

Chemistry 222  
Exam 4: Chapters 11, 13, 14  
80 Points

Name \_\_\_\_\_ Spring 2014

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  $\text{pAg}^+$  at **any two** of the following points in the titration of 50.00 mL of 0.00100 M  $\text{Ag}^+$  with 0.00100 M EDTA at pH 11.00. Select from 33.00 mL, 50.00 mL, 55.00 mL titrant added. For the  $\text{AgY}^{3-}$  complex,  $\log K_f = 7.32$

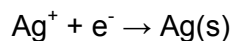
2. A 50.0 mL sample containing  $\text{Cd}^{2+}$  and  $\text{Mn}^{2+}$  was treated with 56.5 mL of 0.0600 M EDTA. Titration of the excess unreacted EDTA required 10.0 mL of 0.0170 M  $\text{Ca}^{2+}$ . The  $\text{Cd}^{2+}$  was displaced from EDTA by the addition of an excess of  $\text{CN}^-$ . Titration 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?

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.

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:

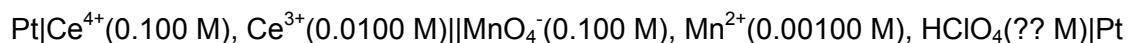
Saturated Calomel Electrode || Titration Solution | Ag (s)

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  $K_{\text{sp}} = 8.3 \times 10^{-17}$ .

5. Consider the electrochemical cell below:



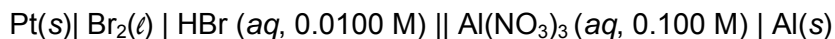
Reaction	E° (volts)
(all species are aqueous unless noted)	
$\text{Ce}^{4+} + \text{e}^- = \text{Ce}^{3+}$	+1.700
$\text{Ce}^{3+} + 3\text{e}^- = \text{Ce(s)}$	-2.336
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- = \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.507
$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- = \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}$	+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)

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:



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

- Calculate  $E_{\text{cell}}$  for the conditions given. (8 points)
- Is the reaction spontaneous in the direction written in part a? How do you know? (2 points)
- Calculate the standard free energy change ( $\Delta G^\circ$ ) and the free energy change ( $\Delta G$ ) for the conditions given. (3 points)
- Is the reaction more favorable under standard conditions, or with the conditions given? How do you know? (3 points)

### Possibly Useful Information

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

### 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																
11 Na 22.9898	12 Mg 24.312																
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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