52

RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Special) Degree in Chemistry
Fourth Year– Semester I Examination – October/ November 2017

CHE 4202 – ADVANCED PHYSICAL CHEMISTRY I

Answer all questions. Time: Two (2) hours

Avogadro Number (N_A) = 6.023×10^{23} mol^{-1}
Planck Constant (h) = 6.63×10^{-34} J s
Universal Gas Constant (R) = 8.314 J K^{-1} mol^{-1}
Velocity of Light (c) = 3×10^{8} m s^{-1}

The use of a non-programmable calculator is permitted.

1. (a) Explain clearly all the terms in the following equation:

$$j = j_0\left(e^{\frac{-\alpha nF\eta}{RT}} - e^{\frac{(1-\alpha)nF\eta}{RT}}\right)$$

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

(c) At very low η values ("± 50 mV)" ,show that the above equation would take the form of .

$$\eta = \frac{RT}{j_0 F} j$$

(d) 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?

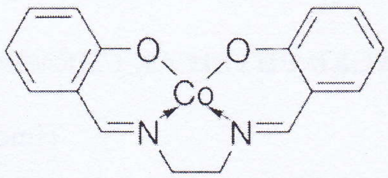
(e) Explain the following terms used in electrochemistry

(i) Ideally polarizable and non polarizable electrode

(ii) Anodic overpotential

(iii) Faradaic and non-Faradaic current

2. (a) Co(II)(salen) shows well-defined two distinct reversible one-electron reduction processes at a glassy carbon working electrode for the change in oxidation states of Co in the solvent DMSO in the presence of 0.1 M tertabutylammonium hexafluorophosphate as a supporting electrolyte.



Co(II)(salen)

Upon addition of Et-Br, an irreversible chemical reaction occurs as follows

$Co(I)(salen)^{-} + EtBr \longrightarrow Et–Co(III)(salen) + Br^{-}$.

Et–Co(III)(salen) can be reduced at a more negative potential than Co(II)(salen).

(i) Draw the schematic diagram of the CV for before addition of Et-Br under nitrogen atmosphere.

(ii) Draw the schematic diagram of the CV for after addition of Et-Br under nitrogen atmosphere.

(iii) Explain the term 'Reversible Electrode Process' in voltammetry

(iv) Briefly explain the role of supporting electrolyte in cyclic voltammetry

(b) In a chronoamperometry experiment, the diffusion coefficient of Co(salen) was calculated to be 1.4 (± 0.3)$\times 10^{-6}$ $cm^2\ s^{-1}$. Describe a cyclic voltammetric method for measuring the active surface area of the glassy carbon working electrode.

$$I_p = (2.69\ \times 10^5)\, n^{\frac{3}{2}}\, A\, D^{\frac{1}{2}}\, v^{\frac{1}{2}} C^*$$

(c) Compare and contrast between cyclic voltammetry and rotating disk voltammetry.

3. (a) List three differences between light-excited and thermally-excited molecules.

(b) List and briefly describe the various intermolecular processes through which an excited-state molecule may be deactivated.

(c) Describe briefly what is meant by the quantum yield of a photochemical reaction?

(d) What are the reasons of low quantum yield?

(e) Considering the deactivation processes of the singlet excited state in the absence and presence of a quencher, derive the **Stern-Volmer** equation which expresses the ratio of the fluorescence quantum yields in the presence and absence of a quencher.

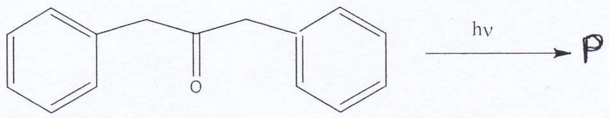
(f) With the help of a fully labeled potential energy surface diagram, briefly explain each process shown from A to F as:

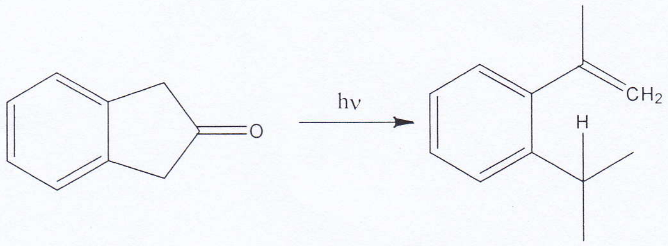
A Spin-allowed absorption, **B** Spin-forbidden absorption, **C** Fluorescence, **D** Phosphorescence, **E** Internal conversion and **F** Intersystem crossing.

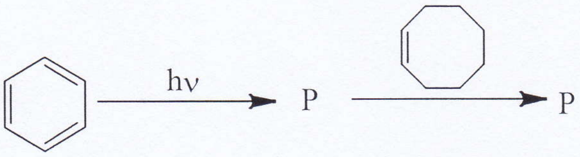
54

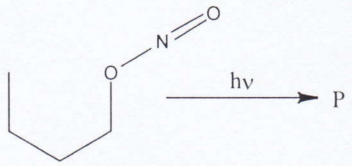
4. (a) Write a short note on how singlet oxygen is photochemically generated and its applications.

(b) Give appropriate mechanisms and the product P for each of the following photochemical transformations.

(i) 

(ii) 

(iii) 

(iv) 

(c) When propionaldehyde is irradiated with light of $\lambda = 3020$ Å, it is decomposed to form carbon monoxide.

$$CH_3\,CH_2\,CHO + h\nu \longrightarrow CH_3CH_3 + CO$$

The quantum yield for the reaction is 0.54.

Calculate the light energy absorbed for the formation of 2.04×10^{-9} mol of CO.