MAASAI MARA UNIVERSITY

REGULAR UNIVERSITY EXAMINATIONS
2018/2019 ACADEMIC YEAR
THIRD YEAR SECOND SEMESTER

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

COURSE CODE: CHE 3226

COURSE TITLE: CHEMICAL KINETICS

DATE: 4TH MAY 2019 TIME: 8.30 AM – 10:30 PM

INSTRUCTIONS TO CANDIDATES

This exam paper consist of two sections A and B. Section A is compulsory. Answer any other TWO questions in section B.

R= 8.314 J mol^{-1} K^{-1}	N_A= 6.022 × 10^{23}/mol	0 K = -273.15 ^{0}C
h = 6.626 × 10^{-34} J.s	c = 2.998 × 10^8 m/s	

This paper consists of 6 printed pages. Please turn over:

SECTION A

QUESTION ONE

a) Give brief definitions of the following chemical kinetics terms giving some examples in each case. (8 marks)

i. Rate-determining step

ii. Half-life

iii. Homogenous catalysis

iv. Activation energy

b)

i. Explain how the order of a reaction is generally determined. For a reaction with multiple reactants, how is the overall order defined?

(3 marks)

ii. It takes 42.0 minutes for the concentration of a reactant in first-order reaction to drop from 0.45M to 0.32M at 25 ^{0}C. How long will it take for the reaction to be 90% complete? (4 marks)

c) The following data were obtained in a kinetics study of the hypothetical reaction

$A + B + C \longrightarrow$ products.

$[A]_0$ (M)	**$[B]_0$ (M)**	**$[C]_0$ (M)**	**Initial Rate (10^{-3} M/s)**
0.20	0.40	0.40	80
0.20	0.40	0.20	40
0.60	0.10	0.20	15
0.20	0.10	0.20	5
0.20	0.20	0.40	20

Using the initial-rate method, determine the rate law expression and the overall order of this reaction. (5 marks)

d) If a temperature increase from 10.0 ^{0}C to 20.0 ^{0}C doubles the rate constant for a reaction, what is the value of the activation barrier for the reaction? (5 marks)

e) A proposed mechanism for the formation of hydrogen iodide can be written in simplified form as

$$I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I \qquad \text{Fast}$$

$$I + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2I \qquad \text{Fast}$$

$$H_2I + I \xrightarrow[k_3]{} 2HI \qquad \text{Slow}$$

What rate law corresponds to this mechanism? (5 marks)

SECTION B

QUESTION TWO

a) For the formation of 1 mol of nitrosyl chloride at a given temperature, ΔH=-41 kJ.

$$NO_{(g)} + \frac{1}{2} Cl_{2(g)} \longrightarrow NOCl_{(g)}$$

The activation energy for this reaction is 57000 J/mol. What is the activation energy for the reverse reaction in kJ? (4 marks)

b) An Industrial chemist is studying the rate of Haber synthesis:

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

Starting with a close reactor containing 1.15 mol L^{-1} of N_2 and 0.35 mol L^{-1} of H_2, she finds that the H_2 concentration had fallen to 0.10 mol L^{-1} after 50 seconds. Estimate the concentration of:

i. N_2 remaining after 100 seconds (3 marks)

ii. NH_3 produced after 50 seconds (3 marks)

c) Consider the chemical equation for the synthesis of methanol at 298 K:

$$CO_2 + 3\ H_2 \longrightarrow CH_3OH + H_2O$$

The experimental rate law is Rate = $k[CO_2][H_2]^2$. If time is measured in seconds and concentration is measured in moles dm^{-3}, what are the units for the rate constant?

(3 marks)

d) The gas phase reaction of NO with F_2 to form NOF and F has an activation energy of E_a=6.3 kJ/mol and the frequency factor of A= 6.0 × 10^6 $M^{-1}S^{-1}$. The elementary reaction is believed to be bimolecular as shown below:

$$NO(g) + F_2(g) \longrightarrow NOF(g) + F(g)$$

i. What is the value of the rate constant at 100 ^{0}C? (3 marks)

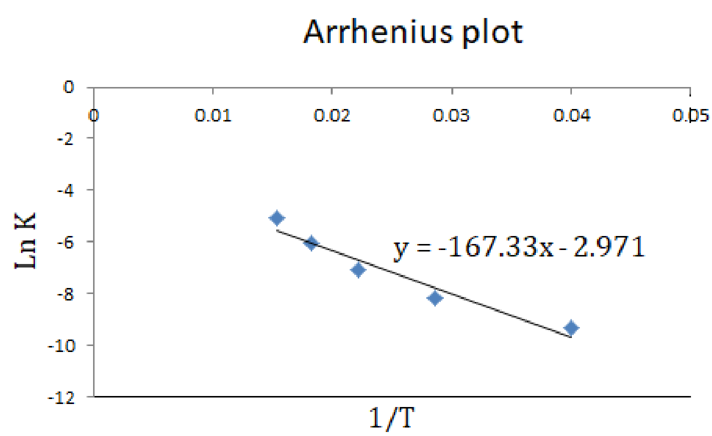
ii. By what factor does the rate of the reaction increase when the temperature increases from 100 ^{0}C to 150 ^{0}C? (4 marks)

QUESTION THREE

a) The diagram below shows an Arrhenius plot for the data that were collected from the kinetics study of the following reaction as a function of temperature. (This reaction is first-order with respect to each reactant).

$$C_2H_5Br\ (aq) + OH^-\ (aq) \longrightarrow C_2H_5OH\ (l) + Br^-(aq)$$

Temp (C)	Rate constant (1/s)
25	0.0000881
35	0.000285
45	0.000854
55	0.00239
65	0.00633



i. Determine the activation barrier and frequency factor for this reaction.

(5 marks)

ii. Determine the rate constant at 15 ^{0}C. (3 marks)

b) A certain biochemical reaction is endothermic and has an enthalpy of reaction that is half the value of the activation energy. 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.* On the same graph, use a dotted line to draw a second curve showing the effect of an enzyme. Briefly discuss the role of the enzyme in changing the reaction. (4 marks)

c) The decomposition of compound **AB** into its constituent atoms **A** and **B** was monitored as a function of time: The order of the reaction was determined graphically and a plot of **1**/[**AB**] versus time only yielded a straight line (best fit line passes through all the data points) and had a slope $7.02 \times 10^{-3}\ M^{-1}\ s^{-1}$.

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

ii. What is the half-life for this reaction at an initial concentration of 0.100 M? (3 marks)

iii. How long will it take for the concentration of AB to decrease to 12.5% of its initial concentration? (3 marks)

QUESTION FOUR

a) Consider the reaction:

$2NH_3(aq) + OCl^-(aq) \longrightarrow N_2H_4(aq) + H_2O(l) + Cl^-(aq)$

This three-step mechanism is proposed.

$NH_3(aq) + OCl^-(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NH_2Cl(aq) + OH^-(aq)$ Fast

$NH_2Cl(aq) + NH_3(aq) \xrightarrow[k_2]{} N_2H_5^+(aq) + Cl^-(aq)$ Slow

$N_2H_5^+(aq) + OH^-(aq) \xrightarrow[k_3]{} N_2H_4(aq) + H_2O(l)$ Fast

i. Show that the mechanism sums the overall reaction. (2 marks

ii. Propose the rate law that is consistent with this mechanism. (5 marks)

b)

i. A rate law is one-half order with respect to a reactant. What is the effect on the rate when the concentration of the reactant is quadrupled (*four times the initial concentration*)? (3 marks)

ii. There are several factors that affect the rates of chemical reactions. Which factor(s) would affect the magnitude of rate constant? Why? (2 marks)

c) 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)

d) At 518 °C and relatively low pressures, the thermal decomposition of acetaldehyde, $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$, is found to be second-order in acetaldehyde. From the following data, determine the value of the specific rate constant. (Give your answer in units of $atm^{-1}s^{-1}$). (4 marks)

Time (s)	**Total Pressure (atm)**
0	0.478
42	0.522
105	0.575
242	0.654
480	0.733