



RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Honours) Degree in Chemistry
Fourth Year– Semester I Examination – September/ October 2019

CHE 4202 – ADVANCED PHYSICAL CHEMISTRY I

Time: Two (02) hours

Answer all questions.

Avogadro Number (N_A) = $6.023 \times 10^{23} \text{ mol}^{-1}$

Planck Constant (h) = $6.63 \times 10^{-34} \text{ J s}$

Universal Gas Constant (R) = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

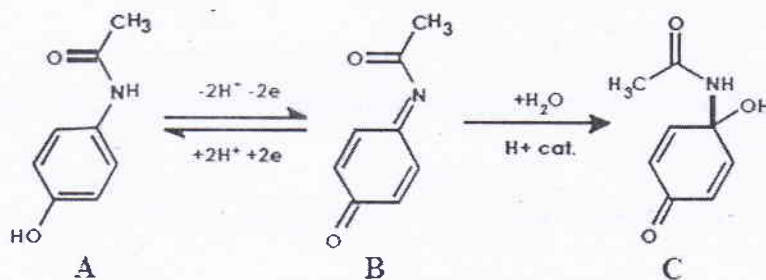
Velocity of Light (c) = $3 \times 10^8 \text{ m s}^{-1}$

The use of a non-programmable calculator is permitted.

- Acetaminophen is an active ingredient over-the-counter pain relief medication. Acetaminophen has largely replaced aspirin (acetylsalicylic acid) as the medication of choice for children and infants because aspirin has, in some cases, been linked to the development of Reye's syndrome.

Part I

Acetaminophen **A** can be electrochemically oxidized to the quinone form **B**, and in the presence of an acid catalyst, **B** is rapidly converted to electro inactive hydrate **C** as given below.



- Briefly explain the three-electrode system and the experimental procedure that you would use to record the cyclic voltammogram (CV) of acetaminophen.
- Draw a completely labeled CV that you would likely to obtain in part (a)
- What changes in the CV (part b) you would expect if acid catalysis is not happened?
- You will be provided with a stock solution of children's acetaminophen medication, whose concentration could be analytically determined. Outline a procedure based on your CV of acetaminophen, for the determination of the concentration of acetaminophen.

(70 marks)

Part II Explain the following:

- a) Cyclic voltammetry is generally carried out in the presence of excess supporting electrolyte for an un-stirred test solution.
- b) Before each CV experiment, nitrogen gas is purged through the analyte for few minutes.

(30 marks)

2. a) The exchange current density (j_0) of the system $\text{Pt(s)} | \text{Fe(CN)}_6^{3-} (2.0 \text{ mmol L}^{-1}), \text{Fe(CN)}_6^{4-} (2.0 \text{ mmol L}^{-1}), \text{NaCl} (1.0 \text{ mol L}^{-1})$ is measured to be 2.0 mA cm^{-2} at 298 K . The transition coefficient (α) of the system is 0.5 .

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

- i. If the concentration of Fe(CN)_6^{3-} and Fe(CN)_6^{4-} is increased to 1.0 mol L^{-1} , calculate the standard current density j_0 . When the concentration of Fe(CN)_6^{3-} and Fe(CN)_6^{4-} are both $10^{-4} \text{ mol L}^{-1}$, calculate the charge-transfer resistance of the reaction.
- ii. How do you graphically prove that $\text{Fe(CN)}_6^{3-} / \text{Fe(CN)}_6^{4-}$ redox reaction is diffusion controlled
- iii. Draw Tafel plot of this system, indicate the exchange current, reversible potential and calculate its Tafel slope.

(60 marks)

- b) Give a comparative account of the Helmholtz, Gouy-Chapman, and the Stern theoretical models of electrical double layer.

(40 marks)

3. a) When propionaldehyde is irradiated with light of $\lambda = 3020 \text{ \AA}$, it is decomposed to form carbon monoxide.



The quantum yield for the reaction is 0.54 .

- i. Calculate the light energy absorbed for the formation of $2.04 \times 10^{-9} \text{ mol}$ of CO .
- ii. What are the reasons of low quantum yield?

(40 marks)

- b) 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.

(30 marks)

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

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

(30 marks)

4. a) Write a brief account of the chemistry involved in photodynamic therapy of cancer

(20 marks)

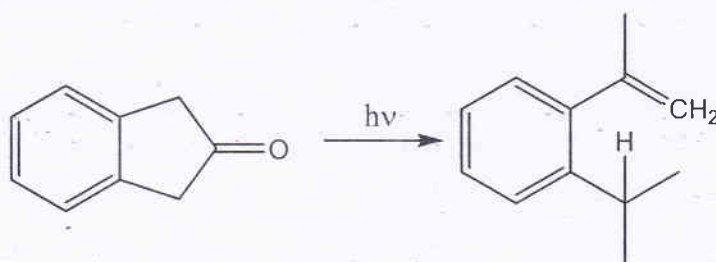
b) Illustrate the following photo processes with appropriate diagrams.

- Photon absorption leading to a bound excited state with energy greater than the bond dissociation energy, resulting bond cleavage.
- Absorption to a dissociative state, resulting bond cleavage.
- Promotion to a stable state followed by crossing to a dissociative state (predissociation)

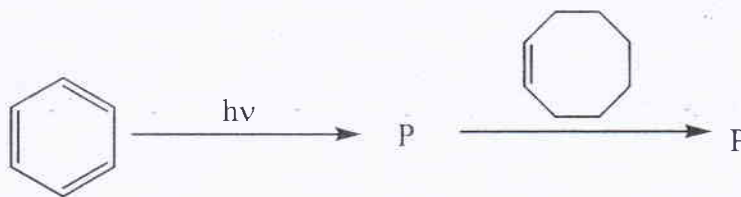
(30 marks)

c) Give appropriate mechanism for part i and the product **P** for parts ii and iii in the following photochemical transformations.

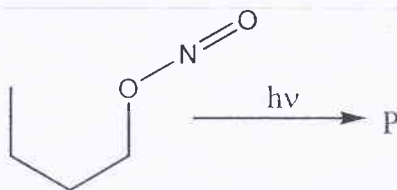
i.



ii.



iii.



(50 marks)

--- END---