MAASAI MARA UNIVERSITY

REGULAR UNIVERSITY EXAMINATIONS
2017/2018 ACADEMIC YEAR
THIRD YEAR SECOND SEMESTER

SCHOOL OF SCIENCE AND INFORMATION SCIENCES
BACHELOR OF SCIENCE AND BACHELOR OF EDUCATION (SCIENCE)

COURSE CODE: CHE 317

COURSE TITLE: CHEMICAL KINETICS

DATE: 20^{TH} AUGUST 2018 TIME: 8.30 AM – 10:30 PM

INSTRUCTIONS TO CANDIDATES

Answer question ONE and any other TWO.

This paper consists of 7 printed pages. Please turn over:

SECTION A

QUESTION ONE

a) Give brief definitions of the following chemical kinetics terms (5 marks)

i. Instantaneous rate

ii. Half-life

iii. Heterogenous catalyst

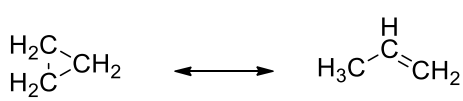
iv. Activated complex

v. Substrate

b)

i. Explain why lizards become sluggish in cold weather. How is this phenomenon related to chemistry? (2 marks)

ii. The isomerization of cyclopropane to form propene



is a first-order reaction. At 773 K, 75% of a sample of cyclopropane changes to propene in 68 min.

Determine the half-life for this reaction at 773K. (For first-order reaction, $t_{1/2}=0.693/k$) (4 marks)

c) The rate constants for the decomposition of a compound **Q** are $6.2 \times 10^{-4}\ s^{-1}$ at 45 ^{o}C and $2.1 \times 10^{-3}\ s^{-1}$ at 55 ^{o}C. Determine the activation energy (in Kilo Joules per mole) and the frequency factor for this reaction. (6 marks)

d) Nitric acid reacts with chlorine to form nitrosyl chloride, NOCl. The following data were obtained in a kinetics study of this reaction.

$$NO + {}^{1}/_{2}\,Cl_2 \longrightarrow NOCl$$

Experiment #	[NO] (M)	[Cl_2] (M)	Initial rate (M/min)
1	0.22	0.065	0.96
2	0.66	0.065	8.6
3	0.44	0.032	1.9

i. What is the order of the reaction? (5 marks)

ii. Write the rate law including the value of k. (3 marks)

e) A given gas-phase reaction is proposed to undergo a three-step mechanism as shown below.

$$Br_{2(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Br_{(g)} \qquad \text{(Fast)}$$

$$Br_{(g)} + H_{2(g)} \xrightarrow{k_2} HBr_{(g)} + H_{(g)} \qquad \text{(Slow)}$$

$$H_{(g)} + Br_{2(g)} \xrightarrow{k_3} HBr_{(g)} \qquad \text{(Fast)}$$

a) What is the overall reaction? (1 mark)

b) Identify the intermediates in the mechanism (1 mark)

c) What is the predicted rate law? (3 marks)

SECTION B

QUESTION TWO

a) A reaction in which A, B and C react to form products is first order in A, second order in B and zero order in C. By what factor does the reaction rate change if:

i. the concentrations of all the three reactants are doubled?

(3 marks)

ii. [C] is tripled and the other reactant concentrations are held constant. (2 marks)

b)

i. Nitric oxide reacts with hydrogen at a measurable rate at 1000 K according to the following equation:

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$$

The experimental rate law is Rate = $k[NO]^2[H_2]$. If time is measured in minutes and concentration is measured in moles per liter, what are the units for the rate constant? (3 marks)

ii. For the reaction $Cl_2(g) + 3F_2(g) \longrightarrow 2\ ClF_3(g)$, when $[Cl_2]$ is decreasing at the rate of 0.012 M/s, how fast is $[F_2]$ decreasing? (3 marks)

c) Consider these two reactions

$$O + N_2 \longrightarrow NO + N \qquad E_a = 315\ kJ/mol$$

$$Cl + H_2 \longrightarrow HCl + H \qquad E_a = 23\ kJ/mol$$

i. Can you suggest a reason why the activation energy barrier for the first reaction is much higher than for the second reaction? (2 marks)

ii. Assuming that the frequency factors for these two reactions are the same, compute the ratio for their rate constants at 25 ^{0}C. (3 marks)

d) The half-life for a radioactive decay (a first-order process) of plutonium-239 is 24,000 years. How many years does it take for one mole of this radioactive material to decay so that just one atom remains? (4 marks)

QUESTION THREE

a) A chemical reaction is exothermic and has an activation energy that is twice the value of the enthalpy of the reaction. Sketch a potential-energy diagram depicting the energy of the reaction as it progresses. Label the following on the diagram: *reactants, products, activation energy* and *enthalpy of reaction.* Using a doted, draw a second curve showing the effect of a catalyst. Discuss the role of the catalyst in changing the reaction. (5 marks)

b) This reaction was monitored as a function of time:

$$\mathbf{XY} \longrightarrow \mathbf{X} + \mathbf{Y}$$

A plot of **1**/[**XY**] versus time yields a straight line.

i. Write the rate law expression and the integrated rate law for this reaction. (2 marks)

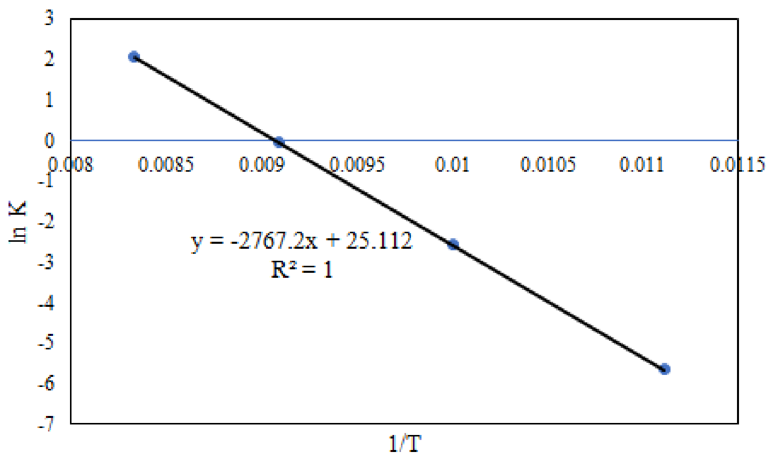
ii. If it took 57s for the concentration to drop 40 percent from its initial value of 0.50M, what is the rate constant (k) for this reaction? (3 marks)

iii. What is the half-life? (3 marks)

c) The diagram below shows an Arrhenius plot for the data that were collected for the following second order reaction:

$$Cl\ (g) + H_2\ (g) \longrightarrow HCl\ (g) + H\ (g)$$

Temperature (K)	Rate Constant (L/mol.s)
90	0.00357
100	0.0773
110	0.956
120	7.781



Determine the activation barrier and frequency factor for this reaction.

(5 marks)

d) There are several factors that affect the rates of chemical reactions. Which factor(s) would affect the magnitude of rate constant? Why?

(2 marks)

QUESTION FOUR

a) Consider the data showing the initial rate of a reaction ($A \longrightarrow$ products) at several different concentrations of A. What is the order and the rate law for this reaction? (5 marks)

[A] (M)	Initial Rate (M/s)
0.12	3.89×10^{-4}
0.18	8.75×10^{-4}
0.28	2.12×10^{-3}

b) Phosgene (Cl_2CO), a poison gas used in World War I, is formed by the reaction of Cl_2 and CO. The proposed mechanism for the reaction is:

Step 1: $Cl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\,Cl$ (fast, equilibrium)

Step 2: $Cl + CO \underset{k_4}{\overset{k_3}{\rightleftharpoons}} ClCO$ (fast, equilibrium)

Step 3: $ClCO + Cl_2 \xrightarrow{k_5} Cl_2CO + Cl$ (slow)

i. What is the overall reaction? (2 marks)

ii. Propose the rate law that is consistent with this mechanism.

(5 marks)

c)

i. Consider the reaction $A \longrightarrow$ products.

Using calculus, derive the first-order integrated rate law for this reaction. (show all derivation steps) (3 marks)

d) Geologists can estimate the age of rocks by their uranium-238 content. The uranium is incorporated in the rocks as it hardens and then decays with first-order kinetics and a half-life of 4.5 billion years. A rock is found to contain 83.2% of the amount of uranium-238 that it contained when it was formed. How old is the rock? (5 marks)