

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,  $\log K_f = 7.32$

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:  
 $Ag^+ + Y^{4-} = AgY^{3-} \quad K_f = 10^{7.32} = 2.09 \times 10^7$

33.0 mL (before equivalence point):

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.

$$33.0 \text{ mL mol } Y^{4-} \times \frac{0.00100 \text{ mol mol } Y^{4-}}{L} \times \frac{1 \text{ mol } Ag^+}{1 \text{ mol } Y^{4-}} = 0.0033 \text{ mmol } Ag^+ \text{ consumed}$$

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

50 mL (at equivalence point)

At the equivalence point, all silver ion has reacted, so we need to account for the dissociation of the complex.

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

$$\begin{array}{lcl} Ag^+ + EDTA & = & AgY^{3-} \\ I & 0 & 0 \\ C & +x & +x \\ E & x & x \end{array} \quad \begin{array}{l} 5.00 \times 10^{-4} \\ -x \\ 5.00 \times 10^{-4} - x \end{array} \quad K_f' = \alpha_{Y4-} K_f = 0.85 K_f = \frac{[AgY^{3-}]}{[Ag^+][EDTA]}$$

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

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

55 mL (after equivalence point)

After the equivalence point, we also have account for the influence of excess EDTA on the dissociation of the complex.

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

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

$$\begin{array}{lcl} Ag^+ + EDTA & = & AgY^{3-} \\ I & 0 & 4.76 \times 10^{-4} \\ C & +x & +x \\ E & x & 4.76 \times 10^{-4} - x \end{array} \quad \begin{array}{l} 4.76 \times 10^{-5} \\ +x \\ 4.76 \times 10^{-5} + x \end{array} \quad \begin{array}{l} 4.76 \times 10^{-4} \\ -x \\ 4.76 \times 10^{-4} - x \end{array} \quad K_f' = \alpha_{Y4-} K_f = 0.85 K_f = \frac{[AgY^{3-}]}{[Ag^+][EDTA]}$$

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

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

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

Since the stoichiometry between EDTA and any metal ion is 1:1, the mmol of  $\text{Cd}^{2+}$  and  $\text{Mn}^{2+}$  in the mixture equals the total mmol of EDTA minus the number of mmol of EDTA consumed in the back titration with  $\text{Ca}^{2+}$ :

$$\begin{aligned}\text{Total EDTA} &= (56.5 \text{ mL EDTA})(0.0600 \text{ M EDTA}) = 3.39 \text{ mmol EDTA} \\ \text{Consumed EDTA} &= 3.39 \text{ mmol} - (10.0 \text{ mL Ca}^{2+})(0.0170 \text{ M Ca}^{2+}) = 3.22 \text{ mmol EDTA}\end{aligned}$$

So, the total moles of  $\text{Cd}^{2+}$  and  $\text{Mn}^{2+}$  must be 3.22 mmol.

The quantity of cadmium must be the same as the quantity of EDTA freed after the reaction with cyanide:

$$\text{Moles Cd}^{2+} = (26.0 \text{ mL Ca}^{2+})(0.0170 \text{ M Ca}^{2+}) = 0.442 \text{ mmol Cd}^{2+}.$$

The remaining moles must be  $\text{Mn}^{2+}$ :  $3.22 - 0.442 = 2.77_8$  mmoles  $\text{Mn}^{2+}$

The initial concentrations must have been:

$$\begin{aligned}(0.442 \text{ mmol Cd}^{2+})/(50.0 \text{ mL}) &= \mathbf{0.00884 \text{ M Cd}^{2+}} \\ (2.77_8 \text{ mmol Mn}^{2+})/(50.0 \text{ mL}) &= \mathbf{0.0556 \text{ M Mn}^{2+}}\end{aligned}$$

3. Outline an experiment for the determination of  $\text{Ca}^{2+}$  using a calcium ion-selective electrode. If the suspected  $[\text{Ca}^{2+}]$  is  $\sim 0.0030 \text{ M}$ , describe (qualitatively) how you would prepare a calibration curve given a standard solution of  $\text{Ca}^{2+}$  ( $\sim 1.0 \text{ M}$ )? 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.

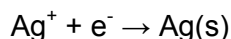
Here are several key points:

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

4. At 25°C, you conduct a titration of 15.00 mL of a 0.0400 M AgNO<sub>3</sub> 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



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

For our electrochemical cell:  $E_{\text{cell}} = E_{\text{Ag/Ag}^+} - E_{\text{SCE}}$

$E_{\text{SCE}} = +0.241$  V

$E_{\text{Ag/Ag}^+}$  is described by the Nernst equation:

$$E_{\text{Ag/Ag}^+} = +0.79993 \text{ V} - \frac{0.05916 \text{ V}}{1} \log \frac{1}{[\text{Ag}^+]}$$

Combining the two:

$$E_{\text{cell}} = +0.79993 \text{ V} - \frac{0.05916 \text{ V}}{1} \log \frac{1}{[\text{Ag}^+]} - (+0.241 \text{ V})$$

So, we need  $[\text{Ag}^+]$  after the addition of the NaI solution to finish our calculation.

The titration reaction is  $\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI(s)}$

The equivalence point occurs at:

$$15.00 \text{ mL Ag}^+ \times \frac{0.0400 \text{ mol Ag}^+}{\text{L}} \times \frac{1 \text{ mol I}^-}{1 \text{ mol Ag}^+} \times \frac{1 \text{ L}}{0.0200 \text{ mol I}^-} = 30.00 \text{ mL}$$

Our given volume is after the equivalence point, therefore, prior to returning to equilibrium, all of the  $\text{Ag}^+$  has been converted to AgI(s) and some excess  $\text{I}^-$  remains.

What is the  $\text{I}^-$  concentration? We have  $35.23 - 30.00 = 5.23$  mL excess  $\text{I}^-$  solution, therefore the concentration must be:

$$\frac{(5.23 \text{ mL})(0.0200 \text{ M I}^-)}{(35.23 + 15.00) \text{ mL}} = 0.00208_2 \text{ M I}^-$$

From the  $K_{sp}$  expression:

$$K_{sp} = [\text{Ag}^+][\text{I}^-]$$

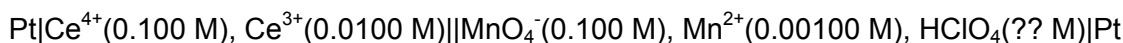
$$[\text{Ag}^+] = K_{sp}/[\text{I}^-] = 8.3 \times 10^{-17}/0.00208_2 = 3.99 \times 10^{-14}$$

Inserting this into our expression above:

$$E_{\text{cell}} = +0.79993 \text{ V} - \frac{0.05916 \text{ V}}{1} \log \frac{1}{3.99 \times 10^{-14}} - (+0.241 \text{ V})$$

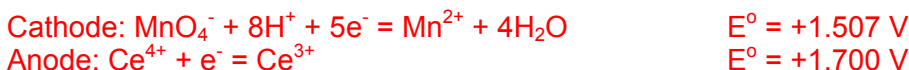
$$E_{\text{cell}} = +0.79993 \text{ V} - (+0.7927 \text{ V}) - (+0.241 \text{ V}) = \mathbf{-0.234 \text{ V}}$$

5. Consider the electrochemical cell below:



Reaction	E° (volts)
(all species are aqueous unless noted)	
$\text{Ce}^{4+} + \text{e}^- = \text{Ce}^{3+}$	+1.700
$\text{Ce}^{3+} + 3\text{e}^- = \text{Ce(s)}$	-2.336
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- = \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.507
$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- = \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}$	+1.692
$\text{MnO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^- = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+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  $E_{\text{cell}}$  is measured to be -0.414 V, what is the pH of the manganese solution? (8 points)

$$E = E^\circ - \frac{0.05916\text{V}}{n} \log \frac{[\text{Ce}^{4+}]^5[\text{Mn}^{2+}]}{[\text{Ce}^{3+}]^5[\text{MnO}_4^-][\text{H}^+]^8}$$

$$-0.414 = -0.193\text{V} - \frac{0.05916\text{V}}{5} \log \frac{[0.100]^5[0.00100]}{[0.0100]^5[0.100][\text{H}^+]^8}$$

$$18.67_9 = \log \frac{[0.100]^5[0.00100]}{[0.0100]^5[0.100][\text{H}^+]^8}$$

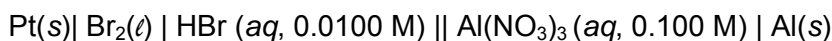
$$[\text{H}^+]^8 = \frac{[0.100]^5[0.00100]}{[0.0100]^5[0.100](4.766 \times 10^{-18})} = 2.0981 \times 10^{-16}$$

$$[\text{H}^+] = (2.0981 \times 10^{-16})^{1/8} = 0.0109_7\text{ M}, \text{pH} = 1.96$$

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

Since  $E^\circ$  is negative under standard conditions, the reaction is not spontaneous in the direction written.

6. Consider the electrochemical cell below:



Reaction	E° (volts)
(all species are aqueous unless noted)	
$\text{Br}_2(\text{aq}) + 2\text{e}^- = 2\text{Br}^-$	+1.098
$\text{Br}_2(\ell) + 2\text{e}^- = 2\text{Br}^-$	+1.078
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- = \text{NO}(\text{g}) + 2\text{H}_2\text{O}$	+0.955
$\text{AgCl} + \text{e}^- = \text{Ag(s)} + \text{Cl}^-$	+0.199 (sat'd KCl)
$2\text{H}^+ + 2\text{e}^- = \text{H}_2(\text{g})$	0.000
$\text{Al}^{3+} + 3\text{e}^- = \text{Al(s)}$	-1.677

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



Nernst equation for each half cell:

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

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

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

If you choose to write a Nernst equation for the overall cell reaction:

$$E_{\text{cell}} = -2.755 \text{ V} - \frac{0.05916 \text{ V}}{6} \log \frac{1}{[\text{Br}^-]^6 [\text{Al}^{3+}]^2} = -2.755 \text{ V} - \frac{0.05916 \text{ V}}{6} \log \frac{1}{[0.0100]^6 [0.100]^2} = -2.893 \text{ V}$$

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 ( $\Delta G^\circ$ ) and the free energy change ( $\Delta G$ ) for the conditions given. (3 points)

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

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

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  $\Delta G$  less positive, the reaction is more favorable under standard conditions.

### Possibly Useful Information

$K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$	$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
$E = E^0 - \frac{2.303RT}{nF} \log Q = E^0 - \frac{0.05916V}{n} \log Q$	$\Delta G^0 = -nFE^0 = -RT \ln K$
$F = 96485 \text{ C mol}^{-1}$	$R = 8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$
$E = \text{const.} + \beta \left( \frac{0.05916V}{n} \right) \log A_{\text{ion}}$	$y = mx + b, \quad m = \frac{\Delta y}{\Delta x}$

### Values of $\alpha_{Y4-}$ for EDTA at 20°C and $\mu = 0.10 \text{ M}$

pH	$\alpha_{Y4-}$	pH	$\alpha_{Y4-}$	pH	$\alpha_{Y4-}$
0	$1.3 \times 10^{-23}$	5	$3.7 \times 10^{-7}$	10	0.36
1	$1.9 \times 10^{-18}$	6	$2.3 \times 10^{-5}$	11	0.85
2	$3.3 \times 10^{-14}$	7	$5.0 \times 10^{-4}$	12	0.98
3	$2.6 \times 10^{-11}$	8	$5.6 \times 10^{-3}$	13	1.00
4	$3.8 \times 10^{-9}$	9	$5.4 \times 10^{-2}$	14	1.00

### PERIODIC CHART OF THE ELEMENTS

PERIODIC CHART OF THE ELEMENTS																INERT GASES	
IA	IIA	IIIB	IVB	VB	VIB	VII B	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	
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
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#### \* 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)
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