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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 :

$$4.5 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

(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)



- (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  $1.6 \times 10^{-3} s^{-1}$  and  $1.625 \times 10^{-2} s^{-1}$  at  $10^\circ C$  and  $30^\circ C$ , 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  $t$ ;

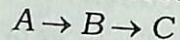
(iii) derive an expression for the half-life of the reaction in terms of  $K$  and  $[A]_0$ .

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,  $A + B \rightarrow \text{products}$ .

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

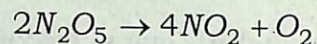
(a) (i) For a reaction of  $n$ th order, show

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

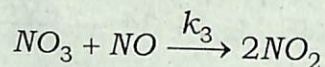
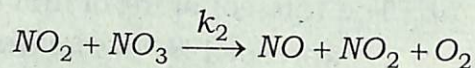
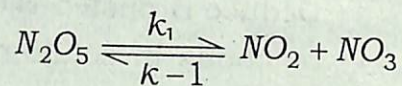
where  $a$ ,  $k$  and  $t_{1/2}$  are the initial concentration of the reactant, rate constant and half-life period of the reaction.

4

(ii) For the reaction



the proposed mechanism is



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

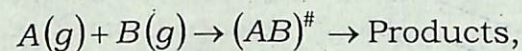
(b) (i) On the basis of the activated complex theory, find an expression for the bimolecular rate constant of the gas phase reaction between  $A$  and  $B$ .

5

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

2

(iii) Show that for a gaseous bimolecular reaction,

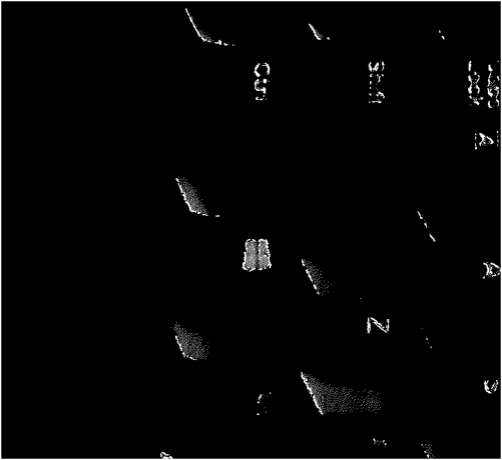


$$E_a = \Delta H_m^{\ddagger} + 2RT \text{ where the}$$

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 :

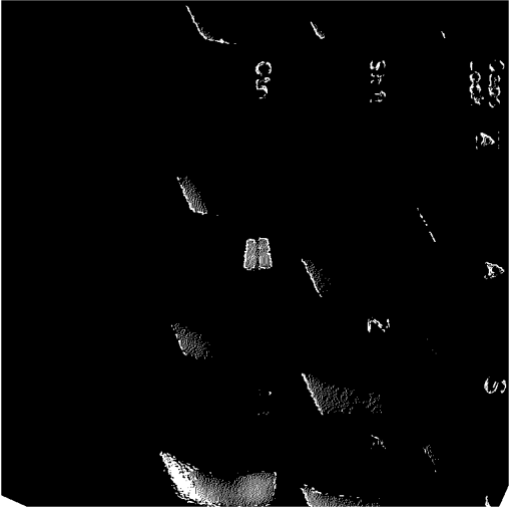
$$A = 1.24 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$

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

(d) (i) The reaction,  $\text{H}_2 + \text{Br}_2 = 2\text{HBr}$  is carried out in a 0.250L reaction vessel. The change in amount of  $\text{Br}_2$  in 0.01s is  $-0.001 \text{ mol}$ . Find (i) the rate of conversion, (ii) the rate of reaction and (iii) the values of  $d[\text{Br}_2]/dt$ ,  $d[\text{H}_2]/dt$  and  $d[\text{HBr}]/dt$ . 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  $3 \text{ s}^{-1}$  and  $1 \text{ s}^{-1}$ . 5





Case  
1000

A

A

63

SHN

Z

CIN

11