Given: Heat of sublimation of Ca is 121 kJ mol^{-1}
 $\Delta H_f^\circ(\text{CaCl}_2) = -795\text{ kJ mol}^{-1}$
 Enthalpy of sublimation of Ca(s) = 121 kJ mol^{-1}
 Bond enthalpy of $\text{Cl}_2(\text{g}) = 242.7\text{ kJ mol}^{-1}$
 The first and second ionization energies of Ca(g) are 589.5 and 1145 kJ mol^{-1} respectively
 Electron enthalpy of $\text{Cl}(\text{g}) = 349\text{ kJ mol}^{-1}$

Show schematically the steps involved in the Born-Haber cycle for the above. 10

- 7.(b) Draw the isomers of $\text{Co}_2(\text{CO})_8$. How many cobalt-cobalt bonds are there in each? 10
- 7.(c) Write the product(s) formed from the following reactions : 10
- (i) $\text{LiBu}^n + \text{ArI} \longrightarrow$
- (ii) $\text{CaC}_2 + \text{N}_2 \xrightarrow{1100^\circ\text{C}}$
- (iii) $\text{Ni}(\text{CO})_4 + 4\text{PF}_3 \longrightarrow$
- (iv) $\text{PCl}_3 + 3\text{CH}_3\text{COOH} \longrightarrow$
- (v) $\text{FeCl}_2 + 2\text{Na}(\text{C}_5\text{H}_5) \xrightarrow{\text{THF}}$

SECTION 'E'

(Attempt any *one* question)

- 8.(a) Outline briefly the functioning of a Geiger-Muller counter. Explain why it cannot be used for alpha and gamma radiation measurements. 15
- 8.(b) What is packing fraction? Depict qualitatively the variation of packing fraction as a function of mass number. How it explains the stability of nucleus? 15
- 9.(a) The absorption band of cerium(III) ion is broad, while that of other lanthanides is sharp. Explain. 5
- 9.(b) Calculate the magnetic moment of gadolinium(III) with its outer electronic configuration being $4f^7 6s^0$ taking into account spin-orbit dependence. 10
- 9.(c) Define bond order. Sketch qualitatively the MO diagram of CN^- ion. Further explain which of the species — CN^- , CN and CN^+ would possess the longest bond distance. 15

SECTION 'F'

(Attempt any *one* question)

- 10.(a) How sodium borohydride is prepared? 5
- 10.(b) State the selection rules for electronic spectral transitions. Why d-d transitions usually lead to weak and broad bands in the electronic spectra of transition metal complexes? 10
- 10.(c) Draw the structures of $\text{Si}_2\text{O}_7^{6-}$, $\text{Si}_3\text{O}_9^{6-}$ and $\text{Si}_6\text{O}_{18}^{12-}$. How these units lead to pyrosilicates, cyclicsilicates and chainsilicates? 15
- 11.(a) At ordinary temperature, the solubility product (K_{sp}) values of copper and manganese sulphides are as follows :
 $\text{CuS} \simeq 10^{-36}$; $\text{MnS} \simeq 10^{-11}$
 Explain how sulphides are selectively precipitated from the mixture of Cu^{2+} and Mn^{2+} ions. 15
- 11.(b) Consider trimethylamine oxide and trimethylphosphine oxide – which of these is more reactive? Justify your answer. 5
- 11.(c) Outline in brief Bronsted-Lowry's concept of acid and base with requisite illustration. 10