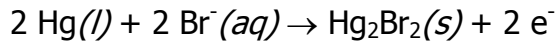


CHEM 221
Instrumental Analysis
Problem Set #2 – Solutions
Spring 2005

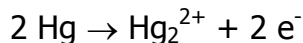
Chapter 25

#11. At $\sim +0.1$ volts, Hg reacts with Br^- :



Since this reaction depends upon Br^- , i_d should vary with $[\text{Br}^-]$ and could be used for the determination of Br^- in solutions.

At $\sim +0.5$ volts, Hg is *oxidized*:



#13. Stripping methods effectively concentrate analyte from a large volume of solution into a tiny electrode, giving large currents when finally oxidized or reduced from the small volume of the electrode. Thus, the sensitivity is much better than that obtained by *directly* oxidizing or reducing dilute analyte in solution.

Additional Problems

#1. Recall that: Amperes = Coulombs/sec

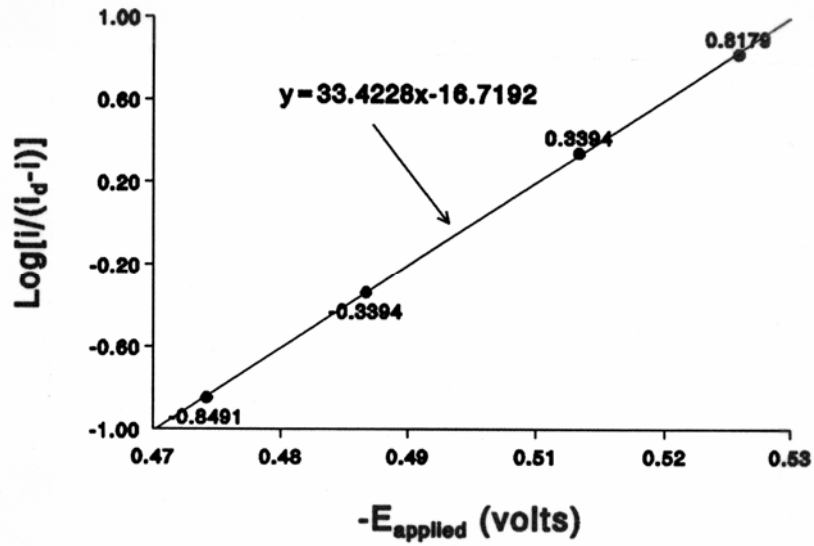
$$\# \text{Coulombs} = \frac{4.0 \times 10^{-6} \text{ C}}{\text{sec}} \times \frac{60 \text{ secs}}{\text{min}} \times 30 \text{ min} = 7.20 \times 10^{-3} \text{ C}$$

$$7.20 \times 10^{-3} \text{ C} \times \frac{\text{equiv. Cd}^{2+}}{96,485.31 \text{ C}} \times \frac{1 \text{ mol Cd}^{2+}}{2 \text{ equiv}} = 3.731 \times 10^{-8} \text{ mol Cd}^{2+} \text{ (electrolyzed)}$$

$$\text{mol Cd}^{2+} \text{ in solution: } 0.050 \text{ L} \times \frac{0.50 \times 10^{-3} \text{ mol Cd}^{2+}}{\text{L}} = 2.50 \times 10^{-5} \text{ mol Cd}^{2+} \text{ (initial)}$$

$$\% \text{ electrolyzed} = \frac{3.731 \times 10^{-8} \text{ mol}}{2.50 \times 10^{-5} \text{ mol}} \times 100 = \underline{\underline{0.15\%}}$$

#2. Plot: $\text{Log}(i/(i_d - I))$ versus $-E_{\text{appl}}$



- Linear plot: *reversible process*
- Slope = $n/0.059 = 33.42$
- **$n = 2$**
- $E_{1/2} = E_{\text{appl}} @ 1/2 i_d$
Solve straight line equation for x when $y = 0$

$$E_{\text{appl}} = -x = \underline{\underline{-0.500 \text{ volts} = E_{1/2}}}$$