Chemistry 222 **Name**_____
Exam 4: Chapters 11, 13, 14 **Spring 2014**
80 Points

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.

1. 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 33.00 mL, 50.00 mL, 55.00 mL titrant added. For the AgY^{3-} complex, log K_f = 7.32

2. A 50.0 mL sample containing Cd^{2+} and Mn^{2+} was treated with 56.5 mL of 0.0600 M EDTA. Titration of the excess unreacted EDTA required 10.0 mL of 0.0170 M Ca^{2+}. The Cd^{2+} was displaced from EDTA by the addition of an excess of CN^{-}. Titration of the newly freed EDTA required 26.0 mL of 0.0170 M Ca^{2+}. What were the molarities of Cd^{2+} and Mn^{2+} in the original solution?

3. 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.

4. At 25°C, you conduct a titration of 15.00 mL of a 0.0400 M $AgNO_3$ solution with a 0.0200 M NaI solution within the following electrochemical cell:

   Saturated Calomel Electrode || Titration Solution | Ag (s)

   For the cell as written, what is the voltage after the addition of 35.23 mL of NaI solution? The reduction potential for the saturated calomel electrode is E = + 0.241 V. The standard reduction potential for the reaction

   $$Ag^+ + e^- \rightarrow Ag(s)$$

   is E^0 = +0.79993 V. The solubility constant of AgI is $K_{sp} = 8.3 \times 10^{-17}$.

5. Consider the electrochemical cell below:

$Pt|Ce^{4+}(0.100\ M), Ce^{3+}(0.0100\ M)||MnO_4^-(0.100\ M), Mn^{2+}(0.00100\ M), HClO_4(??\ M)|Pt$

Reaction (all species are aqueous unless noted)	**E^o (volts)**
$Ce^{4+} + e^- = Ce^{3+}$	+1.700
$Ce^{3+} + 3e^- = Ce(s)$	-2.336
$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$	+1.507
$MnO_4^- + 4H^+ + 3e^- = MnO_2(s) + 2H_2O$	+1.692
$MnO_2(s) + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	+1.230

a. Write the cell reaction described by this notation (in the appropriate direction). (5 points)

b. A voltmeter is used to measure the potential of this cell, using standard convention for assigning the anode and cathode. If E_{cell} is measured to be -0.414 V, what is the pH of the manganese solution? (8 points)

c. Is the reaction spontaneous under *standard conditions* in the direction written in part a? How do you know? (3 points)

6. 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)

Possibly Useful Information

$K_w = 1.0 \times 10^{14} = [H^+][OH^-]$	$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
$E = E^o - \frac{2.303RT}{nF}\log Q = E^o - \frac{0.05916V}{n}\log Q$	$\Delta G^o = -nFE^o = -RT\ln K$
$F = 96485\ C\ mol^{-1}$	$R = 8.31441\ Jmol^{-1}K^{-1}$
$E = const. + \beta\left(\frac{0.05916V}{n}\right)\log A_{ion}$	$y = mx + b$, $m = \frac{\Delta y}{\Delta x}$

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