RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Joint-major) Degree-Chemistry and Physics
Fourth Year - Semester II Examination – February/March 2019

CHE 4202– ADVANCED PHYSICAL CHEMISTRY-I

Answer ALL questions Time: Two (02) hours

Avogadro's number (N_A) = 6.022×10^{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.

Use of a non-programmable calculator is permitted.

1. Voltammetry is the general name given to a group of electroanalytical methods in which the current is measured as a function of applied potential wherein the polarization of the indicator or working electrode is enhanced.

a) (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. Explain

(20 marks)

(ii) Explain the term (a) exchange current density and (b) anodic over potential with reference to the reaction, $M^{n+} + ne^- \rightleftharpoons M$.

(30 marks)

b) (i) Describe the essential details, including a diagram of the apparatus, of how cyclic voltammetry may be used to determine the concentration of electroactive species A.

(20 marks)

(ii) Sketch a cyclic voltammogram of a hypothetical reversible redox process

$$A + e^- \leftrightharpoons A^-.$$

(10 marks)

(iii) Draw the expected CV shape at 50 mV s^{-1} when a species Z is added to the solution that rapidly reacts with A^- in the reaction $A^- + Z \rightarrow$R. **(20 marks)**

2.

a) 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:

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

(i) Explain clearly all the terms in the above equation.

(20 marks)

(ii) Outline all the steps involved in an experimental method in the determination of n, j_0, and α.

(25 marks)

(iii) At very low η values, show that the above equation would take the form of

$$\eta = \frac{RT}{J_{oF}} j$$

(15 marks)

The exchange current density for Pt/ $H_2(g)/H^+(aq)$ system at 298 K is 0.79 mA cm^{-2}. What current flows through a standard electrode of total area 5.0 cm^2 when the potential difference across the interface is + 5.0 mV?

(15 marks)

b). Give an account of the Gouy-Chapmen theory and the Stern theory of electrical double layer.

(25 marks)

3.

a)

(i) 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)

(ii) 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?

(25 marks)

(iii) Draw a completely labeled potential energy levels diagram to illustrate fluorescence and phosphorescence from organic molecules in solution. Luminescence generally occurs from the lowest excited singlet (S1) or triplet (T1) state, irrespective of the energy of the electronic state initially excited.

(20 marks)

b) In an experiment on dynamic fluorescence quenching, the following processes and their rate constants have to be considered:

$$F + h\nu \rightarrow F^* \qquad 1$$

$$F^* \xrightarrow{K_{IC}} F + heat \qquad 2$$

$$F^* \xrightarrow{K_f} F + h\nu \qquad 3$$

$$F^* + Q \xrightarrow{K_q} F + Q^* \qquad 4$$

(i) Identify the above four steps.

(ii) What is meant by quantum yield for a photochemical reaction? Write down an expression for the fluorescence quantum yield (Φ).

(iii) Apply the steady state kinetics to derive an equation for Φ.

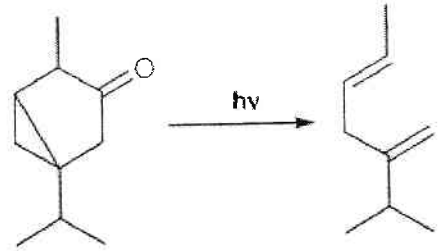
(iv) In the absence of a quencher, fluorescence quantum yield is Φ_0. Obtain an expression for Stern-Volmer rate constant (K_{SV}).

(35 marks)

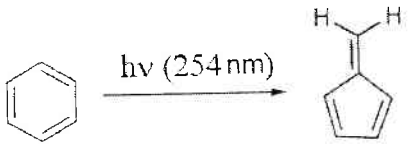
4.

a) Provide a mechanism for each of the photochemical transformations.

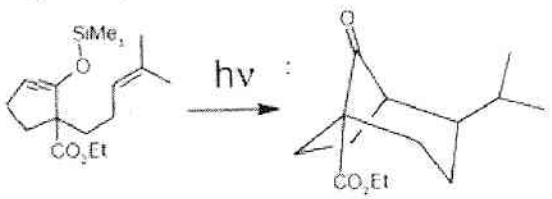
(i)



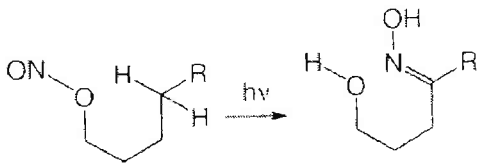
(ii)



(iii)

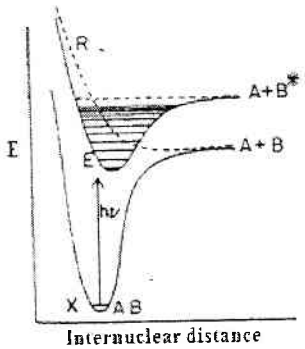


(iv)



(60 marks)

b) Explain the photochemical process takes place in the figure given below



(40 marks)