RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Honours) in Chemistry
Fourth Year - Semester I Examination – January / February 2021

CHE 4202 – ADVANCED PHYSICAL CHEMISTRY I

Time: Two (02) hours

Answer **any four (04)** questions. Use of a non-programmable calculator is permitted.

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

1.

a) Define the terms,
i. equilibrium potential ii. overpotential iii. charge transfer resistance
(05× 3 marks)

b) For large negative values of overpotentials ≥100 mV, the current density increases exponentially with the overpotential according to the equation,

$$J = -J_0 e^{-\alpha\eta F/RT}$$

i. Identify all the terms involved 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+} ions 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

(60 marks)

2.

a) Compare and contrast the models proposed for electrical double layer at the electrode-solution interphase.

(50 marks)

b) Draw a labeled electrical equivalent circuit for an electrochemical cell.

(10 marks)

c) Describe the electrocapillary curves. Outline the information which can be obtained from electrocappilary curves?

(40 marks)

3.

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.

(15 marks)

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

(10 marks)

b) A well-defined reversible cyclic voltammogram (CV) at around -0.75 V was obtained for a $O_2/O_2^{\cdot-}$ couple at a glassy carbon electrode for an oxygen saturated non-aqueous solution. Potential scanning was performed from +0.0 V to -1.00 V.

i. Draw a labelled CV for the $O_2/O_2^{\cdot-}$ couple.

(10 marks)

ii. Ninhydrine was found to scavange superoxide radical anion. Draw and explain the change in shape of CVs for the $O_2/O_2^{\cdot-}$ couple, before and after each successive addition of ninhydrine to the solution.

(20 marks)

iii. How do you experimentally prove, in CVs obtained for the above reaction, that the electron-transfer rate is diffusion controlled and the electrochemical reversibility.

(20 marks)

c) A simplified equation for the peak current i_p at 25 °C for a totally reversible couple is given by, $i_p = (2.69 \times 10^5)n^{3/2}A\,D^{1/2}v^{1/2}C_0^*$. From the CVs recorded at different scan rates for a solution of $Ru(NH_3)_6^{3+}$, a Randles-Sevcik graph of i_p against $v^{1/2}$ was drawn using i_p 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.

i. Calculate the diffusion coefficient D of of $Ru(NH_3)_6^{3+}$ in the electrolyte.

(15 marks)

ii. If the CV is recorded for one-electron reduction of $Ru(NH_3)_6^{3+}$ at a Pt microelectrode, draw the shape of CV.

(10 marks)

4.

a) The molecule AB is electronically excited to AB^*. Briefly describe four processes by which the excited molecule AB* could lose the excitation energy.

(15 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 (S_1) or triplet (T_1) 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)

i. What is meant by the quantum yield of a photochemical reaction?

(10 marks)

ii. For the gas phase photoreaction $HI + h\nu \rightarrow \frac{1}{2} H_2 + \frac{1}{2} I_2$, the quantum yield at 254 nm is found to be bc 2.0. Suggest a reaction scheme to explain this result justifying both the steps you include and those you omit.

(20 marks)

iii. State the factors contributing to fluorescence behavior.

(15 marks)

d) Briefly discuss,

i. photoinduced electron transfer

ii. excitation energy transfer

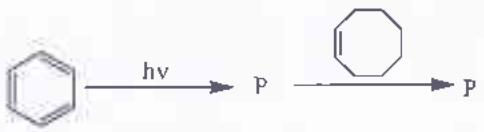
with two applications from each.

(20 marks)

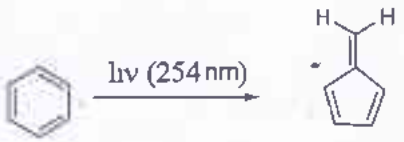
5.

a) Give appropriate mechanisms and the product (P) for **three** of the following photochemical transformations.

i.



ii.



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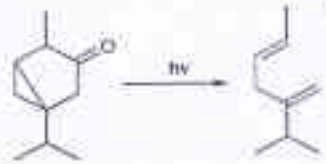
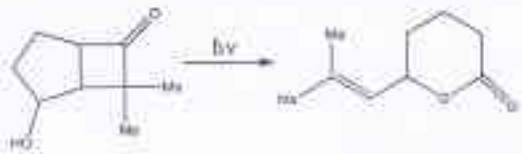


iv.



(3 ×20 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) Discuss the two applications of **Stern-Volmer** equation in chemistry.

(10 marks)

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