



(University of Choice)

**MASINDEMULIROUNIVERSITY OF
SCIENCE AND TECHNOLOGY
(MMUST)**

UNIVERSITY EXAMINATIONS

2021 /2022 ACADEMIC YEAR

FIRST YEARFIRST SEMESTER EXAMINATIONS

FOR THE DEGREE

OF

MASTERS OF SCIENCE (CHEMISTRY)

COURSE CODE: SCH 840

COURSE TITLE: ADVANCED CHEMICAL KINETICS

DATE: Tuesday, 19th April 2022

TIME: 9.00 am – 12.00 (noon)

INSTRUCTIONS TO CANDIDATES

- Answer all the Questions

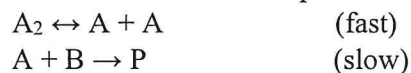
TIME: 3 Hours

MMUST observes ZERO tolerance to examination cheating

This Paper Consists of 3 Printed Pages. Please Turn Over. ▶

QUESTION ONE (15 MARKS)

- a) How is the standard enzyme kinetic scheme modified to incorporate competitive inhibition? What plot is used to establish competitive inhibition and to determine the kinetic parameters associated with inhibition? [5 marks]
- b) The reaction mechanism for the decomposition of A_2



involves an intermediate A. Deduce the rate law for the reaction in two ways by:

- Assuming a pre-equilibrium [3 marks]
- Making a steady-state approximation [3 marks]

- c) The initial rate of a reaction depended on concentration of a substance B as follows:

$[B]_0/(\text{mmol dm}^{-3})$	5.0	8.2	17	30
$v_0/(10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1})$	3.6	9.6	41	130

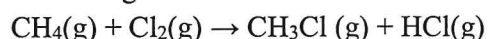
Determine the order of the reaction with respect to B and calculate the rate constant [4 marks]

QUESTION TWO (15 MARKS)

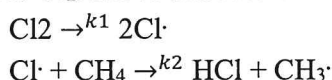
- a) The following questions relate to the quantum yields of molecules or substances.
- Distinguish between the primary quantum yield and overall quantum yield of a chemical reaction. [4 marks]
 - Describe an experimental procedure for the determination of the quantum yield. [3 marks]
 - What is the expected variation in excited state lifetime with quencher concentration in Stern-Volmer plot? [3 marks]
- b) In a photochemical reaction $A \rightarrow B + C$, the quantum yield with 500 nm light is $1.2 \times 10^2 \text{ mol einstein}^{-1}$. After exposure of 200 mmol A to the light, 1.77 mmol B is formed. How many photons were absorbed by A? [5 marks]

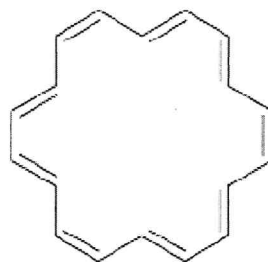
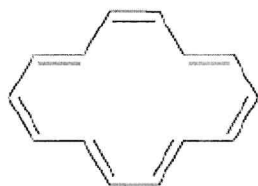
QUESTION THREE (15 MARKS)

- a) Explain the main factors that influence the electron transfer rate constant according to Marcus theory? [5 marks]
- b) Summarize the factors that govern the rates of resonance energy transfer according to Förster theory. Can you find similarities between Marcus and FRET theories? [5 marks]
- c) Consider the following reaction of methane with molecular chlorine

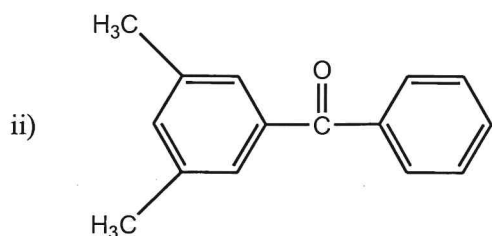
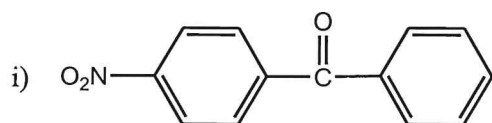


Experimental studies have shown that the rate law for this reaction is one-half order with respect to Cl_2 . Prove this rate law using the following mechanism [5 marks]



**QUESTION TWO (17 Marks)**

- a) What combination of acyl chloride or acid anhydride and arene would you choose to prepare each of the following compounds by a Friedel–Crafts acylation reaction?

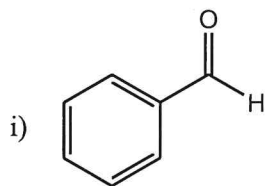
(6 marks)

- b) Give a Friedel Crafts alkylation reaction using the following reagents. Indicate a simple mechanism to justify your products.

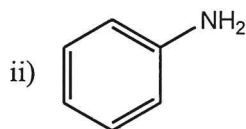
(4 marks)

- c) Using benzene and any necessary organic or inorganic reagents, suggest efficient syntheses of the following compounds

(7 marks)



benzaldehyde

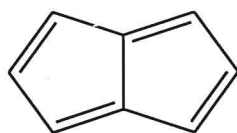


aniline

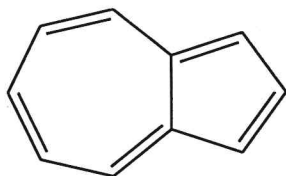
QUESTION THREE (18 Marks)

a) What are the aromatic heterocycles and polycyclic aromatic compounds? Give an example of each **(4 marks)**

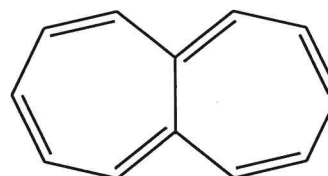
b) Pentalene, azulene, and heptalene are conjugated hydrocarbons that do not contain a benzene ring. Which hydrocarbons are especially stable or unstable based on the number of π electrons they contain? Explain your choices **(3marks)**



pentalene

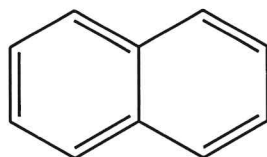


azulene



heptalene

d) The compound below is a poly nuclear aromatic compound



i) Name the compound

1 mark

ii) Identify the reaction product of the compound below using the following reagents:
 CH_3Cl , HNO_3 , Br_2

6 marks