

DEPARTMENT OF CHEMISTRY FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA FIRST SEMESTER EXAMINATION 2021/2022 SESSION COURSE CODE: CHM 512 UNITS: 2 COURSE TITLE: ADVANCED CHEMICAL KINETICS INSTRUCTIONS: TIME ALLOWED: 2 HOURS ANSWER ANY THREE (3) QUESTIONS

Q1. (a). (i) Using the equation of a reaction: $H_2 + I_2 \rightarrow 2HI$ Propose a mechanism for the reaction if the rate law for the formation of

HI is given as

$$\frac{d\{HI\}}{dt} = \frac{k_a[H_2][I_2]^{1/2}}{k_b + [HI][I_2]} \tag{9}$$

marks)

(ii) State which class of reaction does this belongs?

(1 mark)

(iii) Mention the species that may limit the formation of the products in this reaction. (2 marks)

(b) The formation of steam has been identified as an explosive reaction. Using appropriate diagrams and mechanistic pathways, explain how this can be achieved. (6 marks)

(c). Outline those factors that affect the explosion limits in (b) above.(2 marks)

Q2. (a) Explain the significance of the following as related to the formation of activated complex by double sphere model;

- (i) zero entropy of activation
- (ii) negative entropy of activation

(iii) Positive entropy of activation (9 marks)

(b). The rate constant for the reaction $A + 2B^{-} \xrightarrow{K} C + B_{2}$ varies with ionic strength (P) at 25 °C as follows:

P (mol/dm ³)	2.45	3.65	4.45	6.45	8.45	12.45
X 10 ³						
R	1.05	1.12	1.16	1.18	1.26	1.39
(mol/dm ³ /min ⁻						
l)						

(i) Find the charge on A ion (8 marks)

(ii) What is the limiting value of R at infinite dilution? (**3 marks**) [Debye Huckel constant at 25 °C = 0.509]

Q3. (a) Suppose the gaseous decomposition of ethane into ethene and hydrogen gas proceed by the following mechanism

$$\begin{array}{l} C_{2}H_{6} \xrightarrow{k_{1}}{\rightarrow} 2 CH_{3} & (i) \\ CH_{3} + C_{2}H_{6} \xrightarrow{k_{2}}{\rightarrow} CH_{4} + C_{2}H_{5} & (ii) \\ C_{2}H_{5} \xrightarrow{k_{3}}{\rightarrow} C_{2}H_{4} + H & (iii) \\ C_{2}H_{6} + H \xrightarrow{k_{4}}{\rightarrow} H_{2} + C_{2}H_{5} & (iv) \\ C_{2}H_{5} + H \xrightarrow{k_{5}}{\rightarrow} C_{2}H_{6} & (v) \end{array}$$

Derive an expression for the decomposition reaction assuming a steadystate condition that correspond to this rate law: $R = K[C_2H_6]$ (10 marks) (b). In parallel reactions, the reacting species instead of proceeding along one path to yield a given set of products also follows one or more other paths to give different products. Show that for a first order reaction the products are in constant ratio to each other, independent of time and initial concentration of the reactant (**10 marks**)

Q4. (a) (i) Define the term "catalyst" and give the classes of catalysts 03 marks

(ii) List the characteristics of a catalyst **02 marks**

(iii). Explain the catalytic depletion of the Ozone layer by CCl₃F and compare the catalyzed and the uncatalyzed reaction with the aid of a diagram **04 marks**

(b) (i)What are the steps involved in a heterogeneous catalysis? 03 marks

(ii) Given the following reaction: $A_2 + B \rightarrow AB$, explain with the aid of diagrams ONLY, the mechanism of a heterogeneous reaction using

(i) Langmuir-Hinshewood , (ii). Eley-Rideal mechanism 04 marks

(iii) Distinguish between selectivity and specificity in relation to enzyme catalysis 04 marks