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

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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:

$$D + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} D^* + M$$

$$D^* \xrightarrow{k_2} E$$

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:

$$Z + XY \rightarrow ZX + Y$$

(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: $A + B \rightarrow$ 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,

$$A + B \underset{k'_d}{\overset{k_d}{\rightleftharpoons}} \{AB\} \xrightarrow{k_a} \text{Products}$$

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 1.00×10^{-3} kgm^{-1} s^{-1}, calculate the;

1. Diffusion controlled rate constant at 298k for a species. [3]
2. Initial rate, that is $\frac{d[Product]}{dt}$, 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 = $8.314 Jmol^{-1}K^{-1}$.

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

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

Mass of an electron m_e = 9.11×10^{-31} Kg

Mass of proton M_p = 1.67×10^{-27} Kg

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