Birla Institute of Technology and Science, Pilani, Rajasthan 333031
Mid Term Examination 1st Semester, 2015-2016

CHEM F327: ELECTROCHEM FUNDA & APPL **(Closed Book)** **Max. Marks: 50**
Time: 90 mins. **Date: 07.10.2015**

<u>Instructions to the students</u>:

1. There are **three questions** in all. Attempt all the questions.
2. Start answering each question on a fresh page. **<u>Answer all parts of a question together</u>.**
3. Write brief answers to the point with proper justifications.
4. Do not exchange your calculator.
5. Given that, $E^0_{AgBr/Ag} = 0.07$, $E^0_{Br-/Br2} = -0.62$, and $E_{Fe3+/Fe2+} = 0.76$ 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 cm^2 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 / H_2 (1 atm) / H^+ , Cl^- (0.1 M) // H^+ , Cl^- (0.1 M) / O_2 (0.2 atm) / Pt

(ii) Pt / H_2 (1 atm) / Na^+ , OH^- (0.1 M) // Na^+ , OH^- (0.1 M) / O_2 (0.2 atm) / Pt

Q. 2. b. Devise an electrochemical cell for the following chemical reaction (write anode and cathode reactions separately). (i) $Pb + 2H^+ + BQ \rightleftharpoons Pb^{2+} + H_2Q$ (aqueous, where BQ is *p*-benzoquinone and H_2Q is *p*-hydroquinone) **[3]**

Q. 2. c. The following electrochemical cell is given with $E^0_{Hg2Cl2/Hg} = 0.122$ V *vs.* NHE. Calculate the cell potential and equilibrium constant (k_{rx}) for cathode (E_r) reaction at 298 K?

Hg / Hg_2Cl_2 / K+ , Cl- (1 M) // K+ , Cl- (0.1 M) / Hg_2Cl_2 / Hg **[3]**

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

$$Fe^{3+}\ (0.1\ M) + e \rightleftharpoons Fe^{2+}\ (0.01\ M)$$

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/Zn^{2+} , 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, $O + ne \rightleftharpoons R$, the current-overpotential equation is as follows:

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

Answer the following questions:

(1) Write down the cathodic and anodic contribution in the above *(i-η)* equation. (2) Draw the probable i/i_l *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 $\mu A/cm^2$ anodic and cathodic. Assume, $C_R^* = C_O^* = 0.1$ mM, $k^0 = 10^{-3}$ cm/s, $\alpha = 0.5$, n = 1, and neglect mass-transfer effects.

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