RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (General) Degree in Applied Sciences
Third Year– Semester I Examination – September / October 2019

CHE 3207 – ELECTROCHEMISTRY

Time: Two (2) hours

Answer ALL questions
Faraday constant (F) = 9.649 x 10^4 C mol^{-1}, Gas constant = 8.314 J mol^{-1} K^{-1}
Non programmable calculator is permitted

1.

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

(15 marks)

b) Draw and label a free energy versus distance plot for the above reaction where "the reaction is in equilibrium" and "metal dissolution" takes place

(15 marks)

c) Derive the following equation and identify all the terms involved.

$$i_a = i_0 \exp^{\left(\frac{\alpha \eta Fn}{RT}\right)}$$

(20 marks)

d) i Corrosion is a galvanic process, explain
ii Show that dissolution of iron in aerated aqueous media at 298 K is spontaneous. Write all reactions taking place in the process. $E^{\phi}(O_2/H_2O) = 1.23\ V, E^{\phi}(Fe^{2+}/Fe) = -0.45\ V$
iii The reaction (part b) is very rapid in acidic media. Explain

(50 marks)

2.

Consider the following reactions that are possible at the metal "nickel" under aerated wet conditions at 298 K.

$$Ni^{2+} + 2e^- \rightarrow Ni \qquad (1)$$

$$NiO + 2\,H^+ + 2e^- \rightarrow Ni \quad H_2O \qquad (2)$$

$$Ni^{2+} + 2\,H_2O \rightarrow Ni(OH)_2 + 2H^+ \quad (3)$$

$$NiO + H_2O \rightarrow Ni(OH)_2 \quad (4)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (5)$$

$$O_2 + 4\,H^+ + 4e^- \rightarrow 2H_2O \quad (6)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4\,OH^- \quad (7)$$

Chemical potential (μ^θ) values for different species participating in the above reactions are given below.

Ni^{2+} = -46,398.00, NiO = -215,729.00, $Ni(OH)_2$ = -452,694.00, H_2O = -236,964.00, OH^- = -157,147.00, Ni= H_2= H^+= O_2= 0

a) Derive potential or pH dependent equations for the above reactions and construct a pourbaix diagram for the Ni/H_2O system. (concentration of Ni^{2+} = 1.0 mol dm^{-3})

(70 marks)

b) Identify the corrosion, immune and passive zones in your diagram.

(30 marks)

3. a) Discuss the principle of cathodic and anodic protection with the help of potential vs. current diagrams

(40 marks)

b). Compare and contrast between (a) sacrificial anode and (b) impressed current cathodic protection with appropriate diagrams

(30 marks)

c). Explain the band bending when p-type and n-type semiconductors are brought into contact with an aqueous electrolyte with a suitable redox couple.

(30 marks)

4. Answer part (a) and any other one from parts (b) and (c)

a) i. Discuss, briefly with relevant reactions, how electrocoagulation (EC) technique could be employed for the treatment of drinking water contaminated with excess fluoride, calcium and magnesium ions.

ii. State the advantages and disadvantages of EC technique

(60 marks)

b) A sample of unknown fluoride weighing 0.400 g dissolved in 100 ml of de-ionized water and the measured potential was – 0.1823 V. Addition of 5.00 ml of a standard solution of fluoride whose concentration is 5.632×10^{-5} mol dm^{-3} to 25.00 ml of the unknown solution caused the potential to change to – 0.1446 V. Calculate the weight percent of fluoride in the sample.
The Nernst equation describes the level of fluoride ions in the solution corresponding to the measured potential is given by

$$E = k - \frac{0.059}{n} \log C_x$$

Where, k is the reference constant potential, E is the measured potential, C_x is the concentration of unknown solution and n is the number of electrons involved in the electrode reaction. Atomic weight of F is 18.998 g mol^{-1}.

(40 marks)

c)

i. Compare and contrast between a battery and a fuel cell
ii. Discus the working principle and recharging of lead acid battery.
iii. Give three strategies a battery designer can use to obtain a large positive E_{cell} for a battery
iv. Discuss the reactions in a proton exchange fuel cell. Derive an expression for maximum possible energy conversion efficiency of a fuel cell.

(40 marks)

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