# MACHAKOS UNIVERSITY

**University Examinations for 2021/2022 Academic Year**

**SCHOOL OF PURE AND APPLIED SCIENCES**

**DEPARTMENT OF PHYSICAL SCIENCES**

**THIRD YEAR FIRST SEMESTER EXAMINATION FOR**

**BACHELOR OF EDUCATION (SPECIAL NEEDS EDUCATION)**

**BACHELOR OF SCIENCE IN ANALYTICAL CHEMISTRY**

**BACHELOR OF EDUCATION (SCIENCE)**

**SCH 305: CHEMICAL KINETICS**

**DATE: 24/8/2022** **TIME: 11.00-1.00 PM**

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**INSTRUCTIONS:**

Question **ONE** is **COMPULSORY (Section A) (30 marks)**

Answer **ANY** other **TWO** questions from **Section B (each 20 marks)**

**Useful formulae**

$$V_o = \frac{V_{max}[S]}{K_m + [S]}$$

$ln\frac{k_1}{k_2} = \frac{E_a}{R}(\frac{T_1 - T_2}{T_1 T_2})$ where $R = \frac{8.314J}{K}\ mol$

**QUESTION ONE (COMPULSORY) (30 MARKS)**

a) Differentiate between rate of a reaction and rate constant. (2 marks)

b) The initial concentration of $N_20_5$ in the first order reaction $\boldsymbol{N_2O_{5\,(g)} \rightarrow 2NO_{2(g)} + \frac{1}{2}\, O_{2(g)}}$ was $1.2 \times 10^{-2} mol/l$ at 318 K. The concentration of $N_2O_5$ after 60 minutes was $0.20 \times 10^{-2} mol/l$. Calculate the rate constant of the reaction at 318K. (4 marks)

c) The gas-phase decomposition of nitrous oxide $N_2O$ is believed to occur via two elementary steps.

Step 1:$\boldsymbol{N_2O \rightarrow K_1 \rightarrow N_2 + O}$

Step 2: $\boldsymbol{N_2O + O \rightarrow K_2 \rightarrow N_2 + O}$

Experimentally the rate law is found to be, rate=k$[N_2O]$

i. Write the equation for the overall reaction. (2 marks)

ii. Identify the intermediate(s). (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 $1.2 \times 10^{-2} mol\ l^{-1}$

(3 marks)

e) Write the reaction rate expression for the following reactions in terms of disappearance of the reactants and appearance of products. (4 marks)

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

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

f) Derive a rate law for the reaction $H_2 + Br_2 \rightarrow 2HBr$ from the proposed mechanism below

| | |
|---|---|
| $Br_2 \rightleftharpoons 2HBr$ | fast equilibrium $(k_1, k_{-1})$ |
| $H_2 + Br - k_2 \rightarrow HBr + H$ | slow |
| $H + Br - k_3 \rightarrow HBr$ | fast |

(4 marks)

g) State two differences between the order and molecularity of a chemical reaction.

(4 marks)

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)

**QUESTION TWO (20 MARKS)**

a) The following data were obtained during the first order thermal decomposition of $N_2O_{5(g)}$ at constant volume.

$2N_2O_{5(g)} \rightarrow 2N_2O_{4(g)} + O_{2(g)}$

| Time/s | Total pressure/ atm |
|---|---|
| 0 | 0.5 |
| 100 | 0.512 |

Calculate the rate constant (8 marks)

b) An enzyme with a $K_m$ value 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 $min^{-1}$ (4 marks)

c) Discuss briefly two models that have been proposed to explain reaction rates and state two limitations of collision theory. (8 marks)

**QUESTION THREE (20 MARKS)**

a) State and briefly explain four factors that affect the rate of a chemical reaction. (8 marks)

b) 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)

c) The equation for thermal decomposition of acetaldehyde is given by the equation, $CH_3CHO \rightarrow CH_4 + CO$. The chain initiation, propagation and termination equation are given as follows.

$\boldsymbol{CH_3CHO \dashrightarrow k_1 \rightarrow \cdot CH_3 + \cdot CHO}$

$\boldsymbol{\cdot CH_3 + CH_3CHO \dashrightarrow k_2 \rightarrow CH_4 + \cdot CH_2CHO}$

$\boldsymbol{\cdot CH_2CHO \dashrightarrow k_3 \rightarrow \cdot CH_3 + CO}$

$\boldsymbol{\cdot CH_3 + \cdot CH_3 \dashrightarrow k_4 \rightarrow CH_3CH_3}$

Using steady state approximation determine the rate law for the above mechanism(7 marks)

**QUESTION FOUR (20 MARKS)**

a) Use the following reaction mechanism to answer the questions that follow

$$OCl^- + H_2O \leftrightarrow K_1 \leftrightarrow HOCl + OH^- \quad fast$$
$$I^- + HOCl \rightarrow k_2 \rightarrow HOI + Cl^- \quad slow$$
$$HOI + OH^- \leftrightarrow K_3 \leftrightarrow H_2O + OI^- \quad fast$$

i. Determine the overall equation (2 marks)

ii. Use steady state approximation determine the rate law (7 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 ( 2 marks)

ii. Determine the molecularity of each step (2 marks)

iii. Write the rate law for each step (2 marks)

c) Iodine atoms combine to form molecular iodine in the gas phase according to the equation, $I_{(g)} + I_{(g)} \longrightarrow I_2$. The reaction follows second order kinetics and has a high rate constant of $7.0 \times 10^9/m.s$ at $23^0$C.

i. If the initial concentration of iodine was 0.086 M, calculate the concentration after three minutes. (3 marks)

ii. Calculate the half-life of the reaction if the initial concentration of iodine is 0.60 M (2 marks)

**QUESTION FIVE (20 MARKS)**

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

b) 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 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 (5 marks)

ii. Pressure of A after 10 minutes (3 marks)

iii. Rate constant (2 marks)

c) At 378.5°C the half-life period for the first order thermal decomposition of ethylene oxide is 363 minutes and the energy of activation of the reaction is 52,000 cal/mole. Estimate the time required for ethylene oxide to be 75% decomposed at 450°C. (5 marks)