



NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
FACULTY OF SCIENCE AND TECHNOLOGY EDUCATION
DEPARTMENT OF SCIENCE, MATHEMATICS AND TECHNOLOGY
EDUCATION

PST 6342 PHYSICAL CHEMISTRY 5

Main Examination Paper

November 2024

This examination paper consists of 5 pages

Time Allowed: 3 hours

Total Marks: 100

Special Requirements: GRAPH PAPER

Examiner's Name: I. MATIBELA

External Examiner: DR. S. J. MPOFU

INSTRUCTIONS

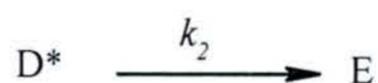
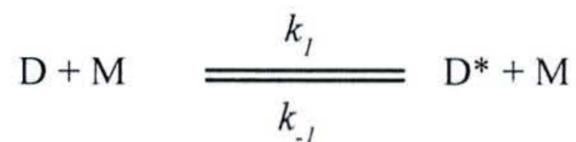
1. Answer **any four** questions
2. Each question carries 25 marks.
3. Begin each question on a new page.

Answer any four questions.

Question 1 [25 marks]

(a) Discuss the model fitting and model free (isoconversional) methods as applied to chemical kinetics. [10]

(b) The mechanism of a unimolecular gas reaction is:



The species D^* is an energized molecule that is present in low concentrations.

Apply the steady-state approximation to D^* and obtain an expression for the rate in terms of $[D]$, k_1 , k_{-1} and k_2 . [6]

(c) Draw and explain the general artificial photosynthesis schematic functional unit. [9]

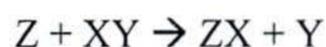
Question 2 [25 marks]

(a) Using diagrams, explain how the Franck-Condon principle, band spectrum, and vibronic progression are related. [10]

(b) Give a detailed explanation, using illustrations and equations, on the shrinking core model and the types of reaction control. [15]

Question 3 [25 marks]

(a) Given a bimolecular reaction below:



(i) Explain in detail the 3D potential energy surface for the reaction. [8]

(ii) Draw a 2D potential energy surface for:

1. Z approaching a vibrating XY molecule but still energy of vibration is insufficient for the reaction. [2]

2. Z approaching non-vibrating XY but with insufficient translational kinetic energy. [2]

(b) Consider the reaction: $A + B \rightarrow \text{Products}$

(i) Derive a theoretical express to calculate the pre-exponential factor using the collision theory. [10]

(ii) Hence, using that theoretical expression, calculate the pre-exponential factor for the rate constant for the reaction at 300K. [3]

[Radius of A = radius of B = 5.0×10^{-10} m. reduced mass = 2×10^{-22} g]

Question 4 [25 marks]

(a) Construct a well labelled diagram showing processes in which energy may be dissipated when an electron is excited. Explain the transitions. [8]

(b) What are the roles of adsorption and desorption in catalysis? [5]

(c) The decomposition of ozone is a unimolecular reaction:

The following values for K_{uni} as a function of pressure were measured as in table 4.1.

Pressure/Bars	0.146	0.280	0.520	1.140
K_{uni}	9.58	10.3	10.8	11.1

Table 4.1 K_{uni} as a function of pressure for the decomposition reaction.

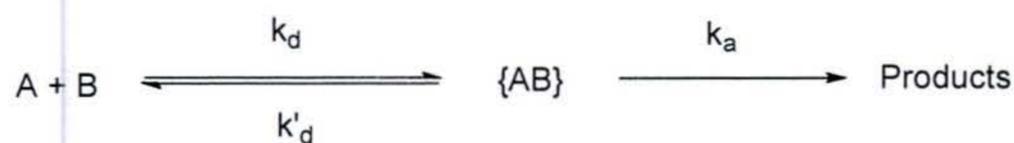
(i) Assuming the Lindemann mechanism accurately describes this decomposition, draw a graph using the given information. [8]

(ii) Hence, use the graph to evaluate the value of k_1 . [2]

(iii) Determine the ratio ok k_{-1}/k_2 . [2]

Question 5 [25 marks]

(a) Consider the reaction below,



Where:

Molecules A and B float through a solvent environment,

{AB} is an activated complex,

k_d = rate constant involved with diffusion of A and B,

k'_d = rate constant of diffusing apart,

k_a = rate constant that AB has sufficient energy to turn into products.

- (i) Show that the diffusibility of reactants in solution and internal energy of activated complex contribute to the overall rate of a reaction. [10]
- (ii) Hence, if the solvent is water which has a viscosity of $1.00 \times 10^{-3} \text{ kgm}^{-1} \text{ s}^{-1}$, calculate the;
1. Diffusion controlled rate constant at 298k for a species. [3]
 2. Initial rate, that is $\frac{d[\text{Product}]}{dt}$, if the initial concentrations of A and B are 0.20M and 0.15M respectively. [2]
- (b) The application of chemistry in designing new materials with desired properties is enhanced using computer simulation programs such as Material Studio. Evaluate the significance of computer simulations in designing materials. [5]
- (c) Discuss the limiting assumptions for progressive conversion model. [5]

END OF EXAMINATION PAPER

Useful information:

Avogadro's number: L = 6.023×10^{23} .

Molar gas constant: R = $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

Planck's constant: h = $6.62 \times 10^{-34} \text{ Js}$

Boltzmann constant K_B = $1.38 \times 10^{-23} \text{ JK}^{-1}$

Mass of an electron m_e = $9.11 \times 10^{-31} \text{ Kg}$

Mass of proton M_p = $1.67 \times 10^{-27} \text{ Kg}$

Speed of light: c = $3.0 \times 10^8 \text{ ms}^{-1}$.