

National Open University of Nigeria
Plot 91, Cadastral Zone, Nnamdi Azikiwe Expressway, Jabi - Abuja
Faculty of Science
OCTOBER/NOVEMBER, 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 $R=8.314 \mathrm{~J} / \mathrm{mol} / \mathrm{K}$

## Question 1 (22 MARKS)

(a) State any FOUR experimental methods of rate studies (4 marks)
(b) State the name of a suitable experimental method that can be followed to monitor the reaction rate in each of the following cases.
i. $\mathrm{H}_{2}(g)+\mathrm{Br}_{2}(g) \rightarrow 2 \mathrm{HBr}(g)$ Hint: Bromine absorbs strongly in the visible region, while hydrogen and hydrogen bromide are not.
ii. $\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}(a q)+\mathrm{OH}^{-}(a q) \rightarrow \mathrm{CH}_{3} \mathrm{COO}^{-}(a q)+\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(a q)$
iii. $\mathrm{CH}_{3} \mathrm{CHO}^{-}(\mathrm{g}) \rightarrow \mathrm{CH}_{4}(\mathrm{~g})+\mathrm{CO}(\mathrm{g})$ (at constant volume conditions) ( $\mathbf{3}$ marks)
(c) The reaction $A+2 B \rightarrow$ products has the rate law: $R=k[A][B]^{3}$. If the concentration of $B$ is doubled while that of A is unchanged, by what factor will the reaction rate increase? ( $\mathbf{2}$ marks)
(d) The rate law for the reaction $2 \mathrm{~A}+\mathrm{B} \rightarrow \mathrm{C}+3 \mathrm{D}$ was expressed as rate $=\mathrm{k}[\mathrm{A}]^{2}[\mathrm{~B}]$, what are the units of $k$ ? ( $\mathbf{3}$ marks)
(e) Given a second-order reaction of the type: $2 \mathrm{~A} \rightarrow$ Products

The initial concentration of A and concentration after time $t$ are $[A]_{o}$ and $[A]_{t}$ respectively. Derive the integrated form of the rate equation. i.e. $\frac{1}{[A]_{t}}=\frac{1}{[A]_{0}}+k t . \quad$ ( 6 marks)
(f) State (i) the Grotthuss-Draper Law of photochemistry (ii) the Stark-Einstein Law of Photochemical Equivalence. (4 marks)

## Question 2 (12 MARKS)

(a) Consider the reaction: $\mathrm{P}_{4}+6 \mathrm{H}_{2} \rightarrow 4 \mathrm{PH}_{3}$. Kinetic study of this reaction was conducted at 298 K . The data that were obtained are shown in the table.

| Expt. | $\left[\mathrm{P}_{4}\right], \mathrm{mol} / \mathrm{L}$ | $\left[\mathrm{H}_{2}\right], \mathrm{mol} / \mathrm{L}$ | Initial Rate, $\mathrm{mol} /(\mathrm{L} \cdot \mathrm{s})$ |
| :--- | :--- | :--- | :--- |
| 1 | 0.0110 | 0.0075 | $3.20 \times 10^{-4}$ |
| 2 | 0.0110 | 0.0150 | $6.40 \times 10^{-4}$ |
| 3 | 0.0220 | 0.0150 | $6.39 \times 10^{-4}$ |

(i) What is the order with respect to $\mathrm{P}_{4}$ ( 2 marks)
(ii) What is the order with respect to $\mathrm{H}_{2}$ ( $\mathbf{3}$ marks)
(iii) Write the rate law for this reaction. ( 2 marks)
(iv) Determine the value and units of the rate constant, k. (2 marks)
(b) At 323 K , the rate of reaction for the decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}$ at a particular instant is $2.74 \times 10^{-4}$ $\mathrm{Ms}^{-1}$. Calculate the rate of formation of $\mathrm{O}_{2}$. The reaction is represented below:
$2 \mathrm{~N}_{2} \mathrm{O}_{5}(g) \rightarrow 4 \mathrm{NO}_{2}(g)+\mathrm{O}_{2}(g)$
(3 marks)

## Question 3 ( 12 MARKS)

(a) Given two parallel reactions depicted below:


Show that the ratio of product concentrations is equal to the ratio of the respective rate constants ( 6 marks)
(b) Differentiate between Physisorption and Chemisorption ( 6 marks)

## Question 4 (12 MARKS)

(a) A solution of the red complex formed by $\mathrm{Fe}^{2+}$ ion with 1,10-phenanthroline is taken in a cell of the thickness 1.00 cm . If e for the complex is $1.11 \times 10^{3} \mathrm{~m}^{2} \mathrm{~mol}^{-1}$ and the absorbance of the solution is 0.391 , calculate the concentration of the complex in $\mathrm{mol} \mathrm{m}^{-3}$. ( $\mathbf{3}$ marks)
(b) In an experiment to measure the quantum efficiency of a photochemical reaction, the absorbing substance was exposed to 320 nm radiation from an 87.5 W source for 28.0 min . The intensity of the transmitted light was 0.257 that of the incident light. As a result of irradiation, 0.324 mol of the absorbing substance decomposed. Determine the quantum efficiency. (9 marks)

## (Question 5

(a) The rate expression for the reaction, below is given as: Overall rate $=k\left[\mathrm{NO}_{2}\right]_{2}$
$\mathrm{NO}_{2}(g)+\mathrm{CO}(g) \rightarrow \mathrm{NO}(\mathrm{g})+\mathrm{CO}_{2}(g)$.
Spectroscopically, $\mathrm{NO}_{3}$ radical has been detected. Suggest a mechanism in keeping with these facts. (4 marks)
(b) (i) What is the difference between positive and negative catalyst? (2 marks)
(ii) In three sentences, state major mechanism or step involved in catalysis (3 marks)
(c) i) Give four examples of complex reactions
(2 marks)
ii) Write equations for the half- life of a second order reaction (1 mark)

## Question 6 ( 12 MARKS)

(a) Discuss briefly the adsorption of gases on solids (5 marks)
(b) In Photochemical decomposition of acetone using 313 nm light, $7.57 \times 10^{-6} \mathrm{~mol}$ of carbon monoxide is formed in 20 minutes. If the light absorbed corresponds to $2.41 \times 10^{-3} \mathrm{~J} \mathrm{~s}^{-1}$, calculate the quantum efficiency for the formation of carbon monoxide. (8 marks)

