MACHAKOS UNIVERSITY

University Examinations 2023/2024

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

THIRD YEAR FIRST SEMESTER EXAMINATION FOR

BACHELOR OF EDUCATION SCIENCE (SPECIAL NEEDS)

BACHELOR OF SCIENCE IN ANALYTICAL CHEMISTRY

BACHELOR OF EDUCATION (SCIENCE)

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) Differentiate between homogenous and heterogeneous catalysis as used in chemical kinetics. (2 marks)

b) Decomposition of ammonia on platinum surface is a zero order reaction with a rate constant of 2.5×10^{-4}. Calculate the rate of production of N_2 and H_2. (4 marks)

c) Explain the following.

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

ii) The probability of a reaction with molecularity higher than three is low. (1 mark)

iii) The rate of any reaction generally decrease during the course of the reaction. (1 mark)

d) For each of the following reactions, use the given rate law to determine the reaction order with respect to each reactant and overall order. (3 marks)

i) $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)} \qquad Rate = K[NO]^2[O_2]^1$

ii) $H_2O_{2(aq)} + 3I^-_{(aq)} + 2H^+_{(aq)} \rightarrow {I_3}^-_{(aq)} + 2H_2O_{(l)} \quad Rate = K[H_2O_2]^1[I^-]^1$

e) The conversion of cyclopropane to propene in gaseous phase is a first order reaction with a rate constant of $6.7 \times 10^{-4} s^{-1}$ at 500°C. Calculate the half-life of the reaction in minutes. (3 marks)

f) The following elementary steps are proposed for a reaction mechanism.

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

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)

g) The rate of a gaseous reaction is halved when the volume of the vessel is doubled. Find the order of the reaction. (4 marks)

h) Write the reaction rate expression for the following reactions in terms of disappearance of the reactants.

(4 marks)

i) $I^-_{(aq)} + OCl^-_{(aq)} \rightarrow Cl^-_{(aq)} + OI^-_{(aq)}$

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

i) An enzyme hydrolyzed a substrate of concentration 0.03 mmol/L, with initial velocity of $1.5 \times 10^{-3}\ mmol\ l^{-1}min^{-1}$ and maximum velocity of $4.5 \times 10^{-3}\ mmol\ l^{-1}min^{-1}$. Calculate the K_m value. (4 marks)

SECTION B

QUESTION TWO (20 MARKS)

a) The rate of reaction $A + 2B \rightarrow C$ was observed at 25°C.

Experiment	Initial$[A]M$	Initial $[B]M$	Rate (M/s)
1	0.100	0.100	5.50×10^{-6}
2	0.200	0.100	2.20×10^{-5}
3	0.400	0.100	8.80×10^{-5}
4	0.100	0.300	1.65×10^{-5}
5	0.100	0.600	3.30×10^{-5}

From the data in the table above determine;

i) The rate law for the reaction (Assume $rate = k[A]^x[B]^y$). (7 marks)

ii) The rate constant. (3 marks)

b) A proposed mechanism for a reaction is

$C_4H_9Br \rightarrow C_4H_9^+ + Br^-$ slow

$C_4H_9^+ + H_2O \rightarrow C_4H_9OH_2^+$ fast

$C_4H_9OH_2^+ + H_2O \rightarrow C_4H_9OH + H_3O^+$ fast

i. State and explain the rate law for this mechanism. (2 marks)

ii. Write the overall balanced equation for this reaction. (2 marks)

iii. Identify intermediates in the proposed mechanism. (2 marks)

c) State and briefly explain two factors that affect the rate of a chemical reaction. (4 marks)

QUESTION THREE (20 MARKS)

a) The decomposition of dinitrogen pentoxide to Nitrogen (IV) oxide and oxygen is a first order reaction with a rate constant of $5.1 \times 10^{-4}s^{-1}$ at 45°C.

i) If the initial concentration of dinitrogen pentoxide was 0.25 M, calculate the concentration after 3.2 minutes? (3 marks)

ii) Determine how long it will take in minutes, for the concentration of dinitrogen pentoxide to decrease from 0.25 M to 0.15 M. (3 marks)

iii) Calculate time taken in minutes, to convert 62% of the starting material. (3 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 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 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)

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

QUESTION FOUR (20 MARKS)

a) The rate of decomposition of azomethane was studied by monitoring its partial pressure as a function of time.

$CH_3 - N = N - CH_{3(g)} \rightarrow N_{2(g)} + C_2H_{6(g)}$.

The data obtained at 300°C is shown in the table below.

Time (s)	Partial pressure of Azomethane (Hg)
0	284
100	220
150	193
200	170
250	150
300	132

i) Using a graph determine if the values are consistent with first order kinetics. (5 marks)

ii) Calculate the rate constant. (3 marks)

b) The equation for thermal decomposition of acetaldehyde is given by,

$CH_3CHO \rightarrow CH_4 + CO$. The chain initiation, propagation and termination equation are as follows.

$CH_3CHO \dashrightarrow k_1 \rightarrow \cdot CH_3 + \cdot CHO$

$\cdot CH_3 + CH_3CHO \dashrightarrow k_2 \rightarrow CH_4 + \cdot CH_2CHO$

$\cdot CH_2CHO \dashrightarrow k_3 \rightarrow \cdot CH_3 + CO$

$\cdot CH_3 + \cdot CH_3 \dashrightarrow k_4 \rightarrow CH_3CH_3$

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

c) The experimental rate law for the reaction $2NO_{2(g)} + F_{2(g)} \rightarrow 2NO_2F_{(g)}$ is $rate = k[NO_2][F_2]$. Given the proposed mechanism below, determine if it is plausible. (5 marks)

$NO_{2(g)} + F_{2(g)} \rightarrow NO_2F_{(g)} + F_{(g)}$ slow

$NO_{2(g)} + F_{(g)} \rightarrow NO_2F_{(g)}$ fast

QUESTION FIVE (20 MARKS)

a) The rate constant of a first order reaction is $3.46 \times 10^{-2}s^{-1}$ at 298 K. Calculate the rate constant at 350 K if the activation energy for the reaction is 50.2 kJ/mol. (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 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) Determine how long it will take for the concentration of the insecticide to decrease to $3.0 \times \frac{10^{-7}g}{cm3}$ (2 marks)