National Open University of Nigeria
Plot 91, Cadastral Zone, Nnamdi Azikiwe Expressway, Jabi - Abuja
Faculty of Science
APRIL/MAY, 2019 EXAMINATIONS

COURSE CODE: CHM407
COURSE TITLE: REACTION KINETICS
CREDIT: 3 Units
TIME ALLOWED: 3 Hours
INSTRUCTION: Answer Question ONE (1) and any other FOUR (4) Questions
In all calculations R = 8.314 J/mol/K

1 (a) State the following laws of photochemistry

i. Draper-Grothus law (2 marks)

ii. Stark-Einstein law (2 marks)

(b) Define the under listed types of catalysis and give one example (equations are required) for each

i. Homogeneous catalysis (2 marks)

ii. Heterogenous catalysis (2 marks)

iii. Enzyme catalysis (2 marks)

iv. Inhibitors (2 marks)

(c) What is a pseudo first order reaction (2 marks)

(d) What are catalyst poison and promoters ? (3 marks)

(e) State four methods that can be used to monitor the rate of chemical reaction (4 marks)

(f) What is the basic requirement for a molecule to be photochemically active (1 mark)

2(a) With the aid of suitable equations, explain two reactions possibilities that can lead to a second order kinetics and write the rate law for each (2 marks)

(b) Show that for a second order reaction, the integrated rate law can be written as

$\frac{1}{A_t} - \frac{1}{A_0} = k_2 t$. (5 marks)

(c) How can you confirm that a given kinetic data represent a second order reaction (2 marks)

(c) Derive an expression for the half-life of a second order reaction. (3 marks)

3. (a) Write short note on quantum efficiency (2 marks)

(b). Calculate the quantum efficiency for the formation of 7.57 x 10^{-6} mole of ethane in 1,200s in a photochemical decomposition of di-n-propyl ketone using 313nm light. The light absorbed is 2.41 x $10^{-3}JS^{-1}$ (N_A = 6.022x10^{23} Mol^{-1}; h = 6.626 x 10^{-34} Js, C=3x10^5 MS^{-1}) (10 marks)

4(a) Define the term, activation energy. Hence write an expression for the exponential form of the Arrhenius equation (2 marks)

(b) Show how you can apply the exponential or logarithm form of the Arrhenius equation to estimate the value of activation energy under the following conditions,

(i) When values of rate constant at various temperatures are known (i.e graphically (2 marks)

(ii) When the rate constants (k_1 and k_2) at two different temperatures are known (4 marks)

(c). The rate constants for the decomposition of $SO2C1_2$ are 0.000101 L/mol/s at 500 K and 0.000385 L/mol/s at 700K. Calculate the activation energy and the frequency factor; assuming them to be independent of temperature. (4 marks)

5.(a) State three basic assumption of the Langmuir adsorption isotherm (3 marks)

b) The mechanism of the formation of HBr from H_2 and Br_2 consist of five steps (given below).

$$Br_2 \xrightarrow{k_1} 2Br^*$$

$$Br^* + H_2 \xrightarrow{k_2} HBr + H^*$$

$$H^* + Br_2 \xrightarrow{k_3} HBr + Br^*$$

$$H^* + HBr \xrightarrow{k_4} H_2 + Br^*$$

$$Br^* + Br^* \xrightarrow{k_5} Br_2$$

Derive integrated rate equation for the following

(i) the formation of Hydrogen bromide, formation of bromide free radical and the formation of Hydrogen free radical **(3 marks)**

(ii) Derive explicit equation in terms of measurable quantities for the rates expressed in (i) above **(6 marks)**

6.(a) (c) Given that an enzyme reaction is represented according to the following equation,

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES^* \xrightarrow{k_2} E + P$$

Answer the following questions

i. Derive rate equation for the formation of the intermediate, ES* ($i.e\ [ES^*] = \frac{k_1[E][S]}{(k_{-1}+k_2)}$)

(5 marks)

ii. Also show that $[ES^*] = \frac{k_1[E_0][S]}{k_{-1}+k_2+k_1[S]}$ **(5 marks)**

iii. Derive the rate equation for the formation of the product (in terms of the rate of disappearance of the substrate) in terms of measurable quantities **(2 marks)**