

CHEMISTRY

(Paper I)

Time Allowed : Three Hours
Maximum Marks : 300

QUESTION PAPER SPECIFIC INSTRUCTIONS

(Please read each of the following instructions carefully before attempting questions)

There are EIGHT questions divided in two Sections.

Candidate has to attempt FIVE questions in all.

Question Nos. 1 and 5 are compulsory and out of the remaining, any THREE are to be attempted choosing at least ONE question from each Section.

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

Wherever any assumptions are made for answering a question, they must be clearly indicated.

Word limit in questions, wherever specified, should be adhered to.

SECTION 'A'

1. Answer any three of the following:
 - (a) What are the criteria to be met for the formation of molecular orbitals? Describe the bonding in N_2 according to MO theory. 20
 - (b) Substantiate the statement that "Hybridization does not enter explicitly into MO theory but mixing of orbitals does occur as in VB theory", taking the example of BeH_2 . 20
 - (c) Describe the X-ray diffraction technique for the determination of crystal structure. 20
 - (d) Explain and bring out the significance of radius ratio rule, lattice energy. Madelung constant and Born-Haber cycle. 20
2.
 - (a) How does a glass electrode develop potential in the solutions of varying hydrogen ion concentrations, and how is pH measured? 20
 - (b) Describe the principle and technique of amperometry and the estimation of lead by this technique. 20
 - (c) Calculate the potential of the following cell and indicate whether it is galvanic or electrolytic $Cu | Cu^{2+} (0.1 M) || Ag^+ (0.2 M) | Ag$ The standard reduction potentials are $E_{Ag} = 0.799 V$ and $E_{Cu} = 0.337 V$ 20
3.
 - (a) For a consecutive unimolecular reaction through the formation of an intermediate I, as in the reaction $A \xrightarrow{K_a} I \xrightarrow{K_b} P$, set up rate laws: (i) for the variation of concentration with time (ii) when $k_a \gg k_b$ and (iii) for steady state approximation. 30
 - (b) Calculate the quantum yield for the photochemical reaction in which 4-heptanone on irradiation with 315 nm radiation, with power output of 50 W for 90 s under the condition of total absorption, produces 2.8 m.mol. of ethane. 15
 - (c) Derive Langmuir adsorption isotherm. How will you find out the isosteric enthalpy of adsorption? 15
4.
 - (a) What is meant by CFSE? Discuss CFSE in weak and strong field cases for various d^n configurations. 30
 - (b) What are chelate complexes? What are the various factors influencing the stability of chelate complexes? 30

SECTION 'B'

5. Answer any three of the following

	(a)	Derive the equation for calculating the entropy change for the isothermal expansion of a perfect gas.	20
	(b)	Derive the Nernst heat theorem.	20
	(c)	Discuss upper and lower critical solution temperatures, with examples. Explain the thermodynamic interpretations of the upper critical solution temperature.	20
	(d)	Derive Clausius-Clapeyron equation for the variation of vapour pressure with temperature.	20
6.	(a)	Explain the principle, construction and uses of hydrogen-oxygen fuel cell and its advantages.	20
	(b)	Explain the factors that influence the stabilization of tetrahedral/octahedral co-ordination in the formation of complexes.	20
	(c)	Explain the technique of cyclic voltammetry and the significance of peak potential, wave slope and reversibility.	20
7.	(a)	Discuss the magnetic and spectral properties of lanthanides. How are they different from those of d-block elements?	20
	(b)	Describe the modern methods adopted for the separation of the lanthanides. Discuss the important oxidation states of lanthanides.	20
	(c)	Describe the photosynthetic process and the role of cytochrome C	20
8.	(a)	What are the important reactions of liquid ammonia and liquid sulphur dioxide as non-aqueous solvents	20
	(b)	Discuss the preparation properties and uses of carbonylate anions.	20
	(c)	Define enthalpy and its implications in thermo chemistry. How will you evaluate an enthalpy change using a differential scanning calorimeter?	20