

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 J/mol/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. $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ **Hint:** Bromine absorbs strongly in the visible region, while hydrogen and hydrogen bromide are not.

ii. CH₃COOC₂H₅ (*aq*) + OH⁻ (*aq*) \rightarrow CH₃COO⁻ (*aq*) + C₂H₅OH (*aq*)

iii. $CH_3CHO^-(g) \rightarrow CH_4(g) + CO(g)$ (at constant volume conditions) (3 marks)

(c) The reaction $A + 2B \rightarrow$ 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? (2 marks)

(d) The rate law for the reaction $2A+B \rightarrow C + 3D$ was expressed as rate = k[A]²[B], what are the units of k? (3 marks)

(e) Given a second-order reaction of the type: $2A \rightarrow$ 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. $\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$. (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: $P_4 + 6 H_2 \rightarrow 4 PH_3$. Kinetic study of this reaction was conducted at 298 K. The data that were obtained are shown in the table.

Expt.	[P ₄], mol/L	[H ₂], mol/L	Initial Rate, mol/(L . s)
1	0.0110	0.0075	3.20 x10 ⁻⁴
2	0.0110	0.0150	6.40 x10 ⁻⁴
3	0.0220	0.0150	6.39 x10 ⁻⁴

(i) What is the order with respect to P_4 (2 marks)

(ii) What is the order with respect to H_2 (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 N_2O_5 at a particular instant is 2.74×10^{-4}

Ms⁻¹. Calculate the rate of formation of O₂. The reaction is represented below: (3 marks)

 $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

Ouestion 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 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 x 10³ m² mol⁻¹ and the absorbance of the solution is 0.391, calculate the concentration of the complex in mol m^{-3} . (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)

- (a) The rate expression for the reaction, below is given as: Overall rate = k [NO₂]₂ NO₂ (g) + CO (g) → NO (g) + CO₂ (g). Spectroscopically, NO₃ 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, $7.57 \ge 10^{-6}$ mol of carbon monoxide is formed in 20 minutes. If the light absorbed corresponds to 2.41 $\ge 10^{-3}$ J s⁻¹, calculate the quantum efficiency for the formation of carbon monoxide. (8 marks)