2025

CHEMISTRY

(Major)

Paper : CHE0500304

(Reaction Dynamics)

Full Marks : 45

Time : 2 hours

The figures in the margin indicate full marks for the questions.

1. Answer the following questions as directed : $1 \times 5 = 5$

   (a) Identify the order of the reaction for which the value of the rate constant is given as :

   $$4 \cdot 5 \times 10^{-3} dm^3 mol^{-1} s^{-1}$$

   (b) The $t_{1/2}$ of a reaction is doubled as the initial concentration of the reactant is doubled. The order of the reaction is

   (i) 1

   (ii) 0

   (iii) 2

   (iv) 1½ *(Choose the correct answer)*

(c) What is a limiting reagent?

(d) Under what condition would the Lindemann theory of unimolecular gaseous reactions show second-order kinetics?

(e) How does the rate of the ionic reaction

$S_2O_8^{2-} + 2I^- \rightarrow$ products performed in aq. $NaCl$ solutions would change with the increasing concentration of $NaCl$ in water? Explain.

2. Answer ***any five*** questions : 2×5=10

(a) On the basis of Arrhenius equation, answer the following :

(i) What is the limiting value of rate constant K as temperature of reaction becomes infinitely large?

(ii) Which reaction will have the greater temperature dependence for the rate constant—one with a small value of Ea or one with a large value of Ea?

(b) The half-life for radioactive decay of ^{14}C is 5730*yr*. An archaeological find contained wood that had only 80% of ^{14}C activity found in living plant. Find the age of the sample.

(c) The conversion $X \rightarrow Y$ follows second order kinetics. If the concentration of X increases 3 times, how will it affect the rate of formation of Y?

(d) What are pseudo first order reactions? Why are they so called? Give *two* examples of pseudo first order reactions.

(e) Can the activation energy of a reaction be zero or negative? Explain.

(f) Why enzymes are highly specific in their action and each enzyme catalyses a particular reaction?

(g) How can the primary and secondary salt effects be differentiated?

(h) The rate constants of a reaction are $1 \cdot 6 \times 10^{-3} s^{-1}$ and $1 \cdot 625 \times 10^{-2} s^{-1}$ at $10°C$ and $30°C$, respectively. Calculate the activation energy of the reaction.

(i) Discuss a method for experimentally determining the order of a reaction.

(j) Explain the concept of steady state approximation.

3. Answer ***any four*** from the following questions : 5×4=20

(a) For the second-order reaction
$aA \rightarrow$ products

(i) integrate the rate law;

(ii) on the basis of this integrated rate law, draw a plot of $\frac{[A]}{[A]_0}$ against t;

(iii) derive an expression for the half-life of the reaction in terms of K and $[A]_0$.

2+1+2=5

(b) How does the reaction rate depend on temperature ? Show how Arrhenius plot of a reaction can be obtained. What is the significance of the pre-exponential factor ? 1+2+2=5

(c) For the consecutive reactions
$A \rightarrow B \rightarrow C$
Obtain the expressions for the concentrations of the species A, B and C. Draw the plots of $[A]$, $[B]$ and $[C]$ against time.

(d) What are chain reactions ? Discuss the kinetics of branching chain reactions.
2+3=5

(e) Discuss the kinetics of enzyme-catalyzed reactions with reference to Michaelis-Menten equation. What do you mean by turnover number ?
4+1=5

(f) Write the postulates of hard-sphere collision theory. On the basis of collision theory, find an expression for the rate constant of the elementary bimolecular gaseous reaction, $A + B \rightarrow$ products.
2+3=5

(g) In what ways encounters in solution are different from those in gas phase ? Deduce Bronsted-Bjerrum equation for reactions in solution. 2+3=5

(h) The rate constant of first order reaction is expressed by the following equation :

$$\log K \left(S^{-1}\right) = 14 \cdot 34 - \frac{1 \cdot 25 \times 10^4}{T} K$$

Calculate (i) the activation energy of the reaction, and (ii) the temperature at which $t_{1/2} = 256 min$. 2+3=5

4. Answer ***any one*** of the following questions : 10

(a) *(i)* For a reaction of nth order, show that $t_{1/2} = \frac{2^{n-1} - 1}{a^{n-1} k(n-1)}$

where a, k and $t_{1/2}$ are the initial concentration of the reactant, rate constant and half-life period of the reaction. 4

(ii) For the reaction

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

the proposed mechanism is

$$N_2O_5 \underset{k-1}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{k_2} NO + NO_2 + O_2$$

$$NO_3 + NO \xrightarrow{k_3} 2NO_2$$

Applying steady-state approximation, derive the rate law. 3

(iii) The rate of the reaction $2A + B \rightarrow 2C$ is doubled when the concentration of B is doubled but increases by a factor of eight when the concentrations of both the reactants are doubled. Find out the rate law of the reaction. What is the overall order of the reaction ? 3

(b) *(i)* On the basis of the activated complex theory, find an expression for the bimolecular rate constant of the gas phase reaction between A and B. 5

(ii) What are the advantages of activated complex theory over collision theory ? 2

(iii) Show that for a gaseous bimolecular reaction,

$$A(g) + B(g) \rightarrow (AB)^{\#} \rightarrow \text{Products},$$

$Ea = \Delta H_m^{\#} + 2RT$ where the subscript m stands for molar. 3

(c) (i) Write the mechanism of unimolecular reaction as proposed by Lindemann. Using this mechanism, deduce an expression for the rate of unimolecular reaction. 2+3=5

(ii) Calculate the activation Gibbs function, enthalpy and entropy of the second-order hydrogenation of ethene at 327°C.
Given :

$$A = 1\cdot24 \times 10^6 M^{-1}S^{-1}$$

$$Ea = 180 kJ\, mol^{-1}$$ 5

(d) (i) The reaction, $H_2 + Br_2 = 2HBr$ is carried out in a $0\cdot250L$ reaction vessel. The change in amount of Br_2 in $0\cdot01s$ is $-0\cdot001 mol$. Find (i) the rate of conversion, (ii) the rate of reaction and (iii) the values of $d[Br_2]/dt, d[H_2]/dt$ and $d[HBr]/dt$. 5

(ii) For a reversible first-order reaction, show how the concentrations of the reactant and the product will change with time. Draw a diagram when the rates of the forward and the backward reactions are respectively $3s^{-1}$ and $1s^{-1}$. 5