Chemistry 222 **Name**_____
Spring 2011 **80 Points**
Exam 4

Complete five (5) of the following problems. Each problem is worth 16 points. CLEARLY mark the problems you do not want graded. You must show your work to receive credit for problems requiring math. Report your answers with the appropriate number of significant figures. You do not need to account for activities in your calculations.

1. Consider the EDTA titration below:

$$Zn^{2+} + Y^{4-} = ZnY^{2-} \qquad K_f = 3.2 \times 10^{16}$$

   a. How many mL of 0.1050 M EDTA solution are required to reach the equivalence point in the titration of 20.00 mL of 0.1433 M Zn^{2+}, buffered at pH 10.00? (α_{Y4-} = 0.36 at pH 10.00) (4 points)

   b. What is the pZn at the equivalence point? (8 points)

   c. How many mL of EDTA solution would have been needed if the analyte solution was 20.00 mL of 0.1433 M Fe^{3+} instead of 20.00 mL of 0.1433 M Zn^{2+}? (4 points)

2. Consider the electrochemical cell below:

$$Pt(s)|\ Br_2(\ell)\ |\ HBr\ (aq,\ 0.0100\ M)\ ||\ Al(NO_3)_3\ (aq,\ 0.100\ M)\ |\ Al(s)$$

Reaction (all species are aqueous unless noted)	**E^o (volts)**
$Br_2\ (aq) + 2e^- = 2Br^-$	+1.098
$Br_2\ (\ell) + 2e^- = 2Br^-$	+1.078
$NO_3^- + 4H^+ + 3e- = NO\ (g) + 2H_2O$	+0.955
$AgCl + e^- = Ag(s) + Cl^-$	+0.199 (sat'd KCl)
$2H^+ + 2e^- = H_2(g)$	0.000
$Al^{3+} + 3e^- = Al(s)$	-1.677

a. Calculate E_{cell} for the conditions given. (8 points)

b. Is the reaction spontaneous in the direction written in part a? How do you know? (2 points)

c. Calculate the standard free energy change (ΔG^o) and the free energy change (ΔG) for the conditions given. (3 points)

d. Is the reaction more favorable under standard conditions, or with the conditions given? How do you know? (3 points)

3. Define the following terms. Include the symbol commonly used to represent each term.
   a. Retention time:

   b. Adjusted retention time:

   c. Dead time:

   d. Retention factor:

   e. Selectivity factor:

4. Calculate the pAg^+ at **any two** of the following points in the titration of 50.00 mL of 0.00100 M Ag^+ with 0.00100 M EDTA at pH 11.00. Select from 0.00 mL, 33.0 0 mL, 50.00 mL, 55.00 mL titrant added. For the Ag/EDTA complex, log K_f = 7.32

5. You are conducting a gas chromatography experiment and have collected the data below. The first three samples are pure compounds, while the third is a mixture of unknown composition. All samples were run under the same conditions. Given this data, what can you say about the composition of the mixture?

Sample	Number of peaks	Retention time(s) (min)
A	1	1.45
B	1	5.62
C	1	10.04
Mixture	3	0.76, 5.58, 7.29

6. Outline an experiment for the determination of Ca^{2+} using a calcium ion-selective electrode. If the suspected [Ca^{2+}] is ~0.0030 M, describe (qualitatively) how you would prepare a calibration curve given a standard solution of Ca^{2+} (~ 1.0 M)? Assume you have a well-stocked laboratory and a collection of salts, acids, and bases to work with. Sketch (qualitatively) how the calibration curve should appear. Include an estimate of the slope you would expect.

Possibly Useful Information

$E = E^o - \frac{2.303RT}{nF}\log Q = E^o - \frac{0.05916V}{n}\log Q$	$\Delta G^o = -nFE^o = -RT\ln K$
$F = 96485\ C\ mol^{-1}$	$R = 8.31441\ Jmol^{-1}K^{-1}$
$E = const. + \beta\left(\frac{0.05916V}{n}\right)\log A_{ion}$	$R_S = \frac{2\Delta Z}{W_A + W_B} = \frac{\sqrt{N}}{4}\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k_B}{1+k_B}\right)$
$\alpha = \frac{K_A}{K_B} = \frac{k_A}{k_B}$	$k_A = \frac{t_R - t_M}{t_M}$

Values of α_{y4-} for EDTA at 20°C and μ = 0.10 M

pH	α_{y4-}	pH	α_{y4-}	pH	α_{y4-}
0	1.3×10^{-23}	5	3.7×10^{-7}	10	0.36
1	1.9×10^{-18}	6	2.3×10^{-5}	11	0.85
2	3.3×10^{-14}	7	5.0×10^{-4}	12	0.98
3	2.6×10^{-11}	8	5.6×10^{-3}	13	1.00
4	3.8×10^{-9}	9	5.4×10^{-2}	14	1.00