Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031

I Semester 2017-2018

CHEM F327 **Electrochemistry: Fundamentals and Applications**

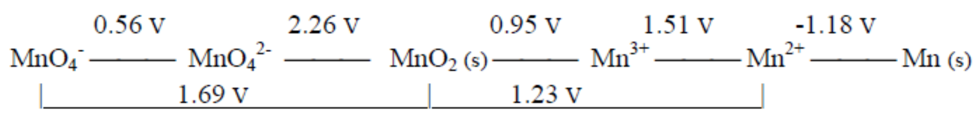
Mid-Semester Examination (Closed Book)

Max. Marks: 90 **Duration: 90 minutes** **Date: 12th October 2017**

NOTE: There are NINE questions in all. Attempt all the questions. Start answering each question on a fresh page and answer all parts of the question together. Pencil should not be used. Symbols have usual meanings. Do not scribble on the question paper.

Useful Data: 1F = 96485 C mol^{-1}; R = 8.314 J K^{-1} mol^{-1}; Standard Reduction Potential in Aqueous Solution at 25°C in V *vs.* NHE: $PbSO_4$/Pb = -0.3505; $PbO_2/PbSO_4$ = 1.697; Ag^+/Ag: 0.7991; Ag/AgI/I^-: -0.1522.

Q. 1 The latimer diagram for manganese in acidic solution is given below at 25°C. Find the standard reduction potential for the reduction of permanganate ion, MnO_4^- to Mn^{2+}. **[8]**



Q. 2 (i) Devise electrochemical cells in which the following reactions could be made to occur. **(ii)** Write the half reactions take place at the electrodes? **(iii)** Determine the standard cell potential. **(iv)** Specify the negative electrode. **(v)** Comment on whether the cell would operate electrolytically or galvanically in carrying out net reaction from left to right. **[4+4+2+2+2]**

(a) $2PbSO_4 + 2H_2O \rightleftharpoons PbO_2 + Pb + 4H^+ + 2SO_4^{2-}$

(b) $Ag^+ + I^- \rightleftharpoons AgI$ (Aqueous)

Q. 3 Consider the cell: Cu/M/Fe^{2+}, Fe^{3+}, H^+//Cl^-/AgCl/Ag/Cu'

(i) Write the half reactions and net reaction. **(ii)** When the cell is open circuit, write all the equilibrium reactions. **(iii)** Use electrochemical potentials to determine whether the cell potential will be dependent on the identity of M; where M is chemically inert. **[3+5+4]**

Q. 4 (i) What is liquid junction potential? **(ii)** What are the classifications in liquid junction? [Show the types of liquid junction with proper schematic diagram] **(iii)** Explain a method to reduce the liquid junction potential with justification. **[3+6+3]**

Q. 5 The exchange current density, j_0, for Pt/$Fe(CN)_6^{3-}$ (2 mM), $Fe(CN)_6^{4-}$ (2 mM), NaCl (1M) at 25°C is 2mA/cm^2. The transfer coefficient, α, for this system is 0.50. Calculate **(i)** k^0; **(ii)** j_0 for a solution 1M each in two complexes; **(iii)** charge transfer resistance of a 0.1cm^2 electrode in a solution 10^{-4} M each in ferricyanide and ferrocyanide. **[3+2+4]**

Q.6 The current-overpotential equation is given by i = $i = i_0[\frac{C_0(0,t)}{C_0^*} e^{-\frac{\alpha F \eta}{RT}} - \frac{C_R(0,t)}{C_R^*} e^{\frac{(1-\alpha) F \eta}{RT}}]$, where η = overpotential, α = Transfer coefficient. **(i)** Write down the approximate form of i-η equation when no mass-transfer effects are present. **(ii)** Draw a qualitative plot of approximate i-η equation (i *vs* η), **(a)** when the exchange current is very large and **(b)** when the exchange current is very small. (Consider α =0.5) and justify the behavior of i-η behavior on exchange current. **(iii)** Starting from the approximate form of i-η equation, justify the conditions required to reach the relation of Tafel form. **(iv)** Derive the Tafel relation for negative potentials. **[2+6+2+3]**

Q. 7 (i) Define inner sphere electrode reaction and outer sphere electrode reaction. **(ii)** For an outer-sphere, single electron transfer from electrode to species O to form the product R, the activation energy is given by $\frac{\lambda}{4}\left(1 + \frac{F(E-E^0)}{\lambda}\right)^2$. Explain the physical interpretation of λ. Derive the expression of transfer coefficient, α, from this equation. **[4+4]**

Q. 8 Define the three modes of mass transfer from one location to another in an electrochemical cell. **[6]**

Q.9 (i) Define Transference number and Mobility. **(ii)** Write the relationship between **(a)** transference number and Conductance and **(b)** Transference number and mobility. **[4+4]**

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