[This question paper contains 4 printed pages.]

Sr. No. of Question Paper : 8469 **C** **Roll No.....**

Unique Paper Code : 217505

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

Name of the Course : B.Sc. (Hons.) Chemistry, Part III

Semester : V

Duration : 3 Hours

Maximum Marks : 75

Instructions for 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) Reactions of third and higher orders are usually not very common.

   (b) Difference between stationary and non-stationary chain reactions.

   (c) Walden's rule is not applicable to cations of small size.

   (d) Equivalent conductance values for alkali metals are in the order

   $$Rb^{+} > K^{+} > Na^{+} > Li^{+}.$$

   (e) Quantum efficiency for the photochemical reaction

   $$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$$

   is low while for the reaction

   $$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

   is very high.

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(f) Why a finely powdered substance is more effective adsorbent ? (3×5)

SECTION A

2. (a) State Kohlrausch's Law of independent migration of ions. How does it help in determination of equivalent conductance at infinite dilution of weak electrolytes.

(b) Specific conductivity of a saturated solution of AgCl at 25°C was found to be 3.41×10^{-6} ohm^{-1} cm^{-1}. The specific conductivity of water used to make the solution was 1.6×10^{-6} ohm^{-1} cm^{-1}. Calculate the solubility of AgCl in water if ionic conductances of Ag^+ and Cl^- at 25°C are 60.3 and 78 ohm^{-1} cm^2 $equiv^{-1}$ respectively. (6,6)

3. (a) What is meant by transference number of ions ? Explain the Hittorf's method to determine experimentally the transference number of ions.

(b) In the moving boundary experiment with HCl following results were obtained

Normality of HCl = 0.1 N

Mass of silver deposited in coulometer = 0.1209 g

Distance moved by the boundary = 7.5 cm

Area of cross-section of tube = 1.24 cm^2

Calculate the transference number of H^+ and Cl^- ions. (6,6)

4. (a) Discuss qualitatively the Debye – Huckel – Onsager theory as applied to the variation of molar conductivity with dilution of a dilute solution of a strong electrolyte.

(b) Specific conductance of N/35 KCl at 25°C is 0.002768 ohm^{-1} cm^{-1} and it had a resistance of 520 ohms. An N/25 solution of a salt kept in the same cell was found to have a resistance of 300 ohms at 25°C. Calculate cell constant of the cell and equivalent conductivity of the salt solution. (6,6)

SECTION – B

5. (a) Derive an expression for the rate constant of a second order reaction with unequal concentrations of the two reactants.

(b) A first order reaction has rate constant 2.2×10^{-5} min^{-1} at 458 K and 3.07×10^{-3} min^{-1} at 510 K respectively. Calculate the energy of activation.

(c) What is the difference between rate constant and rate of reaction ?

(6,4,2)

6. (a) Describe the Activated Complex theory and

(i) Show that it leads to the rate constant

$$k_2 = \left(\frac{RT}{N_A h}\right) \exp\left(\frac{\Delta H^{\neq}}{RT}\right) \exp\left(\frac{\Delta S^{\neq}}{R}\right)$$

Where various symbols have their usual meanings.

(ii) Compare the rate constants as given by Arrhenius equation and activated complex theory and show that

$$E_a = RT + \Delta E^{\neq}$$

(b) In a particular reaction the time required to complete half of the reaction was found to increase nine times when the initial concentration of the reactant was reduced to one third. What is the order of the reaction ? (8,4)

7. (a) Following mechanism was proposed for the decomposition of gaseous N_2O_5

$$\text{i.e. } 2N_2O_5 \rightarrow 4NO_2 + O_2$$

(i) $N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$

(ii) $NO_2 + NO_3 \xrightarrow{k_2} NO_2 + NO + O_2$

(iii) $NO + NO_3 \xrightarrow{k_3} 2NO_2$

Show that it follows the following rate law :

$$\frac{d[O_2]}{dt} = \frac{k_2 k_1}{k_{-1} + 2k_2}[N_2O_5]$$

(b) Explain the effect of temperature on the rate of a chemical reaction.

(c) Distinguish between physical adsorption and chemical adsorption. (6,3,3)

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SECTION – C

8. (a) An organic compound A in benzene when exposed to UV radiations show fluorescence. The intensity of fluorescence (I_f) falls off due to quenching. The suggested mechanism is :

(i) $A + h\nu \xrightarrow{I_{abs}} A^*$

(ii) $A^* \xrightarrow{k_f} A + h\nu$ (Fluoresence)

(iii) $A^* + Q \xrightarrow{k_q} A + Q + h\nu$ (Quenching)

Derive the Stern - Volmer relation for this process i.e.,

$$\frac{I}{I_f} = \frac{I}{I_{abs}} + \frac{k_q[Q]}{k_f I_{abs}}$$

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

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

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.

(c) The Brauauer, Emmett and Teller (BET) equation for multilayer adsorption of gases is given by :

$$\frac{P}{V_{total}(P_0 - P)} = \frac{1}{V_{mono}C} + \frac{C-1}{V_{mono}C}\frac{P}{P_0}$$

Derive Langmuir equation from BET equation specifying its conditions of applicability. (3,6,3)

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

(i) Enzyme Catalysis

(ii) Photosensitized reactions

(iii) Conductometric titrations

(iv) Chemiluminescence (4,4,4)

(2000)****