KISII UNIVERSITY

UNIVERSITY EXAMINATIONS

FOURTH YEAR EXAMINATION FOR THE AWARD OF THE DEGREE OF BACHELOR OF SCIENCE IN PETROELUM CHEMISTRY
FIRST SEMESTER 2022/2023
[SEPTEMBER-DECEMBER, 2022]

CHEM 413: ADVANCED CHEMICAL KINETICS

STREAM: Y4S1 **TIME: 2 HOURS**

DAY: TUESDAY, 12:00 – 2:00 PM **DATE: 20/12/2022**

INSTRUCTIONS

1. Do not write anything on this question paper.
2. Answer Questions ONE and any other TWO Questions.

SECTION A: 40 MARKS

1. Consider the following mechanism of enzyme catalysis

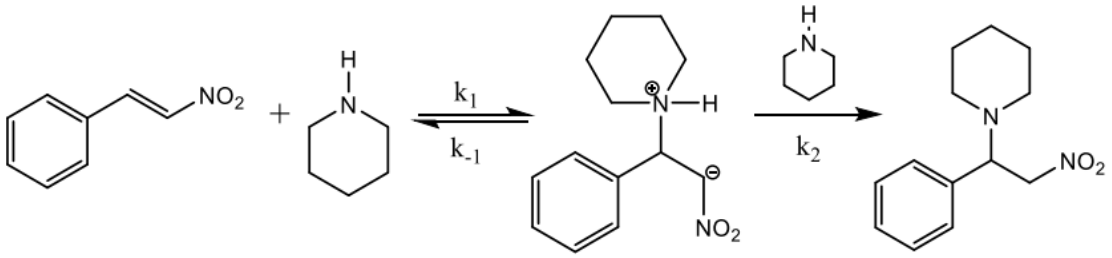
Enzyme [E]+ Substrate[s] $\underset{K^{I}}{\overset{K\text{-}I}{\rightleftharpoons}}$ ES (activated complex) $\xrightarrow{k_2}$ E+Product.

(a) Propose two step kinetic mechanism for above equation (5 marks)
(b) Show that; (15 marks)

$$\text{Rate}=k_2[ES]=\frac{K_2[E_O][S]}{K_M+[S]}$$

K_M is the Michaels constant

2. Study thereaction schemebelow used to investigate β-nitrostyrene and piperidine in Michael reaction kinetics and its transition state



Reaction rate equation;

$$v = \frac{k_1}{k_{-1}} k_2 [\beta - nitrostyrene][piperidine]^2 \qquad \text{(1st equation)}$$

(a) Which is the overall order of the reaction and with respect to β-nitrostyrene and piperidine. (5 marks)

(b) Suggest a method on how the reaction kinetic parameters could be investigated using pseudo first order kinetics. (5 marks)

(c) It is known that the first step of the reaction has established equilibrium, the second step is catalysed by piperidine molecule and it is rate limiting. Both steps are elementary reactions. Derive product rate equation (1st equation). (5 marks)

(d) What is the observed rate constant. (5marks)

SECTION B (15MKS EASCH QUESTION)

3.Consider the following reaction and then answer the questions that follow;

For the reaction **$2NO(g)+H_2(g) \longrightarrow N_2O(g) + H_2O(g)$**

(a) Propose Kinetic mechanism for above equation. (4 marks)
(b) Show that the proposed mechanism leads to the rate law;
$Rate=k[No]^2[H_2]$ (7 marks)
(c) Relate the empirical rate consist **k** to the experimentally determined rate law. (4 marks)

4. For the reaction **$2NO(g)+Cl_2(g) \longrightarrow 2NOCl(g)$** the following mechanism has been proposed

$$NO + Cl_2 \underset{K\text{-}1}{\overset{K_1}{\rightleftharpoons}} NOCl_2$$

$$NO + NOCl_2 \xrightarrow{k_2} 2NOCl$$

Show that the overall rate of reaction is given by **$k[NO]_2[Cl_2]$** assuming that $k_2[NO] <<< K_{-1}$. (15 marks)

5. (a) Consider the following hydrogenation reaction and use it to illustrate catalysis action on nickel surface. (10marks)

$H_2(g) + C_2H_4(g) \longrightarrow C_2H_6(g)$

(b) Explain the following (i) “Complex acid based catalysis which accelerate ionic reactions”
(ii) “Catalyse electron transfer through formation of intermediate radicles”
(5 marks)