CHUKA  **UNIVERSITY**

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

CHEM 323: CHEMICAL KINETICS

STREAMS: **TIME: 2 HOURS**

DAY/DATE: TUESDAY 30/03/2021 **11.30 A.M – 1.30 P.M**

INSTRUCTIONS:

Answer question one and any other two questions

QUESTION ONE (30 MARKS)

1.(a)(i) Discuss the reaction mechanism for the iodination of pro panone in acid solution whose overall stoichiometric equation is given by;$CH_3COCH_3(aq)+I_2(aq) \rightarrow CH_2ICOCH_3aq+HI\,aq$

And its experimentally derived rate equation for this reaction is

Rate = K[CH_3COCH_3¿¿ [3 marks]

(ii) Explain what you understand by the chain reaction. [1½ marks]

(iii) For any radical reaction of your choice. Illustrate the meaning of the terms initiation, propagation, termination, retardation and branching. [5 marks]

(iv) On the basis of the following proposed mechanism account for the experimental fact that the rate law for the decomposition.

$2N_20_5(s) \longrightarrow 4\,NO_2(g)+0_2(g)$ is V = K [N_2O_5¿ [3½ marks]

$N_2O_5 \rightleftharpoons NO_2+NO_3$

$NO_2 + NO_3 \longrightarrow NO_2 + O_2 + NO$

$NO + N_2O_5 \longrightarrow NO_2 + NO_2 + NO_2$

(b) (i) Show that the half life period $t_{½}$ is related to temperature by the equation

$\ln t_{½} = ¿A' + \frac{E_q}{RT}$ where $A' = \frac{2^{n-1}-1}{A(n-1)a^{n-1}}$

A = pre- exponential factor in the Arrhenius equation

E_a= the activation energy

n = nth order

a=Initial concentration [4 marks]

(ii) From the following rate laws write the corresponding stoichiometric equations. The initial concentrations are written as a a,b,c and x represent the concentration unit of A that have reacted

(I) $\frac{dx}{dt} = k(a-x)(b-x)$ [½ mark]

(II) $\frac{dx}{dt} = k(a-x)(b-x)(c-x)$ [½ mark]

(III) $\frac{dx}{dt} = k(a-x)(b-2x)$ [½ mark]

(IV) $\frac{dx}{dt} = kb(a-x)$ [1½ marks]

(V) $\frac{dx}{dt} = kx(a-x)(b-x)$ [1 mark]

(VI) $\frac{dx}{dt} = k_1(a-x) - k_{-1}x$ [½ mark]

(iii) The isotope 19^{k42} has a $t_{½}$ of 12 hours. Determine the fraction of initial concentration of 19^{k42} remains after 60 hours. [1½ hours]

(c) The rate constant for a certain triple when the temperature is increased from 288k to 323k. If the enthalpy of the reaction is 50KJ /mol^{-1}. Calculate the activation energy of the reaction.

{R= 8.31447 J K^{-1} mol^{-1}} [1 mark]

(d) Comment on the following statements.

(i) A catalyst cannot affect the position of equilibrium of a reaction. [2½ marks]

(ii) For the reaction R + C $\longrightarrow$ P, rate = K $C_C C_R$, where R is reactant and C is catalyst and when $C_c = 0$ the rate is zero. [1½ marks]

(iii) If a catalyst catalyzes the forward reaction then it must catalyze the backward reaction. [2 marks]

QUESTION TWO (20 MARKS)

2(a) Comment on the following statements.

(i) Einstein's law of photochemical equivalence is always valid. [2 marks]

(ii) The quantum yield is always greater than one for any chain reaction. [4 marks]

(b) (i) A 1.0 x 10^{-3} M solution of a dye x shows an absorbance of 0.20 at 450 mH and an absorbance of 0.05 at 620 mH. A 1 x 10^{-4} solution of another dye -1 shows 0.00 absorbance at 450 hM and an absorbance of 0.42 AT 620 hM. Calculate concentration of each dye present together in a solution which exhibits an absorbance of 0.38 and 0.71 at 450 hM and 620 hM respectively. The same cell is used in all measurements and its thickening is 1 cm. [4 marks]

(ii) In an experiment of passage of the light through Granyl ozalate actinometer, the actinometry solution consisted of 5.232g of oxalic acid in 50cm^3 of water. After exposure for 4 minutes the remaining solution was titrated with $kmno_4$ and the $kmn0_4$ solution required for complete

oxidation of the remaining oxalic acid was $18cm^3$ of 0.98m solution. Calculate the average intensity of the light used in photons/ sec. Light of wave length 4050 A° was used and the quantum efficiency was reported as 0.55 {1 A° $=10^{-10}m, N_A=6.022\,x\,10^{23}$ h= 6.625 x $10^{-34}\,J\,sec, C=2.9979\,x\,10^8\,m/s$ [4 marks]

(c) The rate of a chemical reaction was followed by measuring the concentration of one of reactants at different intervals. The following data were obtained:

Time in minutes	0	10	20	40	80	120	160
Concentration (10^{-2} ¿ $moles/litre$	3.33	2.22	1.67	1.11	0.667	0.476	0.370

(i) Determine the order of this reaction. [2 marks]

(ii) If this is the only reactant, what is the rate law for the reaction and what is the specific reaction rate. [3 marks]

(iii) What will be the rate of this reaction when the concentrations of the reactant are $10^{-1}m$ and $10^{-3}m$? [1 mark]

QUESTION THREE (20 MARKS)

3.(a) (i) Discus the theory of absolute rate. [4½ marks]

(ii) How is the theory of absolute rate considered superior to the collision theory. [2½ marks]

(iii)Calculate $\Delta H*\Delta G*¿\Delta S*¿$ for second order reaction.

$2NO_2(g)\longrightarrow 2\,NO(g)+O_2(g)$ at 500k. Given A = 2.0 x $10^9\,S^{-1}$ and the energy of activation = 111 KJ mol^{-1} where,

$\Delta H*¿$ a change in activated enthalpy

$\Delta S*¿$ a change in activated entropy

$\Delta G*¿$ a change in activated Gibbs free energy

A = Arrhenius frequency factor

{R = 8.314 $JK^{-1}mol^{-1}$, h= 6.626 x $10^{-34}\,JS$ K = Boltmannis constant = 1.38 x 10^{-23} J K^{-1}}

(b) Explain the following with examples:

(i) Parallel reactions [3 marks]

(ii) Reversible reactions. [4 marks]

(iii)Consecutive reaction [3 marks]

QUESTION FOUR (20 MARKS)

4.(a) (i) Derive the characteristic equations for the second order reaction with two reactions in which the reactants in which the reactants are initially at different concentrations. [4½ marks]

(ii) The following gives 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 rate constant. [3 marks]

(b)(i) A drug is known to be ineffective when it has decomposed to the extent of 30%. The original concentration of the sample is 500 units/ml. When analyzed 20 months later, the concentration was found to be 420 units/ml. Assuming that the decomposition is of first order. What will be expiration time of the sample? What is the half life of this drug? [3 marks]

(ii) A solution containing equal concentration of ethyl acetate and NaoH is 25% saponified in 5 minutes what will be the % of saponification after 10 minutes. [4 marks]

(iv) A certain substance A is mixed with an equal quantity of a substance B. At the end of 1 hour, 75% A reacted . How much A will be left unreacted at the end of 2 hours if the reaction is:

(I) First order in A and independent of B. [2 marks]

(II) First order in A and first in B. [3 marks]

(III) Zero order in A and independent of B. [1½ marks]

(c) A third order reaction is 50% complete after 100 sec calculate the time for 75% and 100% completion.

[1 mark]
