RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES
B.Sc. (Special) Degree in Chemistry
Fourth Year - Semester I Examination – June/July 2018

CHE 4202– ADVANCED PHYSICAL CHEMISTRY-I

Answer all questions Time: Two hours

Avogadro's number (N_A) = 6.0221367×10^{23} mol^{-1}, Faraday constant (F) = 9.6485×10^{4} C mol^{-1}, gas constant (R) = 8.314 J mol^{-1} K^{-1}, Planck constant (h) = 6.63×10^{-34} J s, speed of Light (c) = 3×10^{8} m s^{-1}

Unless specified, other symbols have their usual meaning

1. One of the major research efforts in modern electrochemistry involves studies and applications of redox reactions of electrochemically active species in a suitable electrolyte or confined in stable, ultrathin films attached to an electrode surface.

(a) Explain the following:

(i) Cyclic voltammetry is typically performed in the presence of a large excess of an inert electrolyte and in the absence of any mechanical disturbance in the solution.

(ii) Glassy carbon electrode is a better choice over a Pt for preliminary electrochemical investigation of an inorganic redox system in aqueous acidic solution.

(20 marks)

(b) A cyclic voltammetry experiment was performed by cycling a 10 mM solution of $Ru\,(NH_3)_6^{3+}$ from + 0.8 V to - 0.6 V in 0.1 mol dm^{-3} KCl solution.

$$Ru\,(NH_3)_6^{3+} + e^- \rightleftharpoons Ru\,(NH_3)_6^{2+} \qquad E^{\ominus} = +\,0.10\text{ V}$$

(i) Draw a labelled sketch of the cyclic voltammogram(CV) you would expect to obtain.

(10 marks)

(ii) A series of CVs were recorded at different scan rates. What three parameters could you measure in order to determine whether the electrochemical process was reversible, and how would these parameters differ if it were not?

(30 marks)

(iii) From the CVs recorded at different scan rates a Randles-Sevcik graph of ip against $\nu^{1/2}$ was drawn using ip data for the reduction cycle. The linear part of the graph had a gradient of 6.09×10^{-5} A $(V s^{-1})^{-1/2}$ at 25 °C, and the working electrode area was 0.45 cm^2 Calculate the diffusion coefficient D of of $Ru\,(NH_3)_6^{3+}$ in the electrolyte.

(20 marks)

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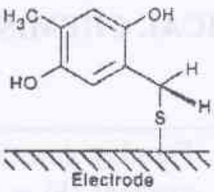
(c) If you record the voltammogram for the same system in part (b)-I at rotating disk electrode, sketch the shape of the voltammogram you would obtain and explain the reasoning behind your answer. (15 marks)

(d) **The molecule 2,5 dihydroxy-4-methylbenzylthiol undergoes irreversible adsorption on Pt electrode to form the species illustrated. Draw the CV for the adsorption process** (05 marks)



2. The Butler-Volmer equation below is the classic kinetic relationship between Faradaic current (I) and the applied potential (E) for an electron-transfer reaction of electroactive species dissolved in solution:

$$i = i_0 \left\{ e^{\frac{(1-\alpha)n\eta F}{RT}} - e^{\frac{-\alpha n\eta F}{RT}} \right\}$$

Where i is the net current, i_0 is the exchange current, α is the transfer coefficient, n is the number of moles of electrons participated and η is the overpotential.

(a) **Explain briefly, what is meant by: (i) Faradaic current (ii) exchange current and (iii) overpotential.** (30 marks)

(b) **What is Tafel plot? The cathodic and anodic Tafel equations are limiting forms of the Butler-Volmer equation. Show how the Tafel equations are derived from the Butler-Volmer equation based on the magnitude of overpotential.** (20 marks)

(c) **The data below refer to the anodic current for the electrode Pt/Fe^{2+}, Fe^{3+} at 25^{0}C. Using the simplified equation in part (b), calculate the exchange current density if the surface area of the Pt electrode is 2.0 cm^2 and the transfer coefficient for the electrode process.**

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

(30 marks)

(d) **The exchange current density of Pt/Fe^{2+}, Fe^{3+} electrode is 2.5 mA cm^{-2}. Calculate the current density at the electrode maintained at 1.00 V at 25^{0}C when [Fe^{2+}] = 0.1 mol dm^{-3} and [Fe^{3+}] = 0.2 mol dm^{-3}. $E^{\ominus}$ (Fe^{3+}, Fe^{2+}) = 0.77 V.** (20 marks)

3.

(a) The molecule AB is electronically excited: $AB + h\nu \rightarrow AB^*$. Briefly describe four processes with which the excited molecule AB* could lose the excitation energy.

(20 marks)

(b) Use the Franck-Condon principle to explain the following observations.

(i) Fluorescence or phosphorescence from organic molecules in solution generally occurs from the lowest excited singlet (S1) or triplet (T1) state, irrespective of the energy of the electronic state initially excited.

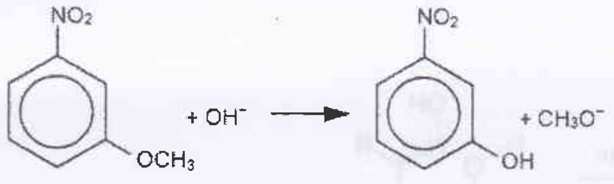
(ii) Intensity of vibrational fine structure ($\nu_0 \rightarrow \nu_0$) is higher than ($\nu_3 \rightarrow \nu_0$). You may use potential energy vs. internuclear distance plots for the illustration.

(20 marks)

(c) State the factors contributing to fluorescence behavior. (20 marks)

(d) When exposed to UV light, m-nitroanisole (I) in aqueous solution is excited to the S_1 state and then 100% of the excited molecules undergo rapid intersystem crossing to the T_1 state. In the presence of hydroxide ion, OH−, and a triplet quencher Q, the molecule in the T_1state has one of the following fates

1. Radiationless decay to the ground state of I (rate constant k_1)
II. Attack by OH− leading initially to m-nitrophenol (II) as indicated below (k_2)
III. Quenching by Q leading to the ground state of I (k_3)



I II

The quantum yield φ of the reaction to produce (II) varies with the triplet quencher concentration and the OH− concentration is held constant.

(i) Draw a vibrational levels of electronic states diagram to illustrate the intramolecular processes mentioned.

(15 marks)

(ii) Derive an expression for the quantum yield of the reaction in terms of the rate constants k_1, k_2 and k_3. (25 marks)

4.

(a) Explain a photosensitization process by which singlet oxygen is produced.

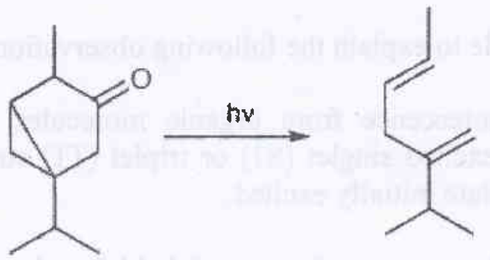
(15 marks)

(b) The energy gap between the triplet ground state and the first excited singlet state for molecular oxygen is 90 kJ mol^{-1}. Calculate the wavelength of photons given off if an excited singlet state relaxes to the ground state with the emission of light. Is the light emitted fluorescence or phosphorescence?

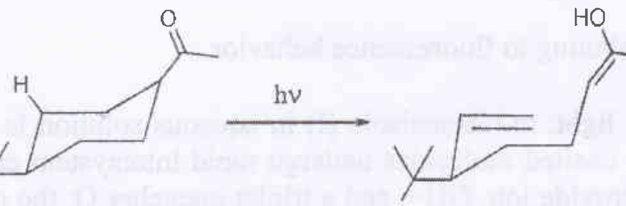
(35 marks)

(c) Provide mechanism for each of the photochemical transformations.

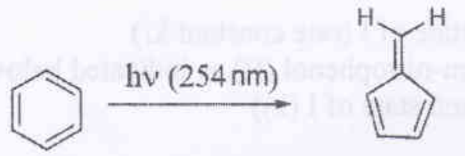
(i)



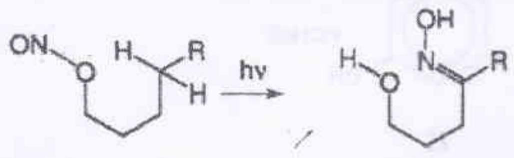
(ii)



(iii)



(iv)



(50 marks)