

**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**

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**INSTRUCTIONS TO CANDIDATES:**

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

**PLEASE TURN OVER**

### Useful Constants

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

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

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

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

### 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  $\text{N}_2\text{O}_5$ ,

$$\frac{-\Delta(\text{N}_2\text{O}_5)}{\Delta t}, \text{ for the reaction:}$$

$2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}(\text{g}) + \text{O}_2(\text{g})$  during the time interval  $t = 600\text{s}$  and  $t = 1200\text{s}$  using the following data.

Time	$[\text{N}_2\text{O}_5]$	$[\text{O}_2]$
600s	$1.24 \times 10^{-2} \text{ M}$	0.0021M
1200s	$0.93 \times 10^{-2} \text{ M}$	0.0036M

(ii) Calculate the rate of formation of  $\text{O}_2$

(2 marks)

(iii) For a reaction of the form  $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$  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) =  $k[\text{A}]^a[\text{B}]^b$ , where  $k$  is the rate constant.

(3 marks).

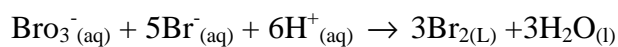
(c) The reaction  $\text{A} \rightarrow \text{B}$  has been found to be second order with respect to A.

(i) Write the rate expression for this reaction.

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

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

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



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 Concentration of $\text{BrO}_3^-$ (moll-1)	Initial Conc. Of $\text{Br}^-$ (moll-1)	Initial Conc. Of $\text{H}^+$ (moll-1)	Measured initial rate $\text{Moll}^{-1}\text{s}^{-1}$
1	0.10	0.10	0.10	$8.0 \times 10^{-4}$
2	0.20	0.10	0.10	$1.6 \times 10^{-3}$
3	0.20	0.20	0.10	$3.2 \times 10^{-3}$
4	0.10	0.10	0.20	$3.2 \times 10^{-3}$

## QUESTION TWO

- (a) (i) Consider the following 3<sup>rd</sup> order reaction;
- $$2\text{FeCl}_3 (\text{aq}) + \text{SnCl}_2 (\text{aq}) \rightarrow 2\text{FeCl}_2 (\text{aq}) + \text{SnCl}_4 (\text{aq})$$

If the initial concentration of  $\text{SnCl}_2$  and  $\text{FeCl}_3$  are equal to  $a$  and  $2a$  respectively, show that the integrated rate law is given by;

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

- (ii) The following data were obtained at  $25^\circ\text{C}$  for the same reaction in a (i) above;

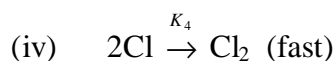
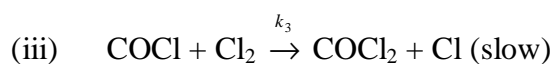
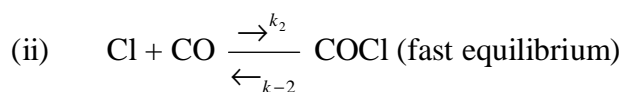
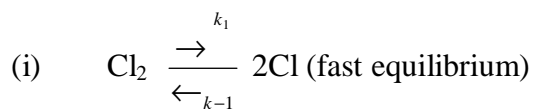
<b>T(min)</b>	1	3	7	11	40
<b>Y</b>	0.01434	0.02664	0.36650	0.04102	0.05058

where  $y$  is the amount of  $\text{FeCl}_3$  reacted in moles per litre. If the initial concentrations of  $\text{SnCl}_2$  and  $\text{FeCl}_3$  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 ( $E_a$ ) (1 mark)
- (ii) The activation energy  $E_a$ , for a certain reaction is  $125\text{KJmol}^{-1}$ . A catalyst is added to the reaction and the rate of the catalyzed reaction is 150 times faster than the un-catalyzed reaction at  $300\text{k}$ . 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  $\text{COCl}_2$  from chlorine  $\text{Cl}_2$  and carbon monoxide  $\text{CO}$  proceeds by the following mechanism.



- (1) What is the overall reaction? (1 mark)
- (2) Which species are intermediates? (1 mark)
- (3) Deduce the rate law for this reaction (6 marks)
- (c) (i) Define the term heterogeneous catalyst. (1 mark)
- (ii) Heterogeneous 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 equilibria
- (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)