CHEMISTRY 447 **Problem Set #2** M. E. Meyerhoff

1. The same medical technologist, who on the last exam had so much trouble measuring potassium by flame emission (she obviously never took Chem 447!) was asked by a doctor to determine the total carbon dioxide content of a particular blood sample. She used a conventional Severinghaus type potentiometric CO_2 sensor, but didn't understand how it worked. Explain, via appropriate diagrams, equations, etc. how this device operates. (10)

2. Consider the following galvanic cell:

$$Pt/Cr^{+3}(0.3M),\ Cr^{+2}(0.01M)/(AgCl(s),\ Cl^{-}(0.025\ M)/Ag$$

Neglecting changes in liquid junction potentials, what would be the qualitative effect of each of the following actions on the overall cell potential, E_{cell} (increase, decrease, remains the same) (10)

a) addition of 10 g of solid AgCl to right half cell (K_{sp} of AgCl = 1.78×10^{-10}).

b) dissolution of 10 g of NaCl in right half cell

c) addition of 10 ml of water to left half cell.

d) addition of soluble Cr^{+3} salt to left hand cell.

e) dissolution of some silver nitrate in right half cell.

3. Suppose you were performing an amperometric titration to determine the copper content of some industrial water sample. If you titrated with a 0.1M solution of sodium sulfide, plot the current vs. ml titrant you would expect to observe. Assume you were using a micro-platinum working electrode in a 3 electrode potentiostat arrangement and E_{appl} was ample to reduce copper. (5)

4. (a) The same medical technologist at the Univ. of Michigan Hospital who had such a difficult time of late explaining her analytical results, was given another problem to solve. She was asked to determine the potassium content in a patient's blood sample using a liquid membrane type ion-selective electrode (ISE) for potassium. The technician used his/her electrode in conjunction with a Ag/AgCl reference electrode and a high input impedance with meter. The electrochemical cell for this analytical system may be represented as follows:

Ag/AgCl(s), KCl(0.1M)// sample soln. / organic liquid membrane / internal ref. soln. , AgCl(s)/Ag

If the internal reference solution of the K^{+}-ISE contained 0.1M KCl and the potential of the cell was measured as $E_{ISE}-E_{ref}$, what would be the cell potential measured when the technician placed the electrode into a blood sample containing $1 \times 10^{-3}M\ K^{+}$. Neglect liquid junction potentials and assume unit activity coefficients. Show all work (E° for Ag/AgCl = 0.222V) (10)

(b) Describe and name the compound in the membrane that makes the electrode selective for potassium. What factor determines the selectivity of this electrode over other mono- and divalent cations? (5)

(c) Suppose the same K^+-ISE was being used to directly determine K^+ in the presence of Cs^+. Unfortunately, the electrode is not very selective for K^+ over Cs^+ with a selectivity coeff. of $k_{K^+/Cs^+} = 0.4$. If the sample to be measured contained 1×10^{-3}M K^+ and 2×10^{-4}M Cs^+, what would be the % error in the potassium value measured? (5)

5. (a) The following membrane electrode-galvanic cell was used to determine calcium ions in solution:

Ag | AgCl, Cl^-(a=1M) ‖ sample $a_{Ca^{++}}$ = .001M | Ion-selective membrane for Ca^{++} | Internal reference soln., AgCl(s) | Ag

The internal solution was 0.1M with respect to both Ca^{++} and Cl^- activities. E° for the Ag/AgCl couple is 0.222V. What would be the measured potential for this cell when hooked up to a high input impedance pH/mV meter? Assume that the anode, as written, is the reference electrode and that the pH meter gives $E_{cell} = E_w - E_{ref}$. Also neglect liquid junction potentials and show work. (15)

b) What type of compound is used within the membrane of the calcium electrode to mak it selective for Ca^{++} ? (5)

6. a) Sketch a typical pulse polarogram for a mixture of Pb^{++} and Cd^{++} ($E_{1/2}$ for Pb^{++} ≈ -0.45V and for Cd^{++} ≈ -0.65V). Assume that the solution is adequately degassed. Appropriately label the various portions of the trace. (8)

b) Explain the reasons why mercury electrodes are so widely used in voltammetric techniques. (5)

c) There are two types of processes which give rise to measureable polarographic currents at a dropping mercury electrode (DME). What are these processes and describe how pulse potential techniques can discriminate one current type from the other and consequently improve detection limits. Use appropriate figures, equations, etc. (12)