DEDAN KIMATHI UNIVERSITY OF TECHNOLOGY
UNIVERSITY EXAMINATIONS 2021/2022
EXAMINATION FOR DEGREE OF MASTERS OF SCIENCE IN LEATHER TECHNOLOGY
SCH 6113: ADVANCED CHEMICAL KINETICS
DATE: FEBRUARY 2022 **TIME:3 Hours**
INSTRUCTIONS: Answer ALL Questions

1) a) Distinguish between parallel and Reversible reaction (2 marks)

b) In a reversible reaction between A and B in which only A is present at time t=0

i) Give an expression for the rate of change of the concentration of A with time t in terms of initial concentration of A and concentration of A at any time t (2 marks)

ii) Derive an expression of the concentration of A at equilibrium in terms of its initial concentration (2 marks)

iii) Show that on integration of your equation in (i) above

$$(k + k_{-1})t = ln\frac{x_e}{(x_e - x)}$$

(5 marks)

iv) Given that the concentration of B at any time t, is given by x=[B]= $\frac{k}{k+k_{-1}}a(1 - e^{-(k+k_{-1})t})$

show that the concentration of A can be given by the expression

$$[A] = a\frac{(k_1 - k_{-1})}{k_{-1}}(1 + \frac{k_1}{k_{-1}}e^{-(k_1+k_{-1})t})$$

(4 marks)

c) Given the values of $k_1 = 3\ s^{-1}$ and $k_{-1} = 1\ s^{-1}$ for the reaction above, What will be the concentration of A after 10 s for an initial concentration of A of 0.5 M (2 marks)

Q2. (a) Define the following terms:

(i) Elementary reaction
(ii) Steady state approximation

(b) In a heterogeneous catalytic reaction , which 5 processes take place and which of these is usually the rate determining (5 marks)

(c) For a unimolecular surface reaction ,

$$A + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AS$$

$$AS \xrightarrow{k_2} A + S \qquad \text{slow}$$

Derive the rate expression in terms of k_1, k_{-1} and k_2 (8 marks)

Q3. a) Differentiate between Chemiluminescence and Phosphorescence (2 marks)

b) With the aid of an example discuss briefly Intermolecular and Intramolecular energy transfer (7 marks)
Intermolecular

c) Discuss quenching of absorbed radiation and with reference to the process below, derive the Stern-Volmer equation, $1 + \frac{k_3}{k_1 + k_2}[Q]$

$$A + h\nu \xrightarrow{I_a} A^*$$
$$A^* \xrightarrow{k_1} A + h\nu'$$
$$A^* \xrightarrow{k_2} A$$
$$A^* + Q \xrightarrow{k_3} A + Q'$$

(6 marks)

Q4 a) Explain the following

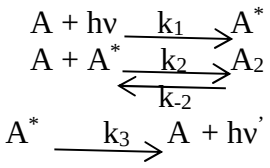
i) Hydrogen and chlorine do not react in darkness yet the reaction is explosive when exposed to light
ii) The quantum yield for the above reaction is very high

(3 marks)

b) Anthracene (A) dimerises and simultaneously fluoresces through the following two different mechanisms
Mechanism 1

$$A + h\nu \xrightarrow{k_1} A^*$$
$$A + A^* \xrightarrow{k_2} A_2$$
$$A^* \xrightarrow{k_3} A + h\nu'$$

Mechanism 2



Derive a rate expression for the two mechanisms based on intensity of light absorbed (12 marks)