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)

$$20.00\ m\cancel{L} \quad \times \quad \frac{0.1433\ \cancel{mol\ Zn^{2+}}}{\cancel{L}} \quad \times \quad \frac{1\ \cancel{mol\ Y^{4-}}}{1\ \cancel{mol\ Zn^{2+}}} \quad = \quad \frac{1\ L}{0.1050\ \cancel{mol\ Y^{4-}}} \quad = \quad \mathbf{27.30\ mL}$$

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

At the equivalence point: $[ZnY^{2-}]$ = (20.00 mL x 0.1433 mol/L)/(47.30 mL) = 0.06059_8 M

	Zn^{2+}	+	Y^{4-}	=	ZnY^{2-}
i	0		0		0.06059
c	+x		+x		-x
e	x		x		0.06059-x

$$K_f' \quad = \quad a_{Y4-}K_f \quad = \quad \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

After plugging in our numbers:

$$K_f' \quad = \quad (0.36)(3.2 \times 10^{16}) \quad = \quad \frac{0.06059-x}{(x)(x)}$$

Solving for x yields $[Zn^{2+}] = 2.29 \times 10^{-9}$M or **pZn = 8.64**

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)

Since EDTA binds with 1:1 stoichiometry with each ion, it should require the same volume of solution to do the Fe titration compared to the Zn titration.

2. Consider the electrochemical cell below:

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

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)

Cathode:	$Al^{3+} + 3e^- = Al(s)$	$E^o = -1.677\ V$
Anode:	$Br_2\ (\ell) + 2e^- = 2Br^-$	$E^o = +1.078\ V$
Cell Rxn:	$6Br^- + 2Al^{3+} = 2Al + 3Br_2$	$E^o = -1.677\ V - 1.078\ V = -2.755\ V$

Nernst equation for each half cell:

$$E_{anode} = +1.078\ V - \frac{0.05916\ V}{2}\log[Br^-]^2 = +1.078\ V - \frac{0.05916\ V}{2}\log[0.0100]^2 = +1.196\ V$$

$$E_{cathode} = -1.677\ V - \frac{0.05916\ V}{3}\log\frac{1}{[Al^{3+}]} = -1.677\ V - \frac{0.05916\ V}{3}\log\frac{1}{[0.100]} = -1.697\ V$$

$$\mathbf{E_{cell} = E_{cathode} - E_{anode} = (-1.697 - 1.196)V = -2.893\ V}$$

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

Since the cell potential is negative, the reaction is not spontaneous.

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

$\Delta G^o = -nFE^o = -(6\ mol\ e^-)(96485\ C/mole)(-2.755\ V) = +1{,}595{,}000\ J =$ **+1,595 kJ**

$\Delta G = -nFE = -(6\ mol\ e^-)(96485\ C/mole)(-2.893\ V) = +1{,}675{,}000\ J =$ **+1,675 kJ**

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

Since E is less negative and ΔG less positive, the reaction is more favorable under standard conditions.

3. Define the following terms. Include the symbol commonly used to represent each term.
   a. Retention time: (t_r), The retention time is the time between injection and the arrival of a component at the detector.

   b. Adjusted retention time: (t_r'), The adjusted retention time is the difference between the retention time and dead time.

   c. Dead time: (t_m), Dead time is the time for an unretained component to reach the detector

   d. Retention factor: (k'), Retention factor is the ratio of the adjusted retention time to the dead time and provides a measure of the tendency of the component to remain on the column.

   e. Selectivity factor: (α), Selectivity factor is the ratio of retention factors (or adjusted retention times) for two components in a separation and provides information of the relative retention of the two components.

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

Because the concentration of Ag^+ and EDTA are the same, it should take 50.00 mL to get to the equivalence point. At any point after the start of the titration, we should consider the following equilibrium: $Ag^+ + Y^{4-} = AgY^{3-}$ $K_f = 10^{7.32} = 2.09 \times 10^7$

0.00 mL: No EDTA has been added, so $[Ag^+] = 0.00100$ M, $pAg^+ = -\log[Ag^+] = 3.00$

33.0 mL: Prior to the equivalence point, therefore some unreacted Ag^+ will remain. Because of this, and because K_f is so large, dissociation of AgY^{3-} will be negligible.

$$33.0\text{ mL mol }Y^{4-} \times \frac{0.00100\text{ mol mol }Y^{4-}}{\text{L}} \times \frac{1\text{ mol }Ag^+}{1\text{ mol }Y^{4-}} = 0\ 0033\text{ mmol }Ag^+\text{consumed}$$

$$[Ag^+] = \frac{(0.0050 - 0.0033)\text{ mmol }Ag^+}{83.0\text{ mL}} = 2.05 \times 10^{-4}\text{ M} \qquad \mathbf{pAg^+ = 3.69}$$

50 mL (equivalence point)

$$[AgY^{3-}] = \frac{(0.0010\text{ M})(50\text{ mL})}{100\text{ mL}} = 5.00 \times 10^{-4}\text{ M}$$

	Ag^+	+	EDTA	=	AgY^{3-}
I	0		0		5.00×10^{-4}
C	+x		+x		-x
E	x		x		5.00×10^{-4} - x

$$K_f' = \alpha_{Y4-} K_f = 0.85\ K_f = \frac{[AgY^{3-}]}{[Ag^+][EDTA]}$$

$$1.78 \times 10^7 = \frac{5.00 \times 10^{-4} - x}{x^2}$$

Solving for x, we find that x = $[Ag^+] = 5.27 \times 10^{-6}$ M, **$pAg^+ = 5.28$**

55 mL (equivalence point)

$$[AgY^{3-}] = \frac{(0.0010\ M)(50\ mL)}{105\ mL} = 4.76 \times 10^{-4}\ M$$

$$[EDTA] = \frac{(0.0010\ M)(5\ mL\ excess)}{105\ mL} = 4.76 \times 10^{-5}\ M$$

	Ag^+	+	EDTA	=	AgY^{3-}
I	0		4.76×10^{-5}		4.76×10^{-4}
C	+x		+x		-x
E	x		$4.76 \times 10^{-5} + x$		$4.76 \times 10^{-4} - x$

$$K_f' = \alpha_{Y4-}K_f = 0.85\ K_f = \frac{[AgY^{3-}]}{[Ag^+][EDTA]}$$

$$1.78 \times 10^{7} = \frac{4.76 \times 10^{-4} - x}{(4.76 \times 10^{-5}+x)(x)}$$

Solving for x, we find that x = $[Ag^+] = 5.54 \times 10^{-7}$ M, **pAg^+ = 6.26**

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

An examination of the retention times of the peaks in the mixture shows that none of the three peaks has similar retention times to compound A or C. This is strong evidence that the mixture does not contain A or C. The fact that the mixture has a peak with retention time close to that of compound B suggests that the mixture may contain B. This is not 100% conclusive because several compounds may share similar retention times. Additional experiments must be done to verify the identity of the “B” peak.

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.

Here are several key points:

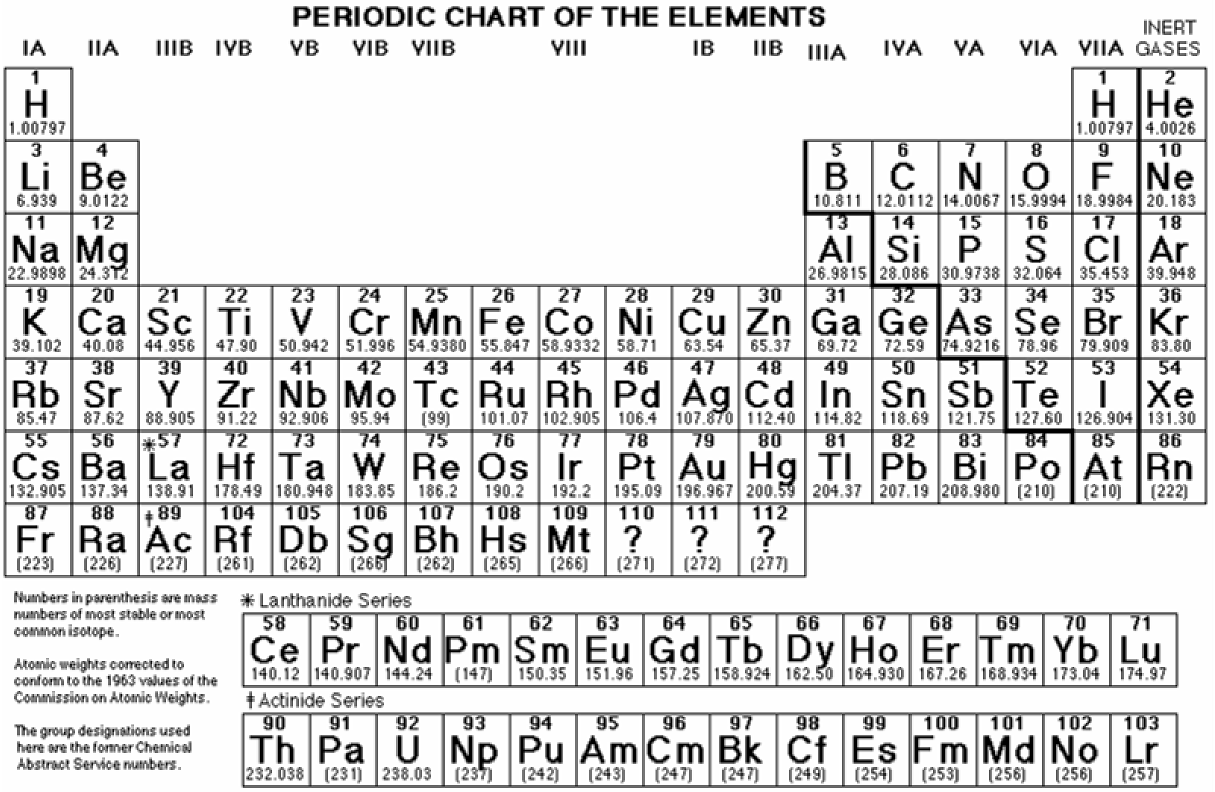
1. Prepare standards of concentrations surrounding 0.0030 M, such as 0.01 M to 0.001 M. Use an inert salt to maintain constant ionic strength.
2. Measure E_{cell} using the calcium ISE and a suitable reference electrode.
3. Plot $\log[Ca^{2+}]$ versus E_{cell}.
4. Slope of calibration plot should be ~0.05916 V/2 or ~0.030 V.
5. Measure E_{cell} for the unknown and calculate an unknown concentration from you r calibration curve.

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



PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES
1 H 1.00797																1 H 1.00797	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	✳57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	‡89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)						

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

✳ Lanthanide Series

58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97

‡ Actinide Series

90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lr (257)