

CHUKA



UNIVERSITY

UNIVERSITY EXAMINATIONS

**THIRD YEAR EXAMINATION FOR THE AWARD
OF DEGREE OF BACHELOR OF SCIENCE**

CHEM 323: CHEMICAL KINETICS**STREAMS: BSC****TIME: 2 HOURS****DAY/DATE: MONDAY 02/12/2019****2.30 P.M. – 4. 30 P.M.****INSTRUCTIONS: Answer question ONE and any other TWO questions****QUESTION ONE (30 MARKS)**

- (a) (i) State the first and the second laws of photochemistry [1 mark]
- (ii) Give two reasons for validity of law of photochemical equivalence [1 mark]
- (iii) When a sample of 4-heptanone was irradiated for 100 sec with 313 nm radiation with a power output of 50W under conditions of total absorption, it was found that 2.8 mmol C_2H_4 was formed. Calculate the quantum yield for the formation of ethane

[20 marks]

- (b) (i) For the reaction following mechanism has been proposed

On the basis of the above mechanism devise the rate law of N_2 [4 marks]

- (ii) Consider the parallel reaction

In an experiment, it was observed that 80% decomposition of A takes place in 40 min and analysis of product showed that 60% of B and 40% of C are present.

Calculate K_1 and K_2

[2 marks]

(c) Write short notes on catalytic poisoning [3 marks]

(d) Predict how the total pressure varies during the gas phase decomposition in a constant volume container [2 marks]

(e) The data below was obtained during formation of urea from ammonium cyanate initially 22.9g of ammonium cyanate was dissolved in enough water to prepare 1.0 dm³ of solution. Determine the order of the reaction, the rate constant and the mass of ammonium cyanate left after 300 min

t/min	0.0	20.0	50.0	65.0	150.0
	0.0	7.0	12.1	13.8	17.7

QUESTION TWO (20 MARKS)

(a) (i) Distinguish between excited singlet and excited triplet [1½ marks]

(ii) Briefly discuss with help of Jabloniski diagram the different photochemical processes [6

marks]

(b) (i) How can you explain the decrease in rate of reaction with temperature observed in the photochemical chlorination of benzene and some other reactions of this type?

[2½

marks]

(ii) (I) An actinometer uses a solution of in which is reduced and the oxalate ion is oxidized. Assuming at 310nm, calculate the intensity of the incident light which produces mole

of in

36.5 min.

(II) The same light source is used to irradiate a sample of for a period of 15.2 min. if the quantum yield of is 1.0 and that if CO is 2.0, determine the amount of each gas produced by the photochemical reaction

[7 marks]

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- (c) An aqueous solution of a compound A of concentration moles/litre absorbs 50% of incident radiation in a cell length 1cm and another compound B of concentration moles/litre absorbs 60% of the incident radiation at a particular wavelength. Calculate the percentage absorbed by a solution containing moles/litre of A and B each in the same cell at the wavelength [3 marks]

QUESTION THREE (20 MARKS)

- (a) (i) A undergoes two simultaneous reactions to produce B and C according to $\text{A} \rightarrow \text{B} + \text{C}$, show that k_{obs} , the observed activation energy for the disappearance of A is given by the equation:

[3½ marks]

- (ii) The second order rate constant for the neutralization of 2 – nitropropane by OH^- ions in aqueous solution at $T^\circ\text{K}$ is given by the expression $k = \frac{A}{T - B}$ where K is expressed in $\text{litre mol}^{-1} \text{min}^{-1}$. Calculate the energy of activation, and the half-life period at 20°C ; when the initial concentration of base and acid are each $0.008 \text{ mole litre}^{-1}$ ($R=8.314$) [1½ marks]

- (b) (i) The decomposition of N_2O_5 at 950K is observed and noting the change in total pressure as a function of time. The reaction is $\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + \frac{1}{2}\text{O}_2$. The following measurements were made on the N_2O_5 system containing only N_2O_5 initially

Time (sec)	0	50	100
	200	299	332

Show that, it is a first order reaction and also calculate the rate constant [4 marks]

- (ii) A third order reaction is 50% completed in 100 sec. calculate the time for 75% and 100% completion [2 marks]

- (c) (i) Briefly discuss the various types of elementary reactions [4 marks]
- (ii) Explain the following observations “when chlorine and ethane are mixed at room temperature there is no detectable reaction whereas when the mixture is exposed to light, the reaction suddenly initiates and explodes”

[4 marks]

- (d) For the thermal decomposition of O_3 , the following mechanism has been suggested

(i)

(ii)

Assuming that show that the rate of the overall reaction is

What could be concluded from the appearance of

[3 marks]

QUESTION FOUR (20 MARKS)

(a) (i) Derive the Michaelis – menten equation

[4 marks]

(ii) The enzyme catalyse catalyzes the decomposition of H_2O_2 . The data obtained is given in the table below

	0.001	0.002	0.005
Initial rate (mol/LS)			

If concentration of catalase is mol/L. determine v_{max} , the constant K_m and the turnover number, K_2 .

[6 marks]

(b) Derive an expression for the rate of reversible reaction given that both reactions are of first order.

[3½ marks]

(c) The following table gives the kinetic data for the reaction between $Na_2S_2O_3$ and CH_3I at 298K, the concentration being expressed in arbitrary units.

Time (min)	0	4.75	10	20	35	55
$Na_2S_2O_3$	35.35	30.5	27.0	23.2	20.3	18.6
CH_3I	18.25	13.4	9.9	6.1	3.2	1.5

Show that the reaction follows a second order kinetics and calculate the mean specific rate constant.

[3½ marks]

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