JL – 7/14

Chemistry

Paper – I

Time : 3 hours

Full Marks : 200

The figures in the right-hand margin indicate marks.

*Answer **five** questions selecting at least **two** each from Section – A and Section – B.*

SECTION – A

1. (a) (i) Differentiate between fugacity and activity. Outline the theoretical basis for the determination of activity coefficient by electrochemical measurements. 10

(ii) Distinguish between molar and partial molar volume. The volume (dm^{-3}) of a mixture of solute and water at 20°C can be expressed as, $V \times 10^3 = 1001.80 + 24.522\ m^{1/2} + 3.486\ m + 40.452\ m^{3/2}$. Calculate the partial molar volumes of solute and water at 0.5 molal concentration. 10

(b) (i) What are thermodynamic excess functions ? Obtain the expression for any four thermodynamic excess functions. 10

(ii) Define γ-space and μ-space. Discuss Einstein treatment of heat capacity of solids. 10

2. (a) (i) Define steric factor and mention its importance in the study of reaction kinetics. If the specific rate of reaction triples when the temperature is raised from $30^{\circ}C$ to $50^{\circ}C$, calculate the energy of activation. 10

(ii) How does the catalyst enhance the rate of reaction ? Outline the application of NMR spectroscopy in the study of kinetics of fast reactions. 10

(b) (i) What is meant by ion association ? Deduce Debye-Huckel-Onsager conductance equation and give its extension for ion-solvent interaction. 10

(ii) Platinum electrode is better reversible electrode than other electrodes.

Give reasons. Explain the mechanism of corrosion prevention by anodic passivation. 10

3. (a) (i) How is CMC related to ΔG, ΔH and ΔS accompanying the process of micelle formation ? Discuss the BET theory of multilayer adsorption. 10

(ii) Define kinetic chain length. Discuss kinetics of anionic polymerization with an example. 10

(b) (i) Distinguish between Schottky and Frenkel defect. Insulin forms crystals of orthorhombic type with unit cell dimensions of 13.00 nm × 7.48 nm × 3.09 nm. If the density of the crystal is 1.315×10^3 kg m^{-3} and there are six insulin molecules per unit cell, what is the molar mass of insulin ? 10

(ii) State the number of components present in an aqueous solution of NaCl and $NaNO_3$. Discuss the application of phase rule to a ternary system of three liquids. 10

4. (a) (i) To which type of system is the perturbation method generally applicable ? An electron moving in a cubic box of side 10Å, what is the ZPE of the particle ? How much energy is required to raise the particle from its lowest state where $n_x = n_y = n_z = 3$? 10

(ii) What are σ, π, σ^* and π^* molecular orbitals ? Give their characteristics. Discuss the application of Huckel theory to cyclobutadiene. 10

(b) (i) Explain what Zeeman is splitting. ψ_i and ψ_j represent the wave functions corresponding to the different states of a particle in a box, show that they are orthogonal to each other. 10

(ii) Obtain the expression for the first order correction in energy of a perturbed system according to perturbation theory. Explain when the inclusion of higher order perturbation corrections becomes essential. 10

SECTION – B

5. (a) (i) Outline the concept of VSEPR model. Based on this, discuss the shapes of ClF_3, SF_4, BrF_5 and XeF_2. 10

(ii) Discuss the Pearson's concept of hard and soft acids and bases. Predict with reasoning, will Cu^{2+} react more strongly with HO^- or NH_3 and with O^{2-} or S^{2-} ? 10

(b) (i) What do you understand by the term 'point group' ? Describe the systematic procedure for the classification of molecules into point groups. To which point groups do the molecules $XeOF_4$, B_2H_6, HCN and CH_3Cl belong ? 10

(ii) Show that two σ_v– operations of C_{2v} point group are non-conjugate while that of three σ_v– operations of C_{3v} group are conjugate. Construct a character table for C_{2v} point group and explain each area in detail. 10

6. (a) (i) Give a comparative account on complex formation, spectral and magnetic behaviours among the elements of d-block and f-block. 10

(ii) Write the important assumptions of CFT and discuss the splitting pattern of metal d-orbitals in the complexes of $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$. Based on CFT, calculate their spin-only magnetic moment values. 10

(b) (i) Explain why an electronic transition for high-spin $[Mn(H_2O)_6]^{2+}$ is spin-forbidden, but for $[Co(H_2O)_6]^{2+}$ is spin-allowed. Discuss the Tanabe-Sugano diagram for $[Ni(OH_2)_6]^{2+}$ and estimate Δ_o and B for the $[Ni(OH_2)_6]^{2+}$ complex ion (Given absorptions at 8500, 15400 and 26000 cm^{-1}). 10

(ii) Set up MO energy level diagram for the complex ion $[CoF_6]^{3-}$ involving only sigma bond. Using the MO diagram, calculate the magnetic moment of the complex. 10

7. (a) (i) Explain stepwise stability and overall stability constants. How are they related ? The stepwise stability constants for

complexes of cadmium with bromide are $K_1 = 36.3$, $K_2 = 3.47$, $K_3 = 1.15$ and $K_4 = 2.34$. Why is $K_4 > K_3$? 10

(ii) Explain the mechanism for base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ and give the evidences in favour of this mechanism. 10

(b) (i) Discuss substitution in square planar complexes with emphasis on the influence of solvent, leaving group and entering group. 10

(ii) Distinguish between (i) inner sphere and outer sphere electron transfer reactions and (ii) nuclear fission and fusion reactions. 10

8. (a) (i) Discuss the nature of bonding and structures of metal carbonyls. How does the vibrational spectroscopy help in structural elucidation of metal carbonyls ? Predict the relative stabilities of $[V(CO)_6]$, $[V(CO)_6]^-$ and $Mo(CO)_7$. 10

(ii) Why is M-C bond in transition metal alkyls unstable ? Explain the different methods for the synthesis of stable transition metal alkyls with an example for each. 10

(b) (i) Describe the therapeutic uses of gold complexes as antiarthritis and platinum complexes as anticancer drugs. Explain the mechanism of each drug action. 10

(ii) Discuss briefly on the structural features and biological roles of hemoglobin, carboxy peptidase, nitrogenase and ferredoxins. 10