UNIVERSITY EXAMINATIONS
2022/2023 ACADEMIC YEAR

SECOND YEAR SECOND SEMESTER
MAIN EXAMINATIONS

FOR THE DEGREE OF B.Sc. (Chemistry)

COURSE CODE: SCH 224

COURSE TITLE: CHEMICAL KINETICS

DURATION: 2 HOURS

DATE: 19/04/2023 **TIME: 2:00-4:00PM**

INSTRUCTIONS TO CANDIDATES

- ANSWER **QUESTION ONE** (COMPULSORY) AND ANY OTHER TWO (2) QUESTIONS.
- INDICATE **ANSWERED QUESTIONS** ON THE FRONT COVER.
- START EVERY QUESTION ON A NEW PAGE AND MAKE SURE QUESTION'S NUMBER IS WRITTEN ON EACH PAGE.
- YOU ARE PROVIDED WITH GRAPH PAPERS WHERE NECESSARY.

SOME CONSTANTS

R= 8.314J/mol/K or 0.082atmL/mol/K

QUESTION ONE (30 MARKS)

(a) Define the following terms as used in chemical kinetics. **(4marks)**

i. Reaction intermediates
ii. Reaction mechanism
iii. Rate of a reaction
iv. Molecularity

(b) Consider the following reaction;

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

The table below shows the results involving different concentrations of reactants.

Experiment number	$[NO_2](M)$	$[F_2](M)$	Initial rate (M/S)
1	0.376	0.196	0.0549
2	0.376	0.413	0.116
3	0.685	0.196	0.100

i. Determine the order of the reaction with respect to NO_2 and with respect to F_2 **(2marks)**
ii. What is the overall order of the reaction? **(1marks)**
iii. Calculate the rate constant. **(2marks)**

(c) (i) Explain why high Molecularity reactions are Rare **(3marks)**
(ii) State the three types of elementary reactions **(3marks)**
(d) Discuss briefly the main postulates of collision theory and how it explains chemical reactions. **(3marks)**

(e) Let us consider a first order reaction of the type

A⟶ Products
Show that its integrated rate law is given by $k = \frac{1}{t}.\ln(\frac{a}{a-x})$ **(5 marks)**

(f) Show that the half-life of a second order reaction of the form A → Products is $t_{½} = \frac{1}{k[A]}$ **(5 marks)**

(g) Give any two examples of heterogeneous catalysis **(2 marks)**

QUESTION TWO (20 MARKS)

(a) The gas-phase reaction between methane (CH_4) and diatomic sulphur (S_2) is given by the equation
$CH_4\,(g) + 2S_2\,(g) \longrightarrow CS_2\,(g) + 2H_2S\,(g)$

At 550°C the rate constant for this reaction is 1.1 l mol^{-1} sec and at 625°C the rate constant is 6.4 l mol^{-1} sec. Calculate E_a for this reaction **(7 marks)**

(b) Consider a three-step reaction mechanism suggested below and use it to answer the questions that follows;

Step 1 fast $2NO_{(g))} \rightarrow N_2O_{2(g)} +$

Step 2 slow $N_2O_{2\,(g)} + H_{2\,(g)} \rightarrow N_2O_{(g)} + H_2O_{\,(g)}$

Step 3 fast $N_2O_{(g)} + H_2\,(g) \rightarrow N_{2(g)} + H_2O_{\,(g)}$

i) Derive the overall reaction **(1 marks).**
ii) Identifying the reaction intermediate **(1mark)**
iii) Define the term reaction intermediate **(1 marks)**
iv) Identify the rate determining step **(1 marks)**
v) Derive the rate law of the above reaction **(1 mark)**

(c) The decomposition of carbon disulfide, CS_2, to carbon monosulfide, CS, and sulfur is first order with $k = 2.8 \times 10^{-7}\ s^{-1}$ at 1000°C.

$CS_2 \rightarrow CS + S$

What is the half-life of this reaction at 1000°C? **(4 marks)**

(d) Provide the reaction profile that shows the catalyzed and uncatalyzed patterns for a given reaction **(4marks)**

QUESTION THREE (20 MARKS)

(a) Describe the half-life method of determining order of reaction **(10 marks)**
(b) i) State any three assumptions of collision theory **(3marks)**
(ii) What are the draw backs of collision theory **(2marks)**
(c) (i) Define the term catalysis **(1 mark).**
ii) State the four common characteristics of catalytic reactions **(4 marks)**

QUESTION FOUR (20 MARKS)

(i) From the following data for the decomposition of N_2O_5 in CCl_4 solution at 48°C, show that the reaction is of the first order **(5marks)**

t (minutes)	0	4500	7140	∞
Vol of O_2 evolved	24.36	29.32	31.72	47.15

(ii) State the three types of complex reactions **(3 marks)**

(iii) In the case of sequential reactions, $A \underset{k_1}{\rightarrow} B \underset{k_2}{\rightarrow} C$ applying steady state approximation show that

$\frac{d[c]}{dt} = k_1[A]$ **(2 marks)**

(iv) Explain the Michaelis-Menten mechanism **(10 marks)**

QUESTION FIVE (20 MARKS)

(a) TST postulates three major factors that determine whether or not a reaction will occur. State these factors are: **(3 marks)**

(b) For a first order reaction of $2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$, has a rate constant of $1.06 \times 10^{-3} min^{-1}$. If the initial$[H_2O_2] = 0.020 molL^{-1}$, then what percentage of it remains after 100 minutes of reaction time? **(5 marks)**

(c) In the reduction of nitric oxide, 50% of reaction was completed in 108 seconds when initial pressure was 336 mm Hg and in 147 seconds initial pressure was 288 mm Hg. Find the order of the reaction **(5 marks)**.

(d) Briefly explain the Ostwald's Isolation method of determining order of reaction **(5 marks)**

(e) Why does the rate constant depend on temperature **(2 marks)**