KIBABII UNIVERSITY

UNIVERSITY EXAMINATIONS
2020/2021 ACADEMIC YEAR

FOURTH YEAR SECOND SEMESTER
SUPPLEMENTARY EXAMINATIONS

FOR THE DEGREE OF BACHELOR OF SCIENCE

COURSE CODE: SCH 441 E

COURSE TITLE: PHOTOCHEMISTRY

DURATION: 2 HOURS

DATE: 12/1/2022 **TIME: 2-4PM**

INSTRUCTIONS TO CANDIDATES

- Answer **QUESTION ONE** (Compulsory) and any other two (2) Questions.
- Indicate **answered questions** on the front cover.
- Start every question on a new page and make sure question's number is written on each page.

This paper consists of **4** printed pages. Please Turn Over

Question 1

a. What is meant by the following; [5mks]

i. Quantum efficiency
ii. Fluorescence
iii. phosphorescence
iv. Quenching
v. Photosensitization

b). Caffeine molecules absorb infrared radiation at 1656 cm^{-1}. Calculate the following:

i. wavelength of this radiation; [2mks]
ii. frequency of this radiation; [2mks]
iii. Energy change associated with this absorption. [2mks]

c) Give five differences between photochemical and thermal reactions. [5mks]

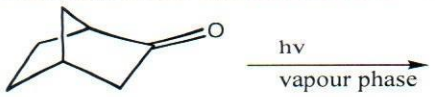
d) State four practical considerations for running photochemical experiments [4mks]

e) In the uranyl oxalate actinometer 5.18×10^{18} molecules were decomposed during the time radiation. 10.58×10^{18} photons of a radiation of 3655A wavelength were absorbed. What is the quantum efficiency of this reaction? [2mks]

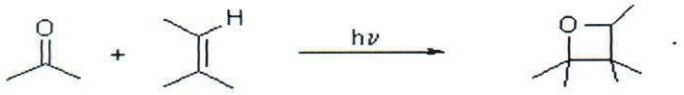
f) Explain four Causes for high quantum yield. [4mks]

g) write the mechanism for each of the following reactions; [4 mks]

i.



ii.



Question 2

a) Explain the validity of Stark-Einstein Law. [2 mks]

b) Derive Beer- Lamberts equation, Given that I is the intensity of incident radiation, x be the thickness of the solution and C be the concentration of the solution. [4mks]

c) The concentration of yeast t-RNA in an aqueous solution is 10 M. the absorbance is found to be 0.209 when this solution is placed in a 1.00cm cuvette and 258nm radiations are passed through it.

i. Calculate the specific absorptivity, including units of yeast t-RNA. [2mks]
ii. What will be the absorbance if the solution is 5M? [2mks]

iii. What will be the absorbance if the absorbance if the path length of the original solution is increased to 5.00cm? [2mks]

d) State four Limitations of Beer-Lambert's law. [4 mks]

e) Using reaction mechanisms, explain the term 'chemiluminescence'. [4 mks]

Question 3

a. State FOUR secondary effects of absorption of radiations by molecules. [4mks]

b. Using mechanisms, discuss the photochemistry of following reactions; [8 mks]

i. methane- chlorine reaction

i. Photolysis of ammonia

C) Discuss Oxidant - smog mechanism of peroxyacyl nitrates (PAN) generation. [8mks]

Question 4

a) Discuss three detectors used for the measurement of intensity of transmitted light. [12mks]

b) In a potassium ferrioxalate actinometer, the quantum efficiency for Fe^{2+} Production, at 480 mn wavelength is 0.95. After irradiating the potassium ferrioxalate solution for 20 minutes, it is completely transferred to a 200 cm^3 volumetric flask, mixed with required quantity of 1,l0-phenanthroline for complex formation and made up to mark with a buffer solution. For colorimetric estimation, a sample of this complex is taken in a cell of 1.00 **cm** thickness. The complex has an absorbance value of 0.391 and its **E** is 1.11×10^3 m^2 mol^{-1}.

Calculate

i) the concentration of the complex. [3mks]

ii) the number of Fe^{2+} ions formed in the actinometer due to irradiation, [2mks]

iii) the rate of formation of Fe^{2+} ions (dNp/dt) [1mk]

iv) ***Ia*** (number of photons absorbed per second). [2mks]

(Assume that one Fe^{2+} ion forms one complex molecule with 1,10-phenanthroline).

Question 5

a) Explain what is meant by fluorescence lifetime [1 mk]

b) List two requirements of photosensitizer in photosensitization reactions. [2mks]

c) Give the physical processes undergone by excited molecules in the following transitions [5mks]

i. $S1 \rightarrow S1$

ii. $S1 \rightarrow S_o + hv$

iii. $S_2 \rightarrow S_1$

iv. $S1 \rightarrow T1$

v. $T1 \rightarrow S_o + hv$

d) State five differences between Singlet and triplet excited states [5mks]

e) Explain two methods to determine fluorescence lifetime of fluorophores [4mks]

f) Give THREE advantages of fluorescence lifetime measurement over intensity-based measurement . [3mks]