

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) Define and differentiate between the following: (i) Normalized and Orthogonal wave functions (ii) Eigen value and Eigen function (iii) Eigen value and Most probable value 12
- (b) The heat of vaporization of ether is $25.98 \text{ kJ mol}^{-1}$ at its boiling point 34.5°C . Calculate the rate of change of vapour pressure of ether with temperature at the boiling point. 12
- (c) Electromagnetic radiation of wavelength 242 nm is just sufficient to ionize the sodium atom. Calculate the ionization energy of sodium in kJ mol^{-1} . 12
- (d) Determine the values of ΔH and ΔE for the reversible isothermal evaporation of 90.0 g of water at 100°C . Assume that water vapour behaves as an ideal gas and heat of vaporization of water is 2.244 kJ g^{-1} . 12
- (e) Set up Born – Haber cycle for determining the enthalpy of solvation of Mg^{2+} ions from MgCl_2 by water. 12
2. (a) The wave function for $1s$ electron of Li is given by $(Z^{3/2})/((\pi a_0^3)^{1/2})e^{-Zr/a_0}$, where a_0 is equal to 52.9 pm . Calculate the value of radius at which the probability of finding $1s$ electron is a maximum. 20
- (b) Metallic sodium crystallises in a body centred cubic lattice and has a density of $1.306 \times 10^3 \text{ kg m}^{-3}$. Calculate the length of the side of the unit cell (a) and the distance between 200 plane (d_{200}). Atomic weight of sodium is 29.99 g mol^{-1} . 20
- (c) Draw molecular orbital diagram for the following molecules and compare bond order, bond length and magnetic properties: CN and CN^- . Explain why the bonding in metal cyanides is between metal and carbon. 20
3. (a)(i) Derive the Langmuir adsorption isotherm for adsorption of a gas on a solid. Also, mention assumptions involved. 10
- (a)(ii) Explain the steps involved in the reaction $\text{A} + \text{B} \rightarrow \text{C}$ occurring under heterogeneous catalysis. 10
- (b) If germanium shows photoconductivity at a wavelength of 1824 nm , calculate the energy gap between the valence band and conduction band in germanium. 20
- (c)(i) Discuss the structure and bonding in diborane. 10
- (c)(ii) Using hybridization, explain what is the shape of XeO_3 . Explain how VSEPR theory accounts for the distortion. 10
4. (a) Evaluate most probable speed and average speed from Maxwell's relation for distribution of speed in a gas. Given: 15

$$dN_c/N = 4\pi(m/2\pi KT)^{3/2} c^2 e^{-mc^2/2KT} dc$$

and

$$\int_0^\infty e^{-ax^2} \cdot x^2 dx = 1/2a^2$$

- (b) Calculate ΔS and ΔS_{surr} for reversibly heating 2 moles of liquid water from 0 °C to 100 °C at a constant pressure of 1 atm. Treat heat capacity of water independent of T and equal to 4.184 J K⁻¹ g⁻¹. 15
- (c)(i) For a pure substance, what is the maximum number of phases that may exist at constant pressure? Explain and illustrate. 10
- (c)(ii) What are partial molar properties? Show that the partial molar free energy is equal to $(\partial H/\partial n_i)_{s,p,n_j(j \neq i)}$. 10
- (d) Show that for a second order reaction $2A \rightarrow \text{products}$, the half-life is inversely proportional to the initial concentration of A. 10

SECTION 'B'

5. (a) When Cl₂ is dissolved in water, it disproportionates, producing Cl⁻ ion and HClO. Find at what H₃O⁺ concentration the potential for the disproportionation changes from a negative value to a positive value, assuming 1.0 atm of pressure and concentration of 1.0 M for all species except hydronium ions. Given: $E_{Cl_2, Cl^-}^0 = 1.36$ and $E_{HClO, Cl_2}^0 = 1.63$ at 25 °C. 12
- (b) The value of temperature coefficient, $((k_{T+10})/k_T)$ at 300 K for a reaction is 2.8. Calculate the energy of activation (E_a) of the reaction. 12
- (c) Volume of nitrogen required to cover through monolayer 1 g of silica gel is 0.129 dm³ at 1 atm and 273 K. Calculate the surface area of the gel if each nitrogen molecule occupies an area of 16.2×10^{-10} m². 12
- (d) With the help of P – V diagram of NH₃ explain the critical temperature. 12
- (e) Explain the term ‘overpotential’. 12
6. (a) Calculate overall voltage output of a hydrogen – oxygen fuel cell which shows free energy change (ΔG) at 25 °C equal to $-273.3 \text{ kJ mol}^{-1}$. Also, write anodic, cathodic and overall reaction taking place in presence of KOH. 12
- (b) Discuss the working of a polarograph. Define $E_{1/2}$ and i_d and mention their application in chemical analysis. 12
- (c) Write a short note on ion selective electrodes and their uses. 12
- (d) Describe the relaxation method for studying kinetics of fast reactions. 12
- (e) Which compound is called ‘inorganic benzene’ and why? 12
7. (a) What are sacrificial anodes? How do they inhibit corrosion? 10
- (b) A certain system absorbs 3.0×10^{18} quanta of light per second. On irradiation for 10 minutes, 2.0×10^{-3} moles of the reactants was found to have reacted. Calculate the quantum efficiency of the process. 15
- (c) What are the functions of carbonic anhydrase and carboxypeptides? Explain. 20
- (d) What molecule is responsible for oxygen transport in molluscs? Give its structure. 15
8. (a) From the following data calculate the solubility product of AgCl at 25 °C: Ag | 0.1 M KCl satd. with AgCl || 0.1 M AgNO₃ | Ag (Given: E_{cell} at 25 °C = 0.455 V, $\log_{10} 2 = 0.3$) 14
- (b) (i) Explain what is lanthanide contraction. (ii) CuCl₂ is coloured but ZnCl₂ is colourless. Explain. 16
- (c) Draw all the stereoisomers of [Co(en)₂Cl₂] and comment on their optical activity. 20

- (d) Compare the 10 Dq values of the following ions with proper justification (At. No. of V, Fe and Os are 23, 26 and 76 respectively) (i) $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ (ii) $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Os}(\text{CN})_6]^{4-}$
 Given: Constants for use: $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$; $h = 6.625 \times 10^{-34} \text{ Js}$; $K_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$; $c = 3.0 \times 10^8 \text{ ms}^{-1}$; $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

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