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# M.Sc. (Part—I) Semester—II (CBCS Scheme) Examination CHEMISTRY (New)

## (Physical Chemistry—II)

## Paper—VII

Time: Three Hours] [Maximum Marks: 80

Note:—(1) All questions are compulsory and carry equal marks.

- (2) Use of log table and scientific calculator is allowed.
- 1. (a) Discuss the kinetics of Thermal Chain reaction of  $H_2 + Br_2$ .
  - (b) In case of general catalytic mechanisms of the reaction of type A + B  $\stackrel{K_{+1}}{\rightleftharpoons}$  C + D,

discuss the kinetics of Arrhenius type intermediates. (Pre-equilibrium treatment) 6

(c) What are fast reaction techniques? Discuss the principle involved in stopped flow method.

#### OR

- (p) What are oscillatory reactions? Discuss the kinetics of Lotka-Volterra model of Prey-Predator interactions.
- (q) Discuss the kinetics of relaxation method.
- (r) Calculate the relaxation time for the reaction

$$\Lambda_{(aq)}^{-} + B_{(aq)}^{-} \stackrel{K_1}{\rightleftharpoons} AB_{(aq)}$$

for a temperature jump experiment to a final temperature 400 K. The solution was initially prepared by adding 0.02 moles of AB to water maintaining total volume to 1 lit. Both forward and backward reactions are first order.  $K_1$  and  $K_2$  are  $8.0 \times 10^{10}$  and  $5.0 \times 10^6 \mathrm{s}^{-1}$  at 400 K respectively.

- (a) Use the Hückel approximation to find the energies of the π-orbitals of cyclobutadiene, and estimate the delocalization energy.
  - (b) Write the Hamiltonian for H<sub>2</sub> (single electron system) and discuss the linear combination of atomic orbitals.

### OR

- (p) Find the delocalization energy for benzene.
- (q) Show that an overlap integral is a measure of the extend of orbital overlap.
- 3. (a) What are macromolecules? What are different types of polymers? Discuss inorganic and chelate polymers in detail.
  - (b) Discuss the osmometric method for determination of molecular weight of polymer.

### OR

- (p) What is oxidation-reduction polymerization? Discuss the kinetics of propagation and termination of chain.
- (q) What are Number average molecular weight  $\overline{M}_n$  and Mass average molecular weight  $\overline{M}_w$  of a macromolecule? Calculate  $\overline{M}_N$  and  $\overline{M}_w$  if equal numbers of molecular weights of 100 and 10000 are mixed.

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- (a) Derive the expression for Debye-Hückel-Onsager equation and discuss the validity of Onsager equation for aqueous solutions.
  - (b) What are the different techniques for corrosion measurements? Discuss the weight loss method in detail.

### OR

- (p) Derive the expression for Buttler-Volmer equation. Discuss graphically the variation of current density with overpotential for activation polarization.
- (q) Write notes on:
  - (i) Electrocardiography
  - (ii) Threshold membrane phenomena.

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- (a) Derive the Bose-Einstein statist cal distribution law for Bosonic particles and discuss Boson condensate.
  - (b) What is partition function? Derive the expression for translational partition function.

#### OR

- (p) Derive the Fermi-Dirac distribution law for fermions and discuss the significance of fermi function in electrical conduction.
- (q) Show that the grand canonical partition function is just an aggregate of canonical partition function.