Sr. No. of Question Paper : 740   G   Your Roll No................

Unique Paper Code : 217505

Name of the Paper : Physical Chemistry – IV (CHHT-513)

Name of the Course : **B.Sc. (Hons.) Chemistry**

Semester : V

Duration : 3 Hours   Maximum Marks : 75

Instructions for the Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.

2. Attempt any **six** questions in all.

3. Question No. **1** is compulsory.

4. Attempt at least **one** question from each section.

5. Use of scientific calculator is permitted.

1. Explain any five of the following :

(a) Higher the activation energy of a reaction, slower is the rate of reaction.

(b) Difference between Order and Molecularity of a reaction.

(c) A DC current cannot be used for conductance measurement.

(d) Role of Uranyl ion in photochemical decomposition of oxalic acid.

(e) Adsorption is an exothermic process.

(f) Walden's rule is not applicable to cations of small size.   (3×5)

Section A

2. (a) What are the various factors affecting conductance of a solution ? How do you account for increase in conductance at high field strength and high frequency ?

(b) The specific conductivity of a saturated solution of CaF_2 was found to be 4.2×10^{-5} ohm^{-1} cm^{-1}. The specific conductivity of water used to make the solution was 2.0×10^{-6} ohm^{-1} cm^{-1}. The equivalent conductivities of Ca^{2+} and F^- ions are 52.0 and 48.0 ohm^{-1} cm^2 equiv^{-1}. Calculate the solubility of CaF_2 in water. (6,6)

3. (a) What do you mean by abnormal transference numbers ? Explain with suitable example.

(b) Explain the moving boundary method to determine the transference number of ions.

(c) During the electrolysis of a solution of potassium chloride between platinum electrodes, 0.0137 g of the chloride was lost from the anodic compartment and 0.0857 g of silver was deposited in a silver coulometer connected in series with the cell. Determine the transference number of K^+ and Cl^- ions. (4,4,4)

4. (a) Draw and discuss the titration curves obtained in the conductometric titration of :

   (i) An aqueous solution of HCl with aqueous solution of NaOH.

   (ii) An aqueous solution of HCl with aqueous solution of NH_4OH.

(b) What are the advantages of conductometric titrations over conventional titrations ?

(c) At 25°C, the equivalent conductance at infinite dilution of HCl and CH_3COOH are 400 and 85 ohm^{-1} cm^2 gequiv^{-1} respectively. If the transport numbers of H^+ and CH_3COO^- are 0.8 and 0.4 respectively, calculate the equivalent conductance of acetic acid at infinite dilution. (4,2,6)

Section B

5. (a) The reaction,

$$\nu A \rightarrow \text{Products}$$

is a first order reaction with respect to A.

(i) Write down its differential rate law and deduce from it the integrated rate law.

(ii) Show that half life of such a reaction is independent of the initial concentration of the reactant A.

(b) For the decomposition of acetone dicarboxylic acid, rate constants are 2.46×10^{-5} at 273 K and 1.63×10^{-3} at 303 K. Calculate the energy of activation of the reaction.

(c) Comment on the statement that ionic reactions are fast while the molecular reactions are slow.   (6,4,2)

6. (a) Derive an expression for the rate constant on the basis of collision theory for bimolecular gaseous reactions.

$$k_2 = p \, N_A \, \pi \sigma_{AB}^2 \left(\frac{8kT}{\pi\mu} \right)^{1/2} \exp\left(\frac{-E_0}{RT} \right)$$

Compare it with that of Arrhenius equation and show that

$$E_a = E_0 + \frac{RT}{2}$$

(b) The following results were obtained for the saponification of ethyl acetate using equal concentration of ester and alkali :

Time (min)	0	4.89	10.07	23.66
mL of acid used	47.65	38.92	32.62	22.58

Show that the reaction is second order.   (8,4)

7. (a) An acid HA catalyses the substrate S to products as follows :

$$S + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^-$$

$$SH^+ + H_2O \longrightarrow Products + H_3O^+$$
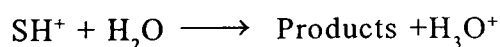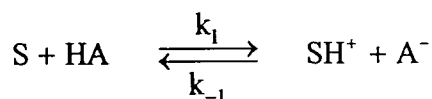
Derive the rate law for the reaction. State when it becomes an example of 'general acid catalysis' and it is 'specific hydrogen ion catalysis'.

(b) Derive an expression for Langmuir adsorption isotherm. Discuss its limitations.

(c) In adsorption of hydrogen over a sample of copper, monolayer – formation volume per gram of powder was found to be 1.36 cm^3 measured at STP. Calculate the specific surface area of copper. Liquid hydrogen has a density of 0.07 g cm^{-3}. (4,4,4)
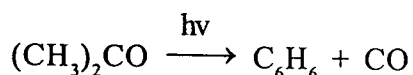
Section C

8. (a) Define Quantum Efficiency. What are the reasons for low and high quantum efficiency ?

(b) The mechanism of photochemical dimerization of Anthracene (A) is given below :

$$A \xrightarrow{hv} A*$$

$$A* + A \xrightarrow{k_2} A_2$$

$$A_2 \xrightarrow{k_3} 2A$$

$$A* \xrightarrow{k_4} A + hv'$$
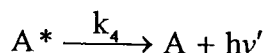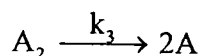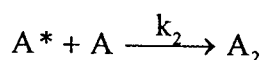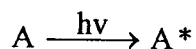
Derive the expression for rate of formation of dimer.

(c) Adsorption of UV radiations decomposes acetone according to the reaction

$$(CH_3)_2CO \xrightarrow{hv} C_6H_6 + CO$$

The quantum yield of the reaction at 280 nm is 0.2. A sample of acetone absorbs monochromatic radiation at 280 nm at the rate of 7.5×10^{-3} J s^{-1}. Calculate the rate of formation of CO. (4,4,4)

9. Write short notes on any **three** of the following :

(a) Enzyme catalysis

(b) Electrophoretic effect

(c) Photostationary state

(d) Quenching of fluorescence (4,4,4)