

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. (a) Deduce the following equation for a particle in a one-dimensional box giving the Hamiltonian explicitly: $\psi_n = A \sin(n\pi x/a)$. Also deduce the energy for the system. 15
- (b) Using VSEPR theory, predict the shapes of PCl_2F_3 and SF_4 . Indicate the state of hybridisation in each case. 15
- (c) How do you account for the fact that the rate of reaction is more than double for a ten degree rise of temperature, whereas the number of collisions increases by only 3–4% for the same rise of temperature? 15
- (d) What are meant by phase, component and degree of freedom? Define Gibbs phase rule. A saturated solution of sodium sulphate with excess salt is at equilibrium with its vapour in a close vessel. How many phases, components and degrees of freedom are there in the system? 15
2. (a) Draw the MO energy-level diagram for N_2 and O_2 molecules. Predict their magnetic behaviours and also calculate the bond orders. 20
- (b)(i) State the essential conditions for hybridisation. Show diagrammatically the possible geometries from hybridisation of s, p and d orbitals. Give examples. 10
- (b)(ii) Half-change time and initial concentrations of a reaction are as follows:

$t_{1/2}$ (sec)	a (mm of mercury)
425	354
275	540
941	158

What is the order of the reaction? Calculate the rate constant. 10
- (c) Lindemann's mechanism for the first-order reaction is given as follows: $A + A \xrightleftharpoons{k_1} A^* + A$ (rapid equilibrium); $A^* \xrightarrow{k_2} \text{product}$ (slow). Show that $d/dt(\text{product}) = k_1 k_2 [A]^2 / (k_{-1}[A] + k_2)$. Under what condition will the reaction show (i) first order and (ii) second order? 20
3. (a)(i) A photochemical reaction with quantum efficiency of one shows no temperature dependence. Explain. 10
- (a)(ii) Calculate the number of moles of $\text{HCl}(\text{g})$ produced by the absorption of one joule of radiant energy of wavelength 480 nm in the reaction $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$ if the quantum yield of the photochemical reaction is 1.0×10^6 . 10
- (b) Give the postulates on which Langmuir's adsorption isotherm is based. Derive the expression for Langmuir's adsorption isotherm. How does this equation account for the adsorption at (i) high pressure and (ii) low pressure? Show that when a diatomic gas 20

adsorbs an atom on the surface of a solid, the Langmuir adsorption isotherm is modified to $\theta = \frac{(Kp)^{1/2}}{[1+(Kp)^{1/2}]}$ where, θ = fraction of surface covered, $K = k_{\text{adsorption}}/k_{\text{desorption}}$, p = pressure of gas

- (c) With proper diagram, calculate and explain briefly the limiting radius ratio values for tetrahedral and octahedral sites. 20
4. (a) Draw the phase diagram of a simple eutectic system. Give an example of such a system. 20
- (b) Using the principle of LCAO, obtain the normalised wave functions for the bonding and the antibonding molecular orbitals for H_2^+ system. 20
- (c)(i) For the reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$, rate $= k[\text{NO}]^2[\text{O}_2]$ Explain that the rate of this reaction decreases with increase of temperature. 10
- (c)(ii) How much will the rate of reaction change if volume of the vessel is reduced to 1/3 of its original volume? 10

SECTION 'B'

5. (a) What are interhalogen compounds? How are they classified? Give structures of IF_5 and IF_7 . 15
- (b) How do you explain the magnetic properties of transition metal ions, Ln^{3+} by the Crystal Field Theory? 15
- (c) Explain what are meant by extensive and intensive properties of a system. Which of the following properties are extensive and which are intensive? (i) Entropy (ii) Gibbs free energy (iii) Viscosity (iv) Chemical potential (v) Heat capacity 15
- (d) What is meant by liquid-junction potential? Why is KCl salt bridge used to eliminate it? Give one example of a concentration cell with transference. 15
6. (a) What is meant by heat capacity? Establish a relationship between heat capacity at constant pressure and constant volume, i.e. $C_p - C_v = [P + (\partial E/\partial V)_T](\partial V/\partial T)_P$ Deduce the relationship for an ideal gas. 20
- (b) (i) Derive Bragg's equation and show that $n\lambda = 2d\sin\theta$ for the reflection of X-rays from the faces of a crystal. (ii) Calculate the interplanar spacing (d-spacing) in a cubic crystal if the second-order reflections from such planes are obtained. $\sin\theta = 0.38$, when X-rays of λ 154 pm are used. 20
- (c) Discuss the different types of isomerism exhibited by coordination compound. Give suitable examples. 20
7. (a)(i) What is Nernst equation? Explain the various terms involved. 5
- (a)(ii) Calculate the potential of the following cell. Write down the cell reaction and indicate the polarities of the electrodes: $\text{Fe} \mid \text{Fe}^{2+}(\text{aq})_{(0.004 \text{ M})} \parallel \text{Cd}^{2+}(\text{aq})_{(0.001 \text{ M})} \mid \text{Cd}$ [$E_{\text{Fe}/\text{Fe}^{2+}} = 0.441 \text{ V}$, $E_{\text{Cd}/\text{Cd}^{2+}} = 0.403 \text{ V}$] 10
- (b) Find the expression for CFSE of d^5 , d^6 and d^7 systems in weak and strong octahedral fields in terms of Dq and P (pairing energy). 20
- (c) What is the effect of temperature on the vapour pressure of a liquid? Derive Clapeyron-Clausius equation for the equilibrium between liquid $\rightleftharpoons$ vapour Give the integrated form of this equation. 15
- (d) Write IUPAC names of the following: (i) $[\text{CoCl}(\text{H}_2\text{O})_2(\text{NH}_3)_4]\text{Cl}_2$ (ii) $[\text{PtCl}(\text{NH}_2\text{CH}_3)_2(\text{NH}_3)\text{Cl}]$ (iii) $[\text{Cr}(\text{en})_3]\text{Cl}_3$ (iv) $[\text{Fe}(\text{CN})_6]^{4-}$ (v) $[\text{Pt}(\text{py})_4][\text{PtCl}_4]$ 10
8. (a)(i) Give a short account of S-N compounds. 10
- (a)(ii) Why are 5f elements important? 5
- (b)(i) Distinguish between chemical cell and concentration cell giving examples. 5

- (b)(ii)** Derive an expression for the e.m.f. of electrode concentration cell without transference. **12**
- (c)** For the equilibrium $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ at 298 K, $K_c = 1.8 \times 10^{-7}$. What is ΔG for the reaction? [$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$] **20**
- (d)** Give reasons for the following: (i) $[\text{Ni}(\text{CN})_4]^{2-}$ is a square planar, while $\text{Ni}(\text{CO})_4$ is tetrahedral. (ii) $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic, while $[\text{Fe}(\text{CN})_6]^{3-}$ is paramagnetic. (iii) Low-spin tetrahedral complexes are not known. (iv) $[\text{FeF}_6]^{3-}$ is colourless, while $[\text{CoF}_6]^{3-}$ is coloured. **8**