KABARAK  **UNIVERSITY**

SUPPLEMENTARY/SPECIAL EXAMINATIONS

2008/2009 ACADEMIC YEAR

FOR THE DEGREE OF BACHELOR OF EDUCATION SCIENCE

COURSE CODE: **CHEM 313**

COURSE TITLE: **CHEMICAL KINETICS**

STREAM: **SESSION III**

DAY: **TUESDAY**

TIME: **2.00 – 4.00 P.M.**

DATE: **17/03/2009**

INSTRUCTIONS TO CANDIDATES:

(1) Attempt all questions.
(2) Graph papers provided (two)

PLEASE TURN OVER

Useful Constants

$h = 6.626 \times 10^{-34}$ JS

$C = 2.998 \times 10^{8}$ ms^{-1}

$N_A = 6.022 \times 10^{23}$ mol^{-1}

$R = 8.314 JK^{-1}$ mol^{-1}

QUESTION ONE

(a) Define the following terms;

(i) Rate law of a reaction (1 mark)

(ii) Order of a reaction (1 mark)

(b) (i) Calculate the average rate of decomposition of N_2O_5,

$\frac{-\Delta(N_2 05)}{\Delta t}$, for the reaction:

$2N_20_{5\,(g)} \longrightarrow 4N0_{(g)} + 0_{2\,(g)}$ during the time interval t = 600s and t = 1200s using the following data.

Time	$[N_2O_5]$	$[0_2]$
600s	1.24×10^{-2} M	0.0021M
1200s	0.93×10^{-2} M	0.0036M

(ii) Calculate the rate of formation of 0_2 (2 marks)

(iii) For a reaction of the form $aA + bB \rightarrow cC + dD$ where a, b, c and d are the number of molecules of substances A, B. C and D respectively, use the law of mass action to prove that r (rate of the reaction) = $k[A]^a[B]^b$, where k is the rate constant.

(3 marks).

(c) The reaction $A \rightarrow B$ has been found to be second order with respect to A.

(i) Write the rate expression for this reaction.

(ii) What are the units of its rate constant if the concentrations are expressed as $moldm^{-3}$ and time in seconds? (2 marks)

(iii) The rat constant of a zero-order reaction is 0.2 $moll^{-1}$ hr^{-1}. What will be the initial concentration of the reactant, if after half an hour, its half life, the concentration is 0.05 $moll^{-1}$? (3 marks)

(d) Consider the following reaction between bromate ions and bromide ions in acidic aqueous solution.

$Bro_3^-{}_{(aq)} + 5Br^-_{(aq)} + 6H^+_{(aq)} \rightarrow 3Br_{2(L)} + 3H_2O_{(l)}$

The table below gives the results of four experiments. Using these data;

(i) Determine the orders with respect to each of the three reactants.

(ii) Determine the overall order of the reaction and

(iii) Calculate the rate constant. (Use initial rates method).

(8 marks)

Experiment	Initial Concetration of BrO_3^-(moll-1)	Initial Conc. Of Br-(moll-1)	Initial Conc. Of H^+(moll-1)	Measured initial rate $Moll^{-1}s^{-1}$)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

QUESTION TWO

(a) (i) Consider the following 3rd order reaction;

$2FeCl_{3(aq)} + SnCl_{2(aq)} \rightarrow 2FeCl_{2(aq)} + SnCl_{4(aq)}$

If the initial concentration of $SnCl_2$ and $FeCl_3$ are equal to a and 2a respectively, show that the integrated rate law is given by;

$$Kt = \frac{1}{8(a-x)^2} - \frac{1}{8a^2}$$ (6 marks)

(ii) The following data were obtained at 25^0C for the same reaction in a (i) above;

T(min)	1	3	7	11	40
Y	0.01434	0.02664	0.36650	0.04102	0.05058

where y is the amount of $FeCl_3$ reacted in moles per litre. If the initial concentrations of $SnCl_2$ and $FeCl_3$ were 0.03125 and 0.0625 moles per litre respectively, show by the method of rate constants that the reaction is indeed third order. (6 marks)

(b) (i) Define the term activation energy (Ea) (1 mark)

(ii) The activation energy Ea, for a certain reaction is $125KJmoL^{-1}$. A catalyst is added to the reaction and the rate of the catalyzed reaction is 150 times faster than the un-catalyzed reaction at 300k. Assuming the frequency factor is the same for both the catalyzed and un-catalyzed reaction, calculate the activation energy for the catalyzed reaction. (6 marks)

QUESTION THREE

(a) Outline the requirements that a reaction mechanism must fulfill in order to be validated. (2 marks)

(b) In the gas phase, the production of phosgene $COCl_2$ from chlorine Cl_2 and carbon monoxide Co proceeds by the following mechanism.

(i) $Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cl$ (fast equilibrium)

(ii) $Cl + CO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} COCl$ (fast equilibrium)

(iii) $COCl + Cl_2 \overset{k_3}{\rightarrow} COCl_2 + Cl$ (slow)

(iv) $2Cl \overset{K_4}{\rightarrow} Cl_2$ (fast)

(1) What is the overall reaction? (1 mark)
(2) Which species are intermediates? (1 mark)
(3) Deduce the rate low for this reaction (6 marks)

(c) (i) Define the term heterogenous catalyst. (1 mark)

(ii) Heterogenous catalysis depends on at least one reactant being adsorbed (usually chemisorbed) and modified to a form in which it readily undergoes reaction. Outline the steps involved in this surface reaction. (5 marks)

QUESTION FOUR

(a) Explain the following terms as used in photochemistry;

(i) Photochemical equillibria

(ii) Photosensitization

(iii) Quantum efficiency (3 marks)

(b) In an experiment to measure the quantum efficiency of a photochemical reaction, the absorbing substance was exposed to 490nm light from a 100w source for 45mins. The intensity of the transmitted light was 40% of the incident light. As a result of irradiation, 0.344 mols of the absorbing substance decomposed. Determine the quantum efficiency. (6 marks)

(c) Explain the meanings of the following terms;

(i) Simultaneous reactions

(ii) Steady state approximation

(iii) Consecutive reaction

(iv) Parallel reactions (4 marks)