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RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Honours) in Chemistry
Fourth Year - Semester I Examination – July / August 2023

CHE 4202 – ADVANCED PHYSICAL CHEMISTRY I

Answer ALL questions **Time: Two hours**

Use of a non-programmable calculator is permited
Gas constant (R) = 8.314 J K^{-1} mol^{-1}, Faraday constant (F) = 9.6485×10^4 C mol^{-1}
Avagadro constant (N_A) = 6.022×10^{23} mol^{-1}

1

a) For a single electron charge - transfer controlled reaction, the current density and overpotential relationship is given in the following Butier-Volmer equation.

$$J = J_0\left[e^{(1-\alpha)\eta F/RT} - e^{-\alpha\eta F/RT}\right]$$

i. Define the terms J_0, α and η in the above equation.

(15 marks)

ii. Re-write the above equation for large positive values of overpotentials.

(10 marks)

iii. The data given below refer to the anodic current through a 2.0 cm^2 Pt electrode in contact with an aqueous solution containing Fe^{2+} and Fe^{3+} at 298 K. Calculate J_0 and α.

η/mV	50	100	150	200	250
I/mA	8.8	25.0	58.0	131	298

(30 marks)

b) Starting from Butler-Volmer equation and taking into account of small overpotentials, show that $\eta = \frac{RT}{j_0 F} j$ and identify the charge-transfer resistance.

(15 marks)

c) Draw a lebelled electrical equivalent circuit for the representation of electrode/solution interface region.

(15 marks)

d) With appropriate current-potential diagrams, distinguish between a polarizable and a non polarizable electrode.

(15 marks)

2. 08

a) Cyclic voltammetry is carried out under diffusion controlled. Comment

(20 marks)

b)

i. Draw a first sweep of a cyclic voltammogram for the oxidation of species A to species A^+ at an electrode where the kinetics are very fast

(15 marks)

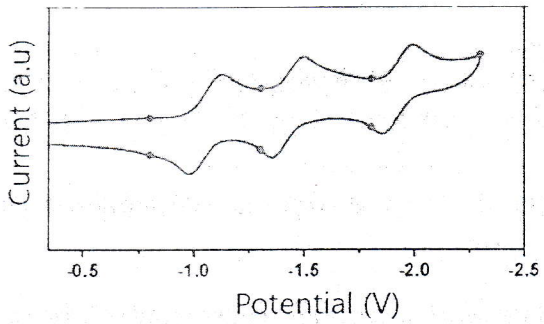
ii. Include in your answer a sketch of the concentration profile of A and A^+ in solution at the start of sweep and at the maximum peak potential in the forward sweep where A is converted to A^+

(15 marks)

iii. How would the voltammogram differ if the electrode reactions were slow electrode kinetics?

(10 marks)

c) The typical cyclic voltammetric response of fullerene molecule (C60) is shown below. Design a simple experiment that can include an electrochemical technique in order to estimate the numbers of electron transfers involved in each voltammetric peak. comment on the cyclic voltammetric response



(40 marks)

3. a) When a substance A was exposed to light, 0.002 mole of it reacted in 20 minutes and 4 seconds. In the same time A absorbed 2.0×10^6 photons of light per second. Calculate the quantum yield of the reaction.

(20 marks)

b) Give reasons for high and low quantum yields for photochemical reactions.

(20 marks)

c) Decomposition of H_2O_2 in the presence of CO occurs in the following reactions,

$$H_2O_2 \xrightarrow{h\upsilon} 2\,OH$$

$$OH + CO \xrightarrow{k_2} COOH$$

$$COOH + H_2O_2 \xrightarrow{k_3} CO_2 + H_2O + OH$$

$$H_2O_2 + OH \xrightarrow{k_4} H_2O + HO_2$$

$$2HO_2 \xrightarrow{k_5} H_2O_2 + O_2$$

If quantum yield $\Phi = \frac{-d[H_2O]/dt}{I_{abs}}$, show that $\Phi = 2\left[1 + \frac{k_2[CO]}{k_4[H_2O_2]}\right]$

(30 marks)

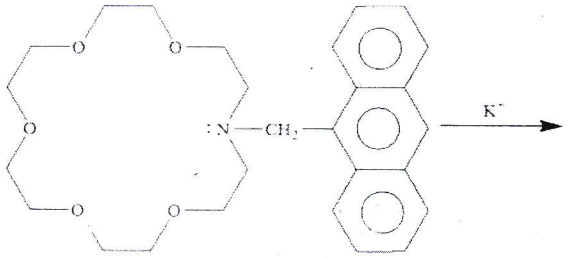
d) Draw completely labelled potential energy surface (PES) diagrams to explain the fluorescence and phosphorescence emission (all photophysical events should be included)

(30 marks)

4. a) What is meant by photosensitization and discuss the mechanism and conditions of photosensitization with reference to singlet oxygen formation?

b) Write a short note on Fluoresence Resonance Energy Transfer (FRET).

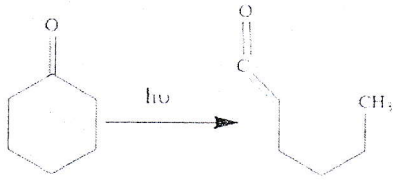
c) Discuss the fluorescence ON-OFF switching mechanism for the following molecular system on binding with K^+ ions.



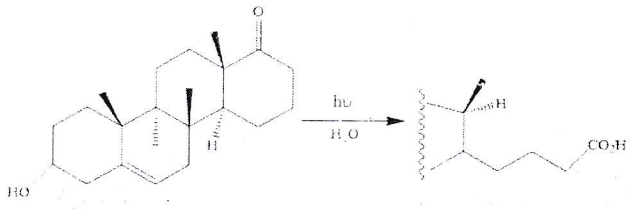
Cation Receptor Fluorophore

d) Give mechanisms for the following photochemical reactions.

i.



ii.



(Each part carries equal 20 marks)

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