[This question paper contains 6 printed pages.]

Sr. No. of Question Paper : 6017 **D** **Your Roll No.....**

Unique Paper Code : 217505

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

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

Semester : V

Time : 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. (a) Fill in the blanks :

   (i) The step with the _____ rate constant value is called the rate-determining step of the reaction.

   (ii) A catalyst cannot alter the _____ of a reaction.

   (iii) The mobility of an ion increases with _____ in hydrodynamic radii in solution.

   (iv) In Photosynthesis of carbohydrates in plants _____ acts as photosensitizer.

   (v) The increase in the rate of chemisorption progressively _____ with increase in pressure. (1×5=5)

   (b) State whether True or False :

   (i) When a molecule emits a photon of frequency, v, it undergoes an energy change given by $\Delta E = hv$.

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(ii) Mobility is the speed of the ion in a field of unit strength.

(iii) Fraction of the total current carried by each type of ion is independent of viscosity of the solution.

(iv) In homogeneous catalysis, doubling the catalyst concentration will not change the rate.

(v) The desorption of a chemisorbed species is always an activated process. (1×5=5)

(c) State reason :

(i) Why does the first order reaction never achieve completion ?

(ii) Why does the Beer's Law fails in case of $K_2Cr_2O_7$ solution ?

(iii) The decomposition of NH_3 on Tungsten is 1^{st} – order.

(iv) The molar conductivities of the alkali metal ions increase on going from Li^+ to Cs^+.

(v) Molar Conductivities of strong electrolytes depends weakly on the concentration of solute ? (1×5=5)

SECTION A

2. (a) Nitrogen pentoxide (N_2O_5) gas decomposes according to the reaction

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

At 328 K, the rate of reaction under certain conditions is 0.75×10^{-4} mol dm^{-3} s^{-1}. Neglecting the concentrations of intermediates determine the values of

$$\frac{d[N_2O_5]}{dt}, \frac{d[N_2]}{dt} \text{ and } \frac{d[O_2]}{dt} ? \quad (2)$$

(b) Using the following data obtain the order w.r.t. each reactant and the total order and rate constant for the reaction

$$CO + Cl_2 \longrightarrow COCl_2$$

Experiment	1	2	3	4
[CO] / mol dm^{-3}	0.1	0.1	0.05	0.05
$[Cl_2]$/mol dm^{-3}	0.1	0.05	0.1	0.05
Rate/mol dm^{-3} s^{-1}	1.2×10^{-2}	4.26×10^{-3}	6.0×10^{-3}	2.13×10^{-3}

(5)

(c) The reaction $SO_2Cl_2(g) \longrightarrow SO_{2(g)} + Cl_{2(g)}$ has a rate constant of 2.24×10^{-5} s^{-1} at 320°C. Calculate the half-life of the reaction. What fraction of a sample of $SO_2Cl_{2(g)}$ remains after being heated for 5.00 hrs at 320°C ? How long will a sample of $SO_2Cl_{2(g)}$ need to be maintained at 320°C to decompose 92.0% of the initial amount present ? (5)

3. (a) Consider two consecutive 1st-order reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$k_1 \neq k_2$ and at time t = 0 only A is present. Derive expression for [A], [B] and [C] at time 't' in terms of rate constants k_1 & k_2. Show graphically the concentration of 'A', 'B' and 'C' as function of time for the condition when $k_2 >> k_1$. (6)

(b) For a reversible first-order reaction

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

$k_f = 10^{-2}$ s^{-1} and $[B]_{eq}/[A]_{eq} = 4$. If $[A]_0 = 0.01$ mol L^{-1} and $[B]_0 = 0$, what will be concentration of B after 30s ? (6)

4. (a) Considering the following mechanism for the thermal decomposition of acetaldehyde :

$$CH_3CHO \longrightarrow CH_4 + CO$$

(i) $CH_3CHO \xrightarrow{k_1} {}^{\cdot}CH_3 + {}^{\cdot}CHO$ *(Initiation)*

(ii) ${}^{\cdot}CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + {}^{\cdot}CH_2CHO$ *(Propagation)*

(iii) ${}^{\cdot}CH_2CHO \xrightarrow{k_3} {}^{\cdot}CH_3 + CO$ *(Propagation)*

(iv) $CH_3 + CH_3 \xrightarrow{k_4} CH_3CH_3$ *(Termination)*

Derive the differential rate law for the formation of CH_4 using steady state approximation and also determine the chain length for the same reaction. (6)

(b) The rate constant for the 1st-order decomposition of ethylene oxide into CH_4 and CO follows the equation :

$$\log k \text{ (in } s^{-1}) = 14.34 - (1.25 \times 10^4)/T.$$

Calculate (i) the activation energy of the reaction (ii) the rate constant at 700 K and (iii) the frequency factor, A. (3)

(c) What conclusion can be reached about adsorption on the surface from the following facts ?

(i) On gold, the rate of decomposition of HI is independent of the pressure of HI.

(ii) The decomposition rate of NH_3 on Pt is proportional to $\frac{p_{NH_3}}{p_{H_2}}$. (3)

SECTION B

5. (a) Discuss the determination of hydrolysis constant of salts from conductometric measurements. (4)

(b) A dilute solution of potassium chloride was placed between two Pt electrodes 10.0 cm apart, across which a potential of 6.0 volts was applied. How far would the K^+ ion move in 2 hours at 25°C ? Molar ionic conductance of K^+ ion at infinite dilution at 25°C is known to be 73.52×10^{-4} S $m^2 mol^{-1}$. (4)

(c) At 25°C, the specific conductance of distilled water is 58.0×10^{-7} S m^{-1} and the λ°_m values for H^+ and OH^- ions are 349.8×10^{-4} and 198.5×10^{-4} S $m^2 mol^{-1}$, respectively. Assuming that A_m differs very little from Λ°_m, calculate the ionic product of water at 25°C. (4)

6. (a) Define Transport Number. How will you determine it by using Hittorf s method ? (6)

(b) Calculate the transport numbers of H^+ ions and Cl^- ions from the following data obtained by the moving boundary method using cadmium chloride as the indicator electrolyte : [Given : Ag = 108 g mol^{-1}]

Concentration of HCl solution	= 0.100 N
Mass of silver deposited in the coulometer	= 0.1209 g
Movement of boundary	= 7.50 cm
Cross-section of the tube	= 1.24 cm^2

(6)

7. (a) Discuss the asymmetric effect and electrophoretic effect. How these effect can be minimized ? (6)

(b) A cell contains 0.10 mol dm^{-3} aqueous KCl, which at that concentration has a molar conductivity of $129 \Omega^{-1}$ cm^2 mol^{-1}. The measured resistance was 28.44 Ω. When the same cell was filled with 0.05 mol dm^{-3} NaOH aqueous solution the resistance was 31.6 Ω. Find the molar conductivity of aqueous NaOH at that concentration. (4)

(c) The molar conductance of sodium acetate, hydrochloric acid and sodium chloride at infinite dilution are 91.0×10^{-4}, 426.16×10^{-4} and 126.45×10^{-4} S $m^2 mol^{-1}$, respectively at 25°C. Calculate Λ°_m at infinite dilution for acetic acid. (2)

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SECTION C

8. (a) State and derive Lambert-Beer's Law for light absorption by solutions. Also, plot the graph for (i) Absorbance ~ concentration and (ii) Transmittance ~ concentration. (6)

(b) Radiation of wavelength 2500 Å was passed through a cell containing 10 ml of a solution which was 0.05 M in oxalic acid and 0.01 M in uranyl sulphate. After absorption of 80 joules of radiation energy, the concentration of oxalic acid was reduced to 0.04 M. Calculate the quantum yield for the photochemical decomposition of oxalic acid at the given wavelength. (4)

(c) In a given absorption cell transmittance of 0.1 mol dm^{-3} of A is 0.75 and that of 0.1 mol dm^{-3} of B is 0.55 at a given wavelength. Calculate the transmittance of a solution that is simultaneous 0.1 mol dm^{-3} in A and 0.1 mol dm^{-3} in B. (2)

9. Write short note on any **three** :

(i) Ostwald's Dilution Law

(ii) Mechanism of Acid-Base catalyzed reactions

(iii) Chemical Actinometer

(iv) Langmuir Adsorption Theory

(v) Collision theory of bimolecular gaseous reactions (3×4=12)