

**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? **+0.247 V**

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  $\text{Ca}^{2+}$  using a calcium ion-selective electrode. If the suspected  $[\text{Ca}^{2+}]$  is  $\sim 0.0030$  M, describe (qualitatively) how you would prepare a calibration curve given a standard solution of  $\text{Ca}^{2+}$  ( $\sim 1.0$  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  $E_{\text{cell}}$  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  $\sim 0.05916$  V/2 or  $\sim 0.030$  V.
5. Measure  $E_{\text{cell}}$  for the unknown and calculate an unknown concentration from your calibration curve.

2. A 50.0 mL sample containing  $\text{Cd}^{2+}$  and  $\text{Mn}^{2+}$  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  $\text{Ca}^{2+}$ . The  $\text{Cd}^{2+}$  was displaced from EDTA by the addition of an excess of  $\text{CN}^-$ . Titration of the newly freed EDTA required 13.1 mL of 0.0200 M  $\text{Ca}^{2+}$ .
- (a) What were the molarities of  $\text{Cd}^{2+}$  and  $\text{Mn}^{2+}$  in the original solution? (12 points)

$$70.0 \text{ mL} \times \frac{0.0500 \text{ mol EDTA}}{\text{L}} = 3.50 \text{ mmol EDTA delivered}$$

$$18.5 \text{ mL} \times \frac{0.0200 \text{ mol Ca}}{\text{L}} \times \frac{1 \text{ mol EDTA}}{1 \text{ mol Ca}} = 0.370 \text{ mmol EDTA in excess}$$

So,  $(3.50 - 0.370) \text{ mmol} = 3.13 \text{ mmol EDTA}$  was used to bind all of the metal. Therefore,  $\text{mol Cd}^{2+} + \text{mol Mn}^{2+} = 3.13 \text{ mmol}$

$$13.1 \text{ mL} \times \frac{0.0200 \text{ mol Ca}}{\text{L}} \times \frac{1 \text{ mol EDTA}}{1 \text{ mol Ca}} \times \frac{1 \text{ mol Cd}^{2+}}{1 \text{ mol EDTA}} = 0.262 \text{ mmol Zn}^{2+}$$

$$[\text{Cd}^{2+}] = 0.262 \text{ mmol}/50.00 \text{ mL} = \mathbf{0.00524 \text{ M Cd}^{2+}}$$

$$(3.13 - 0.262) \text{ mmol} = 2.868 \text{ mmol Mn}^{2+}$$

$$[\text{Mn}^{2+}] = 2.868 \text{ mmol}/50 \text{ mL} = \mathbf{0.0574 \text{ M Mn}^{2+}}$$

- (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)

$\text{Mn}^{2+}$  and  $\text{Cd}^{2+}$  must bind EDTA more strongly than  $\text{Ca}^{2+}$  does, or else the  $\text{Ca}^{2+}$  would displace EDTA from the other ions. Therefore, the  $K_f$  for the Ca-EDTA complex must be less than the  $K_f$  values for Cd-EDTA and Mn-EDTA.

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)

Your discussion should emphasize the role of the glass membrane in the pH measurement, pointing out the presence of weakly acidic silanol groups on the glass surface and how differences in proton concentration (or activity) on opposite sides of the membrane produces a potential difference. This potential difference is measured in series with two reference electrodes and should follow a Nernstian behavior. You may also have included a drawing of a pH electrode.

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

I was looking for any three of the items below.

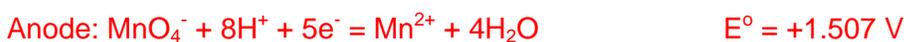
1. Alkaline error: at high pH, other cations (typically  $\text{Na}^+$ ) are present in large excess compared to  $\text{H}^+$ , making it difficult for the glass membrane to distinguish  $\text{H}^+$ .
2. Acid error: at low pH, the silanol groups on the surface of the glass electrode may become saturated with  $\text{H}^+$ , decreasing sensitivity to additional acid.
3. Since the pH electrode responds to activities, differences in the ionic strength of the sample and calibration buffers may lead to large errors.
4. Poorly maintained (or prepared) buffers may actually be at a pH different than that on the label, leading to inaccurate data.
5. Poor handling of the electrode (i.e. dehydration) may also lead to unreliable results as a result of sluggish response.
6. Temperature fluctuations can lead to errors because  $E$  depends on Temperature, too.

4. Consider a solution containing 1.0 M  $\text{Pb}(\text{NO}_3)_4$ , 1.0 M  $\text{Pb}(\text{NO}_3)_2$ , 1.0 M  $\text{KMnO}_4$ , 1.0 M  $\text{Mn}(\text{NO}_3)_2$  and 1.0 M  $\text{HNO}_3$ . For this solution, the following unbalanced reduction half-reactions occur.



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

Since the  $E^\circ$  for the lead reaction is more positive, it is more favorable in the direction written, therefore it will be the cathode half reaction and the manganese reaction will be the anode.



- (b) What is the  $E^\circ$  for the reaction. (4 points)

$$E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = +1.690\text{V} - (+1.507\text{V}) = +0.183 \text{ V}$$

- (c) What is the cell potential for the reaction if the solution is instead 0.15 M  $\text{Pb}(\text{NO}_3)_2$ ,  $1.5 \times 10^{-6}$  M  $\text{Pb}(\text{NO}_3)_4$ ,  $1.5 \times 10^{-6}$  M  $\text{Mn}(\text{NO}_3)_2$ , 0.15 M  $\text{KMnO}_4$ , and 0.83 M  $\text{HNO}_3$ ? Is this more spontaneous or less spontaneous than under standard conditions? (6 points)

$$E = E^\circ - \frac{0.05916\text{V}}{n} \log \frac{[\text{Pb}^{2+}]^5 [\text{MnO}_4^-]^2 [\text{H}^+]^{16}}{[\text{Pb}^{4+}]^5 [\text{Mn}^{2+}]^2}$$

$$E = +0.183\text{V} - \frac{0.05916\text{V}}{10} \log \frac{[0.15]^5 [0.15]^2 [0.83]^{16}}{[1.5 \times 10^{-6}]^5 [1.5 \times 10^{-6}]^2} = -0.016 \text{ V}$$

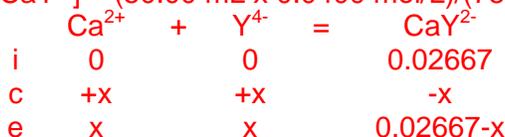
Since the potential is less positive, the reaction is less spontaneous under these conditions than under standard conditions.

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

**First locate the equivalence point:**

$$50.00 \text{ mL} \times \frac{0.0400 \text{ mol } Ca^{2+}}{\text{L}} \times \frac{1 \text{ mol } Y^{4-}}{1 \text{ mol } Ca^{2+}} = \frac{1 \text{ L}}{0.0800 \text{ mol } Y^{4-}} = \mathbf{25.00 \text{ mL}}$$

**At the equivalence point:**  $[CaY^{2-}] = (50.00 \text{ mL} \times 0.0400 \text{ mol/L}) / (75.00 \text{ mL}) = 0.02667 \text{ M}$



$$K_f' = \alpha_{Y^4} K_f = \frac{[CaY^{2-}]}{[Ca^{2+}][Y^{4-}]} = (0.36)(10^{10.65}) = 1.608 \times 10^{10} = \frac{0.02667-x}{(x)(x)}$$

Solving for x yields  $[Ca^{2+}] = 1.28 \times 10^{-6} \text{ M}$  or **pCa = 5.89**

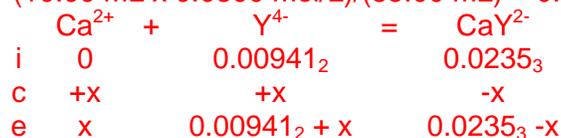
**10 mL before the equivalence point:** we will have consumed 15/25 of the  $Ca^{2+}$ , so 10/25 remains. Since K is large, we can assume that the dissociation of  $CaY^{2-}$  is negligible.

$$50.00 \text{ mL} \times \frac{0.0400 \text{ mol } Ca^{2+}}{\text{L}} \times \frac{10}{25} = 0.01231 \text{ M } Ca^{2+} \text{ or } \mathbf{pCa = 1.91}$$

**10 mL after the equivalence point:** we will have 10 mL extra EDTA.

$$[CaY^{2-}] = (50.00 \text{ mL} \times 0.0400 \text{ mol/L}) / (85.00 \text{ mL}) = 0.0235_3 \text{ M}$$

$$[EDTA] = (10.00 \text{ mL} \times 0.0800 \text{ mol/L}) / (85.00 \text{ mL}) = 0.00941_2 \text{ M}$$



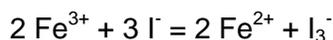
$$K_f' = \alpha_{Y^4} K_f = \frac{[CaY^{2-}]}{[Ca^{2+}][Y^{4-}]} = 1.608 \times 10^{10} = \frac{0.0235_3 - x}{(x)(0.00941_2 + x)}$$

Solving for x yields  $[Ca^{2+}] = 1.56 \times 10^{-10} \text{ M}$  or **pCa = 9.81**

- (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)

Since EDTA always binds metal ions with 1:1 stoichiometry, and since the concentrations of  $Al^{3+}$  and  $Ca^{2+}$  would be the same, it would take the **same volume** of EDTA to reach the equivalence point.

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



Reaction	Standard Reduction Potential
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.771 V
$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe(s)}$	-0.440 V
$\text{I}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	+0.535 V
$\text{I}_3^- + 2\text{e}^- \rightleftharpoons 3\text{I}^-$	+0.535 V

There are multiple approaches to solve this problem, I'll show you two.

**Approach #1:** We can generate our target reaction by combining the first and last reactions above, with the iron half reaction as the cathode and the iodine reaction as the anode:

$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.771 V
$\text{I}_3^- + 2\text{e}^- \rightleftharpoons 3\text{I}^-$	+0.535 V

Therefore, the potential for the overall reaction is  $E_{\text{cathode}} - E_{\text{anode}} = +0.771 \text{ V} - (+0.535 \text{ V}) = +0.236 \text{ V}$ .

Using the relationships between  $\Delta G^\circ$ ,  $E^\circ$ , and  $K$ , we can determine  $K$ :

$$\Delta G^\circ = -nFE^\circ = -(2 \text{ mol e}^-)(96485 \text{ C mol}^{-1})(+0.236 \text{ V}) = -45,540 \text{ J}$$

$$\Delta G^\circ = -RT \ln K, \text{ so } K = e^{-\Delta G^\circ/RT} = 9.60 \times 10^7$$

**Approach #2:** You could also calculate  $\Delta G^\circ$  (or  $K$ ) for each of the half reactions and combine them appropriately.

		$\Delta G^\circ$
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.771 V	$-(1 \text{ mol e}^-)(96485 \text{ C mol}^{-1})(+0.771 \text{ V}) = -74390 \text{ J}$
$\text{I}_3^- + 2\text{e}^- \rightleftharpoons 3\text{I}^-$	+0.535 V	$-(2 \text{ mol e}^-)(96485 \text{ C mol}^{-1})(+0.771 \text{ V}) = -103240 \text{ J}$

To build the overall reaction, we need to double the iron reaction and reverse the iodine reaction before adding them together. We must do the same with the  $\Delta G^\circ$  values.

$$\Delta G^\circ = 2(-74390 \text{ J}) - (-103240 \text{ J}) = -45,540 \text{ J}$$

$$\Delta G^\circ = -RT \ln K, \text{ so } K = e^{-\Delta G^\circ/RT} = 9.60 \times 10^7$$

### Possibly Useful Information

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

### 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

IA	IIA	IIIB	IVB	VB	VIB	VII B	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	INERT GASES	
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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