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.

Step 1: $NO_2Cl_{(g)} \rightarrow NO_{2(g)} + Cl_{2(g)}$

Step 2: $NO_2Cl_{(g)} + Cl_{(g)} \rightarrow NO_{2(g)} + Cl_{2(g)}$

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.

i) $CH_3NC_{(g)} \rightarrow CH_3NC_{(g)}$ (1 mark)

ii) $O_{3(g)} + NO_{(g)} \rightarrow O_{2(g)} + NO_2(g)$ (1 mark)

iii) $O_{3(g)} \rightarrow O_{2(g)} + O_{(g)}$ (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.

i) Why does the rate of a reaction increase with rise in temperature? (1 mark)

ii) Oxygen is available in plenty in air yet fuels do not burn by themselves at room temperature. (1 mark)

iii) Why is the probability of a reaction with molecularity higher than three rare? (1 mark)

iv) 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 $6.8 \times 10^{-4}\ s^{-1}$.

$\boldsymbol{(CH_3)_2O(g) \rightarrow CH_{4(g)} + H_{2(g)} + CO(g)}$. 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)

i) $\boldsymbol{2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}}$

ii) $\boldsymbol{4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}}$

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

$\boldsymbol{C_4H_9Br \rightarrow C_4H_9^+ + Br^-}$ slow

$\boldsymbol{C_4H_9^+ + H_2O \rightarrow C_4H_9OH_2^+}$ fast

$\boldsymbol{C_4H_9OH_2^+ + H_2O \rightarrow C_4H_9OH + H_3O^+}$ fast

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 $A \rightarrow product$, 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 $m^{-1}s^{-1}$. 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. $A_{(g)} \rightarrow \quad B_{(g)} + 2C_{(g)}$. 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	$N_2O + H_2 \rightarrow N_2 + H_2O$	

i) Determine the equation of overall reaction. (2 marks)

ii) Identify the intermediates in this reaction. (2 marks)

iii) Determine the rate law using pre-equilibrium approach. (3 marks)

iv) State the overall order of the reaction. (1 mark)

v) 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 $5.0 \times \frac{10^{-7}g}{cm3}$?

i) Calculate the concentration of the insecticide on June 1 the following year. (3 marks)

ii) How long will it take for the concentration of the insecticide to decrease to $3.0 \times \frac{10^{-7}g}{cm3}$ (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}

i) Deduce the rate law and the value of k when $[Y]$ (M)=0.10. (3 marks)

ii) 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 $3.46 \times 10^{-2} s^{-1}$ 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 mmol/L min^{-1}, calculate the substrate concentration which gives an initial velocity of 0.003 mmol/L min^{-1}. (5 marks)

b) A reaction occurs by the following mechanism

Step 1: $Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + Mn^{3+}$

Step 2: $Ce^{4+} + Mn^{3+} \rightarrow Ce^{3+} + Mn^{4+}$

Step 3: $Ti^{+} + Mn^{4+} \rightarrow Ti^{3+} + Mn^{2+}$

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