Chem 310

6th Homework Set

Due Date: Mar. 11, 2004

Use the following data when appropriate: $E_{SCE} = +0.241$ V; $E_{Ag/AgCl} = +0.199$ V. An extensive table of standard potentials is in Appendix H of Harris (pp. AP23-31).

1. Harris, Problem 14-8.

2. Harris, Problem 14-9. Which electrode is the anode and which electrode is the cathode?

3. Harris, Problem 14-20, part (a) only. Calculate each half-cell potential using the Nernst equation.

4. Sketch (a) a SCE and (b) a Ag/AgCl reference electrode. Label the parts. Indicate the site of the liquid junction potential.

5. The standard potential of the $Cr^{2+/3+}$ half-reaction is -0.408 V. Convert this potential to V vs SCE.

6. What are the advantages and disadvantages of potentiometry?

7. A chloride ISE and a SCE were used to obtain a calibration curve and to determine Cl^- in a sample. Using a spreadsheet, plot the data as ΔE vs log($[Cl^-]$) and fit it to a linear regression line. Attach the plot to your homework. Analyze the data to determine (a) the slope S and its standard deviation, (b) the calibration constant K and its standard deviation, and (c) the molar concentration of Cl^- in the sample.

$[Cl^-]$	ΔE
2.0×10^{-2} M	-73 mV
2.0×10^{-3} M	-19 mV
2.0×10^{-4} M	$+38$ mV
$[Cl^-]$?	$+10$ mV

8. A Mg ISE and a SCE were immersed in a standard containing 2.0×10^{-4} M Mg^{2+}. The cell potential was +0.2714 V. The two electrodes were then rinsed and transferred to a sample; the cell potential was +0.2837 V. Calculate the concentration of Mg^{2+} assuming that the Mg ISE has an ideal slope of 0.02958 V.

9. A Ca^{2+} liquid membrane ISE and a Ag/AgCl reference electrode were immersed in 25.0 mL of solution containing an unknown concentration of Ca^{2+}. The cell voltage was +0.4965 V. Without removing the electrodes, 10.0 mL of $5.0\text{x}10^{-2}$ M Ca^{2+} was added to the solution and mixed. The new cell voltage was +0.5023 V. Assuming that the Ca ISE has an ideal slope of 0.02958 V, calculate the original Ca^{2+} concentration.

10. (a) The cell (SCE ** Ag^+ * Ag) was found to have a potential of +0.485 V. Calculate both the concentration and pAg in the cell given:

$$Ag^+ + e^- \rightleftharpoons Ag \quad E^o = +0.799 \text{ V}$$

(b) If the uncertainty (error) in the cell voltage was ±2 mV, what is the uncertainty (error) in the concentration of silver ion?

11. (a) The cell (Ag/AgCl ref ** SO_4^{2-}, $PbSO_4$(s) * Pb) was found to have a potential of −0.583 V. Calculate the concentration of SO_4^{2-} in the cell given:

$$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-} \qquad E^o = -0.350 \text{ V}.$$

(b) If the uncertainty (error) in the cell voltage was ±2 mV, what is the uncertainty (error) in the concentration of sulfate?

12. What is the role of the membrane in an ion selective electrode?

13. What is the origin of alkaline error in a pH electrode? What is its effect on the pH reading?

14. A pH combination electrode was found to have a cell potential of −0.0214 V in pH 6.865 standard phosphate buffer. An unknown solution yielded a cell potential of −0.1376 V.
(a) Assuming ideal behavior, calculate the pH of the unknown solution.

(b) If the liquid junction potential introduces a minimum error of ±0.002 V in the potential readings, calculate the uncertainty in the pH.