Chemistry 222 **Name**_____
Exam 4: Chapters 11, 13, 14 **Spring 2016**
80 Points

Bonus (5 points):
Monday, Dr. Lamp wrote a potential on the board at 8:30 AM as he started class and said that the potential would be an answer to one of the exam 4 questions. What potential did he put on the board?

Complete five (5) of the following problems. Each problem is worth 16 points. CLEARLY mark the problem 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. 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.

2. A 50.0 mL sample containing $Cd^{2+}$and Mn^{2+} was treated with 70.0 mL of 0.0500 M EDTA. Titration of the excess unreacted EDTA required 18.5 mL of 0.0200 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 13.1 mL of 0.0200 M Ca^{2+}.
   (a) What were the molarities of Cd^{2+} and Mn^{2+} in the original solution? (12 points)

   (b) For this analysis to be successful, what must be true about the relative sizes of the formation constants for the Cd-EDTA and Mn-EDTA complexes compared to the formation constant for Ca-EDTA? (4 points)

3. Given your unnatural passion for analytical chemistry, you have been given the task of explaining to a new quant student, Irma Dorque, the fundamentals of pH measurement with a pH electrode.
   (a) Briefly describe the key components of a pH electrode and how it functions. (10 points)

   (b) Identify at least three potential problems that may occur when making a pH measurement and how to avoid them. (6 points)

4. Consider a solution containing 1.0 M $Pb(NO_3)_4$, 1.0 M $Pb(NO_3)_2$, 1.0 M $KMnO_4$, 1.0 M $Mn(NO_3)_2$ and 1.0 M HNO_3. For this solution, the following unbalanced reduction half-reactions occur.

$$MnO_4^- \rightleftharpoons Mn^{2+} \qquad E^o = +1.507\ V$$

$$Pb^{4+} \rightleftharpoons Pb^{2+} \qquad E^o = +1.690\ V$$

(a) Write the balanced reaction that occurs spontaneously in this solution. (6 points)

(b) What is the E^o for the reaction. (4 points)

(c) What is the cell potential for the reaction if the solution is instead 0.15 M $Pb(NO_3)_2$, 1.5×10^{-6} M $Pb(NO_3)_4$, 1.5×10^{-6} M $Mn(NO_3)_2$, 0.15 M M $KMnO_4$, and 0.83 M HNO_3? Is this more spontaneous or less spontaneous than under standard condition s? (6 points)

5. (a) Calculate pCa^{2+} at **TWO** of the following points in the titration of 50.00 mL of 0.0400 M Ca^{2+} with 0.0800 M EDTA at a pH 10.00: (for Ca-EDTA, log K_f = 10.65) (12 points)
    - At the equivalence point
    - 10.00 mL prior to the equivalence point
    - 10.00 mL after the equivalence point

(b) How would the volume at the equivalence point compare if you had titrated 0.0400 M Al^{3+} instead of Ca^{2+}? (6 points)

6. Calculate the equilibrium constant for the reaction shown below using standard reduction potentials from the table.

$$2\ Fe^{3+} + 3\ I^- = 2\ Fe^{2+} + I_3^-$$

Reaction	Standard Reduction Potential
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771 V
$Fe^{2+} + 2e^- \rightleftharpoons Fe(s)$	-0.440 V
$I_2(s) + 2e^- \rightleftharpoons 2I^-$	+0.535 V
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+0.535 V

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