Potential Step and Polarography Problem Set

Turn in Problems 3, 5, & 7 by Friday, February 20, 2004

1] Solve Fick's 2nd Law of Diffusion for a spherical electrode. From B+F Chapter 5 we have:

$$\frac{\partial C_0(r,t)}{\partial t} = D_0\left(\frac{\partial^2 C_0(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C_0(r,t)}{\partial r}\right)$$

Consider the initial conditions of $C_o(r = r_0, t = 0) = C_o^*$ r_0 = radius of electrode

Boundary conditions $\lim r \rightarrow \infty\ C_o(r,t) = C_o^*$ & $C_o(r = r_0, t > 0) = 0$

Hint: To solve let $v = rC_0$ and rewrite F.S.L. in a liner form (in v). Use reverse substitution to find α and β Laplace constants.

Answer: $i = nFAD_oC_o^* (1/(\pi D_o t)^{1/2} + 1/r_0)$

2] Do problem 5.6 (1980 & 2001 editions) of B+F

3] The concentration of Fe^{3+} ($Fe^{3+} + 3e^- \rightarrow Fe(Hg)$) in a sample of tap water was determined by polarography. The diffusion current in a 10 ml sample was 0.15 μA. After the addition of a 0.5 mM spike of 1.00 ml to the sample the diffusion current was measured 0.30 μA. What is the concentration of ferric ion in the sample? Answer = 4.17e-5 M

4] The following data were obtained from the polarographic analyses of standard Pb^{2+} solutions.

Pb^{2+} mM	i_d uA
0.0	1.32
0.510	5.65
1.02	10.70
2.04	19.08
3.06	27.91
4.08	36.08
5.10	45.82

Two aqueous samples from the Silver Valley area were analyzed and gave id of 7.75 and 40.01 uA respectively. What are the Pb^{2+} concentrations in these samples? Ans = 0.878 mM; 4.62 mM.

5] The Hg flow rate and drop lifetimes were 2.63 mg/s and 2.88 s respectively for the problem above. What is the diffusion coefficient of Pb^{2+}? Ans = 9.8e-6 cm^2/s

6] The following polarographic data were obtained for the reduction of a 2.00e-3 M Pb^{2+}, 0.100 KNO_3 solution and a complexing agent A. From the data below derive the formula and the formation constant of the lead complex.

[A], M	$E_{1/2}$ vs. SCE, V
0.000	-0.405
0.020	-0.473
0.060	-0.507
0.101	-0.516
0.300	-0.547
0.500	-0.558

7] We have mentioned the concept of an analytical microelectrode in lecture. This problem gets that point across. A diffusion current for the reduction of Cd^{2+} is measured as 14 uA. The solution contains 25 ml of 0.50 mM Cd^{2+} and the total analysis time was 3.4 minutes.

a) Calculate the fraction of Cd^{2+} reduced per minute of i_d passage.
b) What is the percentage change in Cd^{2+} concentration after the analysis?