46 – CS/11
Chemistry
Paper – I

Time : 3 hours

Full Marks : 300

The figures in the right-hand margin indicate marks.

*Candidates should attempt Q. No. 1 from Section – A and Q. No. 5 from Section – B which are compulsory and **THREE** of the remaining questions, selecting at least **ONE** from each Section.*

SECTION – A

1. Answer any **five** of the following : 12×5 = 60

   (a) How many unpaired electrons are there in trivalent Dy and Ho ? (At. No. Dy = 66, Ho = 67)

   (b) Actinides have a greater tendency to form complexes than lanthanides. Explain.

(c) How many unpaired electrons do you expect in $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$?

(d) What is the significance of four quantum numbers ?

(e) Write Schrodinger's wave equation and explain each term involved therein.

(f) What are the characteristics of ionic compounds ?

2. (a) How is thermodynamic stability of complexes different from kinetic stability ? 20

(b) Derive the relationship between the stepwise and overall thermodynamic stability constants in relation to the formation of complexes in solution. 20

(c) Explain chelate effect with regard to stability of complexes. 20

3. (a) Draw the structures of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. 10

(b) Explain, with suitable examples, the following types of reactions in liquid ammonia : 30

(i) Acid-Base reaction

(ii) Precipitation reaction

(iii) Solvolysis reaction

(iv) Complex formation reaction

(c) Giving reasons arrange the following in increasing order of crystal field splitting energy : 20

(i) $[Cr(NH_3)_6]^{3+}$

(ii) $[CrCl_6]^{3-}$

(iii) $[Cr(CN)_6]^{3-}$

4. (a) What do you understand by sodium pump in the biological system ? 20

(b) What is **trans** effect ? Predict the products of the following substitution reactions (one mole of each) : 20

$[Pt\ Cl_3\ NH_3]^- + NH_3 \longrightarrow$

$[Pt\ Cl_3\ NO_2]^{2-} + NH_3 \longrightarrow$

(c) What are μ_s and μ_{s+L} values ? Explain why are the μ_{eff} values close to μ_s values for majority of 3d metal complexes. 20

SECTION – B

5. Answer any **three** of the following : 20×3 = 60

(a) Define Joule-Thomson coefficient for real gases in general and deduce its relation with van der Waals constants for gases obeying van der Waals equation of state.

(b) What is Third Law of Thermodynamics ? Discuss some of its important applications.

(c) What are the 'excess thermodynamic functions' ? Describe the experimental procedure for the determination of any one excess thermodynamic function. What are the informations that can be obtained from such excess factions ?

(d) Explain qualitatively the processes that lead to the formation of electrical double layer at metal / electrolyte interface.

Write down the Butler-Volmer (BV) equation for current density resulting from charge transfer reactions occuring at a working electrode and explain the terms involved. Deduce the limiting form of BV equation applicable under low field and mention the inference that can be drawn from this limiting equation about the polarizability of the electrode.

6. (a) What is meant by Effusion ? Derive the equation for the rate of effusion using Maxwell's distribution function of speed and comment whether the predictions of this equation is in agreement or not with Graham's law of effusion. 20

(b) What is meant by canonical partition function ? Deduce the expression for entropy of a system in terms of partition function. 20

(c) Illustrate the principles of relaxation method for the determination of rate constants of very fast reactions. 20

7. (a) Draw and discuss the phase diagram of phenol-water system and define 'Critical Solution Temperature(CST)'. How can you determine the relative amounts of the two conjugate solutions for a given phenol-water mixture of known overall composition maintained at a particular temperature below CST ? 20

(b) What is meant by active centres in the cases of solid catalysts ? Describe the procedure for the determination of surface area of a catalyst (powder). 20

(c) (i) What is Debye-Hückel model for the solution of strong electrolytes ? Write down the Debye-Hückel limiting law for activity coefficient of ions in electrolyte

solutions and comment about its applicability and limitations with reasoning. 12

(ii) Calculate the mean activity co-efficient ($\gamma\pm$) of 0.01 mol/kg aqueous $CaCl_2$ solution at 25° C using Debye-Hückel limiting law. (Given : A = 0.51). 8

8. (a) Derive the rate equation for a parallel reaction involving only first order reactions and illustrate how the rate constants of individual reactions can be determined. 20

(b) How cyclic voltammograms of a compound are determined ? Illustrate how from such voltammograms one can ascertain whether the test compound can undergo reversible or irreversible redox reaction. What are other parameters that can be evaluated from cyclic voltammograms ? 20

(c) What are the different routes of decay of excited state of a molecule and what are the utilities of knowing these modes of decay in various cases ? 20