



MACHAKOS UNIVERSITY
University Examinations 2022/2023

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

**THIRD YEAR FIRST SEMESTER EXAMINATION FOR BACHELOR OF EDUCATION
(SCIENCE), BACHELOR OF EDUCATION SCIENCE (SPECIAL NEEDS) AND
BACHELOR OF SCIENCE IN ANALYTICAL CHEMISTRY**

SCH 305: CHEMICAL KINETICS

DATE:

TIME:

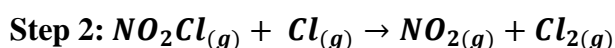
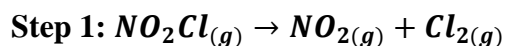
INSTRUCTIONS:

- The paper consists of **two** sections.
- Section **A** is **compulsory** (30 marks).
- Answer any **two** questions from section **B** (each 20 marks).

SECTION A

QUESTION ONE (30 MARKS)

- a) State one condition under which a bimolecular reaction is kinetically first order reaction. (2 marks)
- b) The following elementary steps are proposed for a reaction mechanism.



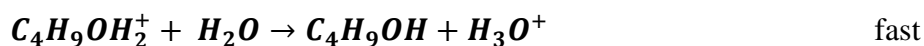
- i) Write the overall balanced equation. (1 mark)
- ii) Determine the molecularity of each step. (2 marks)

- c) Write the rate laws for the following elementary reactions.
- $CH_3NC_{(g)} \rightarrow CH_3NC_{(g)}$ (1 mark)
 - $O_{3(g)} + NO_{(g)} \rightarrow O_{2(g)} + NO_2(g)$ (1 mark)
 - $O_{3(g)} \rightarrow O_{2(g)} + O_{(g)}$ (1 mark)
- d) The rate constant of a zero order reaction is $1.2 \times 10^{-3} mol\ l^{-1} s^{-1}$. Calculate the half-life of the reaction if the initial concentration of the reactant is $1.2 \times 10^{-2} mol\ l^{-1}$ (4 marks)
- e) Explain the following.
- Why does the rate of a reaction increase with rise in temperature? (1 mark)
 - Oxygen is available in plenty in air yet fuels do not burn by themselves at room temperature. (1 mark)
 - Why is the probability of a reaction with molecularity higher than three rare? (1 mark)
 - Why does the rate of any reaction generally decrease during the course of the reaction? (1 mark)
- f) The decomposition of dimethyl ether $(CH_3)_2O$ is a first order process with a rate constant of $6.8 \times 10^{-4} s^{-1}$.
 $(CH_3)_2O(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$. If the initial pressure of dimethyl ether is 135 torr, what is its pressure after 1420 seconds? (4 marks)
- g) Write the reaction rate expression for the following reactions in terms of disappearance of the reactants and appearance of products. (4 marks)
- $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$
 - $4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$
- h) Differentiate between homogenous and heterogenous catalysis as used in chemical kinetics. (2 marks)
- i) An enzyme hydrolyzed a substrate of concentration 0.03 mmol/L, the initial velocity was $1.5 \times 10^{-3} mmol\ l^{-1} min^{-1}$ and the maximum velocity was $4.5 \times 10^{-3} mmol\ l^{-1} min^{-1}$. Calculate the K_m value. (4 marks)

SECTION B

QUESTION TWO (20 MARKS)

- a) A proposed mechanism for a reaction is



- i. Write and explain the rate law expected for this mechanism. (2 mark)
 - ii. What is the overall balanced equation for this reaction? (2 marks)
 - iii. What are the intermediates in the proposed mechanism? (2 marks)
- b) For the reaction $A \rightarrow \text{product}$, the first two half-times are 10 minutes and 20 minutes respectively. At the beginning of the reaction, the $[A]$ was 0.10M
- i) Giving a suitable reason, write the rate law for this reaction. (2 marks)
 - ii) Calculate the $[A]$ at $t=80$ minutes. (3 marks)
- c) State and briefly explain three factors that affect the rate of a chemical reaction. (6 marks)
- d) The reaction $A \rightarrow B$ is a second order in $[A]$ and the rate constant is $0.039 \text{ m}^{-1}\text{s}^{-1}$. If the concentration of A was 0.30 M at 23 seconds, calculate the concentration of A. (3 marks)

QUESTION THREE (20 MARKS)

- a) At 60°C the following reaction was observed to be first order and proceeds to completion. $A_{(g)} \rightarrow B_{(g)} + 2C_{(g)}$. When a pure substance A is decomposed in an empty vessel, it is found that at the end of 10 minutes the total pressure of the system is 180 torr and 300 torr after a very long time. Calculate
- i) The initial pressure of A. (4 marks)
 - ii) Pressure of A after 10 minutes. (3 marks)
 - iii) Rate constant. (2 marks)

b) Given the following mechanism

Step 1	$2NO \rightarrow N_2O_2$	
Step 2	$N_2O_2 + H_2 \rightarrow N_2O + H_2O$	slow
Step 3	$N_2O + H_2 \rightarrow N_2 + H_2O$	

- Determine the equation of overall reaction. (2 marks)
 - Identify the intermediates in this reaction. (2 marks)
 - Determine the rate law using pre-equilibrium approach. (3 marks)
 - State the overall order of the reaction. (1 mark)
 - State the molecularity of the rate determining step. (1 mark)
- c) Differentiate between rate of a reaction and rate constant. (2 marks)

QUESTION FOUR (20 MARKS)

a) The decomposition of a certain insecticide in water follows first order kinetics with a rate constant of 1.45 per year. The insecticide was washed into a lake on June 1, leading to a concentration of $5.0 \times \frac{10^{-7}g}{cm^3}$?

- Calculate the concentration of the insecticide on June 1 the following year. (3 marks)
- How long will it take for the concentration of the insecticide to decrease to $3.0 \times \frac{10^{-7}g}{cm^3}$ (3 marks)

b) The kinetics of the reaction $2x + y \rightarrow Z$ was studied and the results are as follows.

Expt	$[X]_o$ (M)	$[Y]_o$ (M)	Initial rate (M/s)
1	0.20	0.10	7.0×10^{-4}
2	0.20	0.20	1.4×10^{-3}
3	0.40	0.20	1.4×10^{-3}
4	0.60	0.60	4.2×10^{-3}

- Deduce the rate law and the value of k when $[Y] (M)=0.10$. (3 marks)
- The following mechanism was proposed for the above reaction. By filling in the missing gaps, check if the mechanism is plausible. (6 marks)

	Elementary step	Speed	Molecularity
Step 1	$Y \rightarrow M$	slow	

Step 2	$M + X \rightarrow N$	fast	
Step 3	$N + X \rightarrow Z$	fast	
Overall reaction			
Rate law			

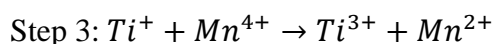
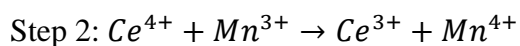
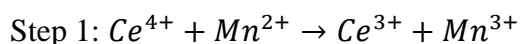
- c) The rate constant of a first order reaction was $3.46 \times 10^{-2} \text{s}^{-1}$ at 298 K. Determine the rate constant at 350 K if the activation energy for the reaction is 50.2 kJ/mol.

(5 marks)

QUESTION FIVE (20 MARKS)

- a) An enzyme with a K_m of 0.06 mmol/L hydrolyzed a substrate of concentration 0.03 mmol/L. If the initial velocity of the reaction was $0.0015 \text{ mmol/L min}^{-1}$, calculate the substrate concentration which gives an initial velocity of $0.003 \text{ mmol/L min}^{-1}$. (5 marks)

- b) A reaction occurs by the following mechanism



- i. Write the overall equation for the reaction. (2 marks)
- ii. Identify each of the following components of the above reaction as a reactant, product, intermediate or a catalyst. (4 marks)
 - I. Mn^{2+}
 - II. Ce^{4+}
 - III. Mn^{3+}
 - IV. Ti^{3+}
- iii. Assuming that the catalyst is involved in the rate determining step, write the rate law for this reaction. (2 marks)

iv. Explain why the uncatalyzed reaction is slow. (Hint: look at the molecularity)

(2 marks)

c) The rate of decomposition of a gas was 7.25 mol s^{-1} when 5% had reacted and 5.14 mol s^{-1} when 20% had undergone decomposition. Calculate the order of the reaction. (5 marks)

END