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1 (Sem-5/FYUGP) CHE03MJ

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 :
1×5=5

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

$$4.5 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad \frac{(\text{mol})^{-1} \text{ s}^{-1}}{\text{L}} \quad 5$$

(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) $1\frac{1}{2}$ (Choose the correct answer)

$$t_{1/2} = \frac{0.693}{k \cdot \frac{A_0}{2k}}$$

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Contd.

(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 : $2 \times 5 = 10$

(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 E_a or one with a large value of E_a ?

- (b) The half-life for radioactive decay of ^{14}C is 5730yr. 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 $1.6 \times 10^{-3} \text{s}^{-1}$ and $1.625 \times 10^{-2} \text{s}^{-1}$ 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
 $aA \rightarrow \text{products}$

(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



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 :

$$\log K (S^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T} K$$

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

2+3=5

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

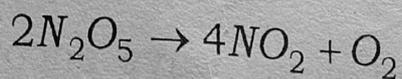
(a) (i) For a reaction of n th order, show

$$\text{that } t_{1/2} = \frac{2^{n-1} - 1}{a^{n-1} k(n-1)}$$

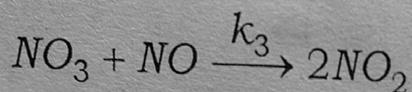
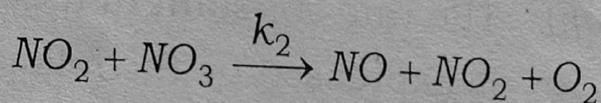
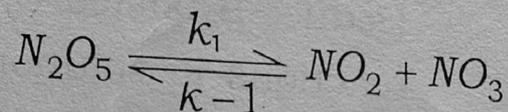
where a , k and $t_{1/2}$ are the initial concentration of the reactant, rate constant and half-life period of the reaction.

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(ii) For the reaction



the proposed mechanism is



Applying steady-state approximation, derive the rate law.

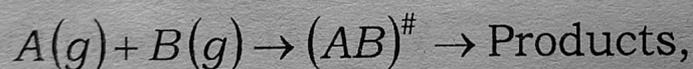
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(iii) The rate of the reaction $2A + B \rightarrow 2C$ is doubled when the concentration of B is doubled but increases by a factor of eight when the concentrations of both the reactants are doubled. Find out the rate law of the reaction. What is the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



$E_a = \Delta H_m^{\#} + 2RT$ 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 :

$$A = 1.24 \times 10^6 M^{-1} S^{-1}$$

$$E_a = 180 kJ mol^{-1} \quad 5$$

(d) (i) The reaction, $H_2 + Br_2 = 2HBr$ is carried out in a 0.250L reaction vessel. The change in amount of Br_2 in 0.01s is $-0.001 mol$. 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