[This question paper contains 8 printed pages.]

Your Roll No......

Sr. No. of Question Paper : 1387

Unique Paper Code : 32171403

Name of the Paper : Physical Chemistry – IV

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

Semester : IV

Duration : 3½ 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. Use of scientific calculator is permitted.

1. (i) Comment on the following :

(a) Elementary reaction with molecularity greater than three are unknown.

(b) In the steady state, the concentration of the reactive intermediate though small remains the same for an appreciable time. (2+2)

(ii) Predict the overall order of reaction for which half-life period depend inversely on the concentration and derive the expression for its half-life. (4)

(iii) The rate constant for a certain reaction is found to be tripled when the temperature is increased from 288K to 323K. If the enthalpy of reaction is 80 kJ/mol, calculate the activation energy of the reaction. (4.5)

2. (i) Differentiate the following **(any two)** :

(a) Stationary and non-stationary chain reaction

(b) Order and molecularity

(c) Average rate and Instantaneous rate of reaction (2+2)

(ii) Under what conditions a given catalytic reaction may be classified into a general acid catalysis and a specific hydrogen-ion catalysis, if the acid catalysed reaction follows the mechanism :

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

$$SH^+ + H_2O \xrightarrow{k_2} P + H_3O^+ \quad (4)$$

(iii) Derive the Michaelis - Menten equation for enzyme catalysed reactions. The mechanism involves the following steps :

$$E + S \underset{k_{-1}}{\overset{k_1}{\leftrightarrows}} ES$$

$$ES \xrightarrow{k_2} P + E$$

Show that the enzyme catalysed reaction is first-order and zero-order with respect to S at low and high concentrations of S, respectively. (4.5)

3. (i) Explain the role of catalyst with the help of potential energy diagram? (4)

(ii) Hydroxide ion is involved in the mechanism but not consumed in this reaction in aqueous solution.

$$OCl^-(aq) + I^-(aq) \xrightarrow{OH^-} OI^-(aq) + Cl^-(aq)$$

(a) From the data in the table, determine the order of reaction with respect to OCl^-, I^-, and OH^-, and the overall order.

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$[OCl^-]$ /(M)	$[I^-]$/ (M)	$[OH^-]$ /M	Rate of formation of OI^- (mol L^{-1} s^{-1})
0.004	00.0020	1.00	4.8×10^{-4}
0.002	00.0040	1.00	5.0×10^{-4}
0.002	00.0020	1.00	2.4×10^{-4}
0.002	00.0020	0.50	2.4×10^{-4}
0.002	00.0020	0.25	9.4×10^{-4}

(b) Write the rate law. (4)

(iii) The following mechanism has been suggested for the decomposition of O_3

$$O_3 \underset{k_{-1}}{\overset{k_1}{\leftrightarrows}} O_2 + O$$

$$O_3 + O \xrightarrow{k_2} 2O_2$$

(a) Assuming $k_{-1}[O_2] > k_2[O_3]$, show that the rate of the all-overall reaction is

$$-\frac{d[O_2]}{dt} = \frac{k[O_3^2]}{[O_2]}.$$

(b) What could be concluded from the appearance of $\frac{1}{[O_2]}$ in the rate equation? (4.5)

4. (i) Derive the relation between Arrhenius activation energy E_a and the minimum energy E_0 of the collision theory of bimolecular reaction theory. (4)

(ii) (a) What are the two conditions that are necessary for effective collisions?

(b) Why the value of steric factor p is usually less than 1 ? (2+2)

(iii) Show that for a first order reaction, the time required for 99.9% completion of the reaction is 10 times the time for 50.0% completion. (4.5)

5. (i) Write a short note on **any three** :

(a) Effect of temperature on Photochemical Reactions

(b) Activated Complex Theory

(c) Conductometric titration of mixture of HCl and CH_3COOH against NaOH

(d) Kohlrausch Law of Independent Migration of Ions (3×3)

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(ii) Why does the transport number of Cd^{2+} ions in concentrated solutions of CdI_2 is negative? (3.5)

6. (i) State and derive Lambert-Beer's Law. (4)

(ii) 2.0×10^{-3} m thickness of a certain glass transmits 10% of the incident light of wavelength 300 nm. What percentage of light of the same wavelength will be absorbed by a 1.0×10^{-3} m thickness of the glass? (4)

(iii) The proposed mechanism of photochemical reaction between H_2 and Br_2 is

$$Br_2 \xrightarrow{h\nu} 2\,Br$$

$$Br + H_2 \xrightarrow{k_2} HBr + H$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br$$

$$H + HBr \xrightarrow{k_4} H_2 + Br$$

$$Br + Br \xrightarrow{k_5} Br_2$$

Derive the quantum yield of reaction. (4.5)

7. (i) Explain, giving reasons : **(any two)**

(a) Specific conductance decreases while equivalent conductance increase on dilution.

(b) Molar conductance values for alkali metal cations are in the order $Rb^+ > K^+ > Na^+ > Li^+$.

(c) ADC current cannot be used for conductance measurements. (2+2)

(ii) What are the various factors affecting the conductance of a solution? How do you account for the increase in conductance of solutions at high field strength and at high frequency? (4)

(iii) A conductance cell when filled with 0.05 M solution of KCl records the resistance of 410.0 ohm at 25°C. When filled with $CaCl_2$ solution (11g $CaCl_2$ in 500 mL) it records 990 ohm. If the specific conductance of 0.05 M KCl solution is 0.00189 mho/cm, calculate (a) Cell constant, (b) specific conductance and (c) Molar conductance of $CaCl_2$. (4.5)

8. (i) Discuss **(any two)** applications of conductance measurements :

(a) Solubility and solubility product of a sparingly soluble salt.

(b) Determination of Ionic product of water.

(c) Degree of hydrolysis and hydrolysis constant of a hydrolysable salt. (4+4)

(ii) A solution of HCl acid is electrolysed in a transport cell using platinum electrodes. 20.175 g of the cathode solution contained 0.175g of Cl^- ion before electrolysis and 18.466 g of the cathode solution contained 0.146 g Cl^- ion after electrolysis. A silver coulometer connected in series had a deposit of 0.2508 g Ag. Calculate the transport number of Cl^- and H^+ ions. (4.5)

9. (i) Describe Hittorf's method or Moving boundary method employed in determining the transport number of an ion. (4)

(ii) Which of the following pairs will have higher molar conductance and why?

(a) LiCl or NaCl

(b) Cl^- ion in HCl or in NaCl (2+2)

(iii) The resistance of a 0.02 mol/dm^3 solution of acetic acid in a cell having cell constant 0.2063 cm^{-1} was found to be 888ohm. What is the degree of ionization of the acid at this concentration? (Given Λ_m^0 for acetic acid = 387.9 $\times 10^{-4}$ $Smol^{-1}m^2$). (4.5)