TECHNICAL UNIVERSITY OF MOMBASA

FACULTY OF APPLIED AND HEALTH SCIENCES

DEPARTMENT OF PURE & APPLIED SCIENCES

UNIVERSITY EXAMINATION FOR THE BACHELOR OF TECHNOLOGY IN APPLIED CHEMISTRY

(BTAC 14S & BTAC 15S2)

ACH 4201 : CHEMICAL KINETICS AND REACTION DYNAMICS

END OF SEMESTER EXAMINATION

SERIES: APRIL 2016

TIME: 2 HOURS

DATE: Pick Date Apr 2016

Instructions to Candidates

You should have the following for this examination

-Answer Booklet, examination pass and student ID

This paper consists of **FIVE** questions. Attempt question ONE (Compulsory) and any other TWO questions.

Do not write on the question paper.

QUESTION ONE

a) The reaction between bromate ions and bromide ions in acidic aqueous solution is given by the equation

$$\underset{(aq)}{BrO_3^-} + \underset{(aq)}{5Br^-} + \underset{(aq)}{6H^+} \longrightarrow \underset{(l)}{3Br_2} + \underset{(l)}{3H_2O}$$

The following data was obtained at 25^oC.

Experiment	Initial [BrO^{3-}] (M)	Initial [Br^{-}] (M)	Initial [H^{+}] (M)	Initial rate ($mol/dm^3.s$)
1	0.1	0.1	0.1	8.0×10^{-3}
2	0.2	0.1	0.1	1.6×10^{-3}
3	0.2	0.2	0.1	3.2×10^{-3}
4	0.1	0.1	0.2	3.2×10^{-3}

Using this data at this temperature, determine the rate law and overall order of reaction.

(6 marks)

b) Mercury (II) is eliminated from the body by a first-order process that has a half-life of 6 days. A farming family accidentally ingests mercury (II) by eating contaminated grain. What percentage of the mercury (II) would remain in their bodies after 30 days if therapeutic measures were not taken? (4 marks)

c) Dimerization of butadiene follows either first-order or second-order kinetics. The reaction is as shown below.

$$2C_4H_6\ (g) \longrightarrow C_8H_{12}\ (g)$$

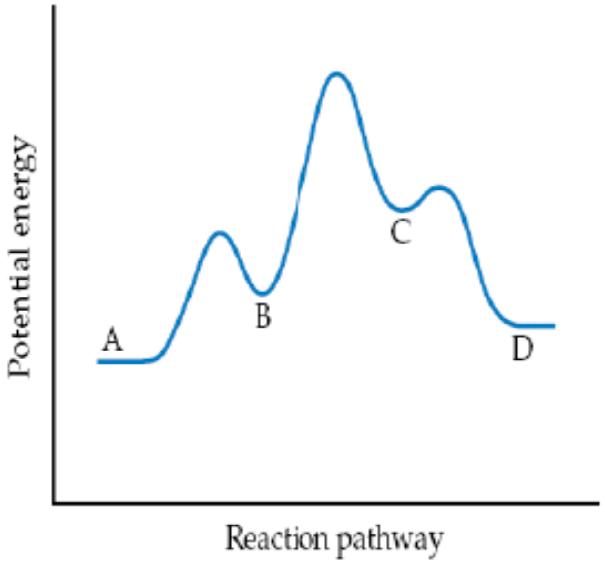
At 500°C, the following data was collected.

Time (s)	[C_4H_6] (mol/dm^3)
0	0.01000
1000	0.00625
1800	0.00476
2800	0.00370
3600	0.00313
4400	0.00270
5200	0.00241
6200	0.00208

Using this data and assuming constant temperature, determine the rate law and rate constant.

(7 marks)

d) The following is the energy profile of a reaction mechanism for the transformation of A to D.



From the energy profile above:

i. Illustrate the number of elementary reactions in this mechanism (1.5 marks)
ii. Identify the reaction intermediates (1.0 mark)
iii. Identify the rate limiting step (0.5 mark)
iv. Identify the fastest step (0.5 mark)
v. State whether the reaction is endothermic or exothermic (0.5 mark)

e) Using a hot nickel catalyst, illustrate the mechanism of addition of 1 mole of hydrogen gas to the alkyne $R_1—C\equiv C—R_2$

(5 marks)

f) State four properties of catalysts (4 marks)

QUESTION TWO

a) The reaction

$$2NOBr_{(g)} \longrightarrow 2NO_{(g)} + Br_{2(g)}$$

follows second-order kinetics with initial concentration of NOBr = 7.5×10^{-3}M and rate constant k = $0.810 M^{-1}.s^{-1}$ at 10^oC. Determine the:

i. Amount of reactant left after 10 minutes (4 marks)
ii. Half-life of this reaction (2 marks)

b) The activation energy of a first-order reaction is 50.2kJ/mol at 25^oC. At what temperature will the rate constant double? (Given R=8.314J/K.mol). (6 marks)

c) Explain how each of the following affects rate of enzyme catalyzed reactions
   i. Coenzymes (2 marks)
   ii. Competitive inhibitors (2 marks)
   iii. Cofactors (2 marks)
   iv. Temperature (2 marks)

QUESTION THREE

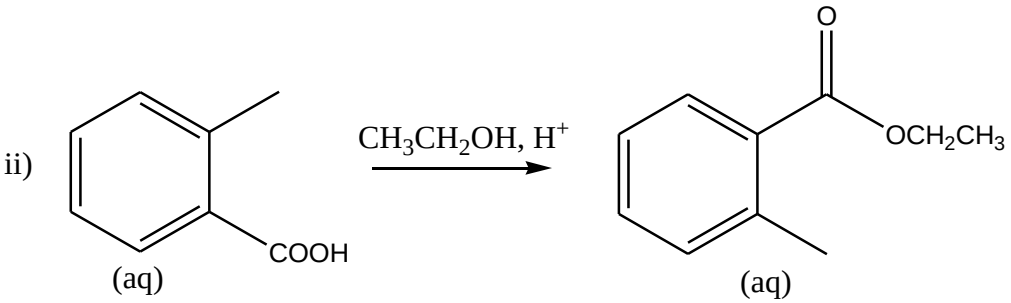
a) Differentiate between each of the following:
   i. Positive and negative catalysis (3 marks)

   ii. Homogeneous and heterogeneous catalyst (3 marks)

b) The second order rate constant for the decomposition of nitrogen dioxide to nitrogen monoxide and oxygen at 300^{o}C is 0.54L/mol.s. Calculate the
   i. Time for an initial nitrogen dioxide concentration of 0.20M to decrease to one-tenth of its value (6 marks)
   ii. Half-life of the reaction from an initial nitrogen dioxide concentration of 0.20M (2 marks)

c) Describe any suitable technique that can be used to measure the rate of each of the following reactions.

i) $Pb(NO_3)_2$ (aq) + $2NaCl$ (aq) $\longrightarrow$ $PbCl_2$ (s) + $NaNO_3$ (aq)

ii) 

(aq) (aq)

(6 marks)

QUESTION FOUR

a) Consider the reaction

$4PH_3$ (g) $\longrightarrow$ P_4 (g) + $6H_2$ (g)

Suppose that, at a particular moment during the reaction, molecular hydrogen is being formed at the rate of 0.078M/s.
   i. At what rate is P_4 being formed? (3 marks)
   ii. At what rate is PH_3 reacting? (3 marks)

b) Ethyl iodide (C_2H_5I) decomposes at a certain temperature in the gas phase as follows

$$\underset{(g)}{C_2H_5I} \longrightarrow \underset{(g)}{C_2H_4} + \underset{(g)}{HI}$$

The following data was collected at this temperature.

Time (min)	$[C_2H_5I]$ (mol/dm^3)
0	0.36
15	0.30
30	0.25
48	0.19
75	0.13

Determine the:

i. Rate law (9 marks)
ii. Rate constant (2 marks)
iii. Half-life of the reaction (3 marks)

QUESTION FIVE

a) The rate constants for the decomposition of acetaldehyde

$$\underset{(g)}{CH_3CHO} \longrightarrow \underset{(g)}{CH_4} + \underset{(g)}{CO}$$

were measured at five different temperatures. The data is shown in the table below:

k ($1/M^{1/2}.s$)	T (^oC)
0.011	427
0.035	457
0.105	487
0.343	517
0.789	537

From this data assuming constant temperature, calculate the:

i. Activation energy in kJ/mol (Given R=8.314J/K.mol). (11 marks)

ii. Frequency factor (3 mark)

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

$$N_2O \xrightarrow{k_1} N_2 + O$$

$$N_2O + O \xrightarrow{k_2} N_2 + O_2$$

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 intermediates (1 mark)
iii. What can you say about the relative rates of steps 1 and 2? (3 marks)