effect. How these effects can be minimized? (4)

(c) Write short notes on any **one** of the following :

(i) Pseudo-unimolecular reactions

(ii) Chemical Actinometer (4)

[This question paper contains 12 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 3108 **H**

Unique Paper Code : 32171403

Name of the Paper : Physical Chemistry – IV

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

Semester : IV

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 **six** questions in all.
3. Question No. **1** is compulsory.
4. Attempt at least **one** question from each Section.
5. Use of scientific calculators is permitted.

NOTE:

$R = 8.314\ JK^{-1}mol^{-1}$, $h = 6.626 \times 10^{-34}$ Js, $k_B = 1.381 \times 10^{-23}\ JK^{-1}$, $F = 96485\ C\ mol^{-1}$

1. Explain any **five** of the following :

(a) Quantum efficiency of Fluorescence decreases with the increase in concentration of the solution.

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

(c) The first order reaction never achieves completion.

(d) The activation energy of a reaction cannot be zero or negative.

(e) The molar conductivity of Li^+ ion is less than that of Cs^+ ion in aqueous medium.

(f) The transport number of Cd^{2+} in concentrated solution of CdI_2 is negative. (5×3)

SECTION A

2. (a) Compare the rate constants as given by Collision Theory and the Activated Complex Theory. Hence, the steric factor p of collision theory may be interpreted in terms of entropy of activation. (5)

interval of time, 7×10^{-5} J were absorbed by the reactant chlorine. If φ_{HCl} is 2.6×10^6 J, how many moles of HCl are formed per joule of energy absorbed. (4)

(c) The quantum yield for the photochemical reaction

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

Is ~ 0.01 while that for the reaction.

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

is $\sim 10^4 - 10^6$. Explain. (3)

9. (a) A monochromatic light of certain wavelength was passed through a solution of certain concentration using a cell of 0.5 m and 25% of the incident light was absorbed. What is its absorbance? If the concentration of the solution is doubled, what will be the length of the cell which absorbs 60% of the incident light. (4)

(b) Discuss the asymmetric effect and electrophoretic

8. (a) Given the following mechanism

(i) $HI + h\nu \xrightarrow{I_{abs}} H + I$

(ii) $H + HI \xrightarrow{k_2} H_2 + I$

(iii) $I + I \xrightarrow{k_3} I_2$

(iv) $H + I_2 \xrightarrow{k_4} HI + I$

Show that the quantum efficiency of the decomposition of HI is

$$\varphi_y = \frac{2}{1 + \frac{k_4}{k_2}\frac{[I_2]}{[HI]}} \qquad (5)$$

(b) A mixture of hydrogen and chlorine was irradiated with radiation of wavelength 400 nm. In a given

(b) The reaction $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$

is first order and has a rate constant 2.24×10^{-5} s^{-1} at 320°C. What fraction of a sample of $SO_2Cl_2(g)$ remains after being heated for 5 Hrs. at 320°C? How long will a sample of SO_2Cl_2 (g) take to decompose 92.0% of the initial amount present at 320°C? (4)

(c) Derive an expression for half-life time of a n^{th} order reaction. (3)

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

$CH_3CHO \longrightarrow CH_4 + CO$

i. $CH_3CHO \xrightarrow{k_1} \cdot CH_3 + CHO$

ii. $\cdot CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + \cdot CH_2CHO$

iii. $\cdot CH_2CHO \xrightarrow{k_3} \cdot CH_3 + CO$

iv. $\cdot CH_3 + \cdot CH_3 \xrightarrow{k_4} CH_3CH_3$

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. (4)

(b) For a reversible first-order reaction

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

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

(c) The rate constant for the dissociation of ethane

$$C_2H_6 \longrightarrow 2\ CH_3$$

is given by $k = 5 \times 10^6 \exp\left(\frac{-368\ kJ}{RT}\right)$.

Calculate the entropy of activation for this reaction at 850 K. (4)

conductance and equivalent conductance at infinite dilution of Potash alum $[K_2SO_4.Al_2(SO_4)_3.24H_2O]$? How are they related to each other? (4)

(c) At 25°C a solution of KCl having a conductivity of 0.14088 S/m exhibits a resistance of 654 ohm in a particular conductivity cell. In this same cell, a 0.10 mol/L solution of NH_4OH has a resistance of 2524 ohm. Calculate

(i) the cell constant

(ii) the molar conductivity of NH_4OH solution

(iii) the degree of dissociation of the 0.10 mol/L NH_4OH

(iv) the dissociation constant of NH_4OH.

(Limiting molar ionic conductivities of NH_4^+ and OH^- are 73.55×10^{-4} and 198.3×10^{-4} $Sm^2\ mol^{-1}$ respectively) (4)

SECTION C

transference number is related to the absolute velocity of the ion. Derive the related expression. (4)

(c) A solution of 0.10 M in LiCl with conductivity 1.06×10^{-2} S/cm is placed in a moving boundary cell of cross-sectional area 1.17 cm^2. It was electrolyzed for 131 minutes with a constant current of 9.42 milliamperes. The Li^+ was observed to move a distance of 2.08 cm. What is the transport number of Li^+ in the solution? (4)

7. (a) (i) State Faraday's Laws of Electrolysis.

(ii) How does ionic mobility differ from ionic speed? What is the unit of ionic mobility? (2+2)

(b) State Kohlrausch Law of independent migration of Ions. How will you calculate the molar

4. (a) The initial rate of oxidation of sodium succinate to form sodium fumerate in presence of the enzyme succinate dehydrogenase at different sodium succinate concentrations is given below

Sodium succinate conc $\times 10^3$/mol dm^{-3}	10.0	2.0	1.0	0.5	0.33
Initial rate $\times 10^6$ mol s^{-1}	1.17	0.99	0.79	0.62	0.50

Determine the Michaelis constant and the limiting rate of equation. (5)

(b) Given below is the mechanism of acid-base catalysis

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

$$SH^+ + H_2O \xrightarrow{k_2} P + H_3O^+$$

P.T.O.

Derive the expression for the rate of formation of product.

$$\frac{dP}{dT} = \frac{k_2 k_1 [S][HA]}{k_{-1}[A^-] + k_2}$$

Show under what conditions a given catalytic reaction may be classified into general acid catalysis and a specific hydrogen ion catalysis.

(4)

(c) Define Turnover number of enzymes. (3)

SECTION B

5. (a) (i) The amide ion in liquid ammonia has an abnormally high transference number. Explain.

(ii) In the conductometric titration, the solution to be added from the burette is much stronger than the solution taken in the conductometric cell. Why? (2+2)

(b) Discuss Hittorf's method to determine the transference number of ions. (4)

(c) The specific conductance of a saturated solution of BaSO, is 3.48×10^{-4} S/m. The conductivity of pure water is 0.50×10^{-4} S/m. Calculate the solubility and solubility product of $BaSO_4$ (Limiting ionic conductance of Ba^{2+} and SO_4^{2-} are 127.26×10^{-4} and 160.04×10^{-4} Sm^2mol^{-1} respectively). (4)

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

(b) What is Transference number? How the