Chemistry 222 **Name**____
Exam 4: Chapters 11, 13, 14, a little separations **Spring 2021**
80 Points

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 as well as a voltmeter and reference electrode. 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+}. You may assume that each of the titration reactions goes to completion.
   (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 reduction half-reactions occur.

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \qquad E^o = +1.507\text{ V}$$

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

(a) Write the balanced reaction that occurs spontaneously in this solution. (4 points)

(b) What is the E° 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 conditions? (8 points)

5. (a) Calculate pCa^{2+} at **<u>TWO</u>** 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+}? (4 points)

6. Answer each of the following regarding chromatography. Two or three sentences per answer should be sufficient: (4 points each)
   a. Why is it important for sample to be introduced to the separation column in as narrow of a "plug" as possible?

   b. Why is longitudinal diffusion a more serious problem in gas chromatography than in liquid chromatography?

   c. Consider liquid chromatography with a packed column. Why does plate height increase and separation efficiency decrease at very low flow rates?

   d. Consider liquid chromatography with a packed column. Why does plate height increase and separation efficiency decrease at very high flow rates?

Possibly Useful Information

$K_w = 1.0 \times 10^{14} = [H^+][OH^-]$	$x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
$E = E^o - \dfrac{2.303RT}{nF}\log Q = E^o - \dfrac{0.05916V}{n}\log Q$	$\Delta G^o = -nFE^o = -RT\ln K$
$F = 96485\ C\ mol^{-1}$	$R = 8.31441\ Jmol^{-1}K^{-1}$
$E = const. + \beta\left(\dfrac{0.05916V}{n}\right)\log A_{ion}$	$y = mx + b\ ,\quad m = \dfrac{\Delta y}{\Delta x}$
$N = L/H$	$H = \dfrac{\sigma^2}{L} = L\left(\dfrac{W}{4t_R}\right)^2$
$N = \left(\dfrac{4t_R}{W}\right)^2 = \left(\dfrac{2.35t_R}{W_{1/2}}\right)^2$	$H \approx A + \dfrac{B}{u} + Cu$

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