

CHEM F327: ELECTROCHEM FUNDA & APPL
Time: 90 mins.

(Closed Book)

Max. Marks: 50
Date: 07.10.2015

Instructions to the students:

1. There are **three questions** in all. Attempt all the questions.
2. Start answering each question on a fresh page. **Answer all parts of a question together.**
3. Write brief answers to the point with proper justifications.
4. Do not exchange your calculator.
5. Given that, $E_{\text{AgBr/Ag}}^0 = 0.07$, $E_{\text{Br}^-/\text{Br}_2}^0 = -0.62$, and $E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.76$ V vs. NHE.

Q. 1. a. Justify your answer, "oxidation and reduction current occur due to the flow of electron between electrode and electrochemical solution". [4]

Q. 1. b. Consider each of the following electrode-solution interfaces, and write the equation for the **electrode reactions** that occurs first when the potential is moved in (1) a negative direction, (2) a positive direction, and (3) at zero potential from the open-circuit potential. Draw the expected i - E curve for the same electrochemical cell. Pt / H⁺, Br⁻ (1 M) / AgBr / Ag [5+2]

Q. 1. c. Suppose a mercury pool of 1 cm² area is immersed in a 0.1 M sodium perchlorate solution. Assume 10 C charge is required to change its potential by 1 mV. What would be the value of capacitance (C) and charge density (σ) when the electrolyte concentration changed to 0.01 M? [2+2]

Q. 2. a. What are the anodic and cathodic reactions in the following cell systems (assume all systems are in aqueous) [2+2]

(i) Pt / H₂ (1 atm) / H⁺, Cl⁻ (0.1 M) // H⁺, Cl⁻ (0.1 M) / O₂ (0.2 atm) / Pt

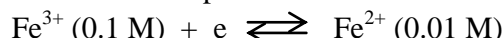
(ii) Pt / H₂ (1 atm) / Na⁺, OH⁻ (0.1 M) // Na⁺, OH⁻ (0.1 M) / O₂ (0.2 atm) / Pt

Q. 2. b. Devise an electrochemical cell for the following chemical reaction (write anode and cathode reactions separately). (i) $\text{Pb} + 2\text{H}^+ + \text{BQ} \rightleftharpoons \text{Pb}^{2+} + \text{H}_2\text{Q}$ (aqueous, where BQ is *p*-benzoquinone and H₂Q is *p*-hydroquinone) [3]

Q. 2. c. The following electrochemical cell is given with $E_{\text{Hg}_2\text{Cl}_2/\text{Hg}}^0 = 0.122$ V vs. NHE. Calculate the cell potential and equilibrium constant (k_{rx}) for cathode (E_{r}) reaction at 298 K?

Hg / Hg₂Cl₂ / K⁺, Cl⁻ (1 M) // K⁺, Cl⁻ (0.1 M) / Hg₂Cl₂ / Hg [3]

Q. 2. d. Define formal potential. Calculate formal potential for the following half reaction at 298 K. [1+2]



Q. 2. e. At equilibrium, derive an expression for cell potential (E_{cell}) for the following electrochemical cell.

(Hint: start with the idea of electrochemical potential) Cu/Zn/Zn²⁺, Cl⁻/AgCl/Ag/Cu' [4]

Q. 2. f. Why liquid junction potential (LJP) is required in an electrochemical cell? Sketch the movement of cation and anion in a LJP when "two solutions at the same concentration with different electrolytes having an ion in common". [1+2]

Q. 3. a. For one-step one-electron process, $\text{O} + ne \rightleftharpoons \text{R}$, the current-overpotential equation is as follows:

$$i = i_0 \left[\frac{C_{\text{O}}(0, t)}{C_{\text{O}}^*} e^{-\alpha f \eta} - \frac{C_{\text{R}}(0, t)}{C_{\text{R}}^*} e^{(1-\alpha) f \eta} \right]$$

Answer the following questions:

- (1) Write down the cathodic and anodic contribution in the above (i - η) equation. (2) Draw the probable i/i_0 vs. η curve and identify the cathodic and anodic component. (3) What would be the approximated form of i - η equation when the overpotential (η) is very large. [1+2+3]

Q. 3. b. Define outer-sphere electron transfer mechanism and sketch the nature of inner-sphere and outer-sphere electron transfer on electrode surface. [1+2]

Q. 3. c. A general expression for the current as a function of overpotential (η), including mass-transfer effects, can be obtained from, $\frac{i}{i_0} = \left(1 - \frac{i}{i_{l,c}}\right)e^{-\alpha f\eta} - \left(1 - \frac{i}{i_{l,a}}\right)e^{(1-\alpha)f\eta}$ and yields [4+2]

$$i = \frac{\exp[-\alpha f\eta] - \exp[(1-\alpha)f\eta]}{\frac{1}{i_0} + \frac{\exp[-\alpha f\eta]}{i_{l,c}} - \frac{\exp[(1-\alpha)f\eta]}{i_{l,a}}}$$

(i) Derive this expression. (ii) Draw $\log |j|$ vs. η curves for currents up to $100 \mu\text{A}/\text{cm}^2$ anodic and cathodic. Assume, $C_R^* = C_O^* = 0.1 \text{ mM}$, $k^0 = 10^{-3} \text{ cm/s}$, $\alpha = 0.5$, $n = 1$, and neglect mass-transfer effects.

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