

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:

20×3=60

- (a) Give the Schrödinger's wave equation for H-atoms in cartesian and polar co-ordinates. With the help of a diagram show the relation between the two co-ordinates.
- (b) Explain on the basis of MO theory, why: (i) Liquid oxygen sticks to the poles of a magnet while liquid nitrogen does not do so. (ii) He_2 and Be_2 molecules do not exist. (iii) The bond order in oxygen is 2, while that of nitrogen is 3. (iv) Hydrogen molecule is more stable than H_2^+ ion.
- (c) Derive Bragg's equation. Using X-ray powder pattern of a compound describe how do you calculate the spacing between the planes.
- (d) One mole of a perfect gas is ten-fold expanded isothermally and reversibly at 300 K. Calculate w , q , Δu , ΔH , ΔS , ΔA and ΔG .

2. (a) What do you mean by quantum numbers? Discuss different types of quantum numbers and their significance. **20**

(b) Define dipole moment. Explain the following: (i) Why is dipole moment of BF_3 zero? (ii) Why is dipole moment of NH_3 greater than that of NF_3 ? (iii) Why does SO_2 have dipole moment while CO_2 does not? **20**

(c) Derive an expression to estimate the frequency of collisions of gas molecules with a surface. Describe the relaxation method for studying fast reactions. **20**

3. (a) What are stoichiometric and non-stoichiometric defects? Explain Schottky defects and Frenkel defects and mention their consequences. **20**

(b) Derive an equation for surface tension exerted by a liquid in a glass capillary tube placed in the liquid when there is a rise. **20**

(c) (i) Which among the following are intensive properties: pressure, volume, temperature, internal energy, free energy and chemical potential? (ii) Define Gibbs free energy function. Explain its significance. **20**

4. (a) Show that (i) $(\partial u / \partial v)_T = T(\partial P / \partial T)_v - P$ (ii) $C_p - C_v = [P + (\partial u / \partial v)_T](\partial v / \partial T)_p$ **20**

(b) (i) The vapour pressures of water at 298 K and 308 K are 3167 Pa and 5599 Pa respectively. Calculate the enthalpy of vaporisation of water. (ii) Define excess free energy. What is its significance? **20**

- (c) (i) Nitrogen gas gets cooled as it expands whereas hydrogen gas gets warmer as it expands. Justify the observation. (ii) The standard free energy change for the following reaction is 8.7 kJ mol^{-1} : $2 \text{ C (graphite)} + 2 \text{ H}_2\text{O} \rightleftharpoons \text{CH}_4 (\text{g}) + \text{CO}_2 (\text{g})$. Calculate the equilibrium constant of the reaction at 900 K.

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SECTION 'B'

5. Answer any three of the following:

20×3=60

- (a) (i) Define transport number of anion and describe how it is measured. (ii) Explain the basis of polarography. How is it used in diffusion measurements? (iii) What is the principle behind ion selective electrode and how is it used as a reference electrode? (iv) Define overpotential and exchange current density.
- (b) Derive the rate constant of a second order reaction when (i) two different reactants have same initial concentrations. (ii) two different reactants have different initial concentrations.
- (c) (i) Explain the pattern of splitting of d orbitals in a square planar ligand field. (ii) Calculate the Crystal Field Stabilisation Energy and Spin-only Magnetic Moment of $[\text{Co}(\text{NH}_3)_6] \text{Cl}_2$.
- (d) (i) Mention the most stable oxidation state of each of the metals Ce, Eu, Th, U and Pu. (ii) "Magnetic susceptibility measurements are of little use in the structural elucidation of lanthanide complexes." Justify the statement.
6. (a) Explain collision theory of reaction rates. What are the factors which cause failure of this theory in certain cases? How do you make allowance for the deviation from the ideal behaviour?
- (b) (i) Describe the structure of electric double layer and define outer potential and inner potential. (ii) Calculate the emf of the following cell and predict whether the given cell representation is correct or wrong. If wrong, write the correct reaction. $\text{Cu (s)} | \text{Cu}^{2+} (\text{aq}) || \text{Zn}^{2+} (\text{aq}) | \text{Zn (s)}$ Given $E_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$, $E_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$
- (c) (i) What are photochemical reactions? Explain quantum efficiency. (ii) The quantum efficiency of the reactions between hydrogen and chlorine is 10^5 whereas that between hydrogen and bromine is 0.01. Explain the reason for this difference.
7. (a) Derive an equation for Langmuir's adsorption isotherm. Discuss the causes for deviations observed.
- (b) (i) What are prosthetic groups of cytochromes and haemoglobin? (ii) Taking into consideration electron transfer and catalytic function, write in brief on ferredoxins.
- (c) (i) Explain why octahedral Co(II) complexes have rather higher magnetic moment than tetrahedral Co(II) complexes. (ii) Explain the origin of the colour of permanganate.
8. (a) (i) Write IUPAC nomenclatures of $\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$, $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$, $[\text{Co}(\text{en})_2\text{Cl}_2] \text{Cl}$, $[\text{Pt}(\text{py})_4]$, $[\text{PtCl}_4]$. (ii) Explain the terms 'chelate effect' and 'lability' in complexes with examples.
- (b) Explain the structure and bonding in (i) Hexachlorocyclotriphosphazene (ii) Xenon hexafluoride
- (c) Explain the salient features of the structure of $[\text{Re}_2\text{Cl}_8]^{2-}$ and $\text{H}_2\text{Ru}_6(\text{CO})_{18}$.

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