

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 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.

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. Note that the slope is positive for cations, negative for anions
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  $\text{Ca}^{2+}$ . You may assume that each of the titration reactions goes to completion.
- (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,  
 $\text{mol Cd}^{2+} + \text{mol Mn}^{2+} = 3.13 \text{ mmol}$

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

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

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

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

- (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)

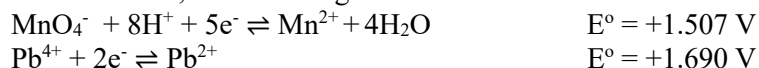
Your discussion should emphasize the role of the glass membrane in the pH measurement, pointing out the presence of weakly acidic silanol groups on the glass surface and how differences in proton concentration (or activity) on opposite sides of the membrane produces a potential difference. This potential 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.

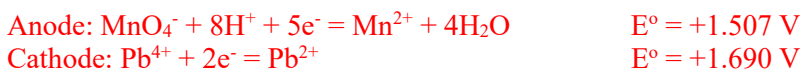
1. Alkaline error: at high pH, other cations (typically  $\text{Na}^+$ ) are present in large excess compared to  $\text{H}^+$ , making it difficult for the glass membrane to distinguish  $\text{H}^+$ .
2. Acid error: at low pH, the silanol groups on the surface of the glass electrode may become saturated 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 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 reduction half-reactions occur.



- (a) Write the balanced reaction that occurs spontaneously in this solution. (4 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? (8 points)

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

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

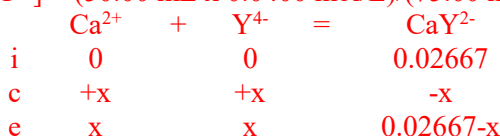
Since the potential is less positive, the reaction is less spontaneous under these conditions than under standard conditions.

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:**

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

**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**

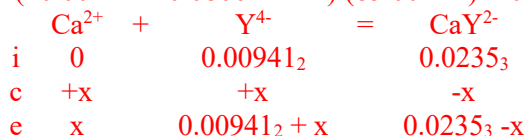
**10 mL before the equivalence point:** we will have consumed 15/25 of the  $Ca^{2+}$ , so 10/25 remains. Since K is large, we can assume that the dissociation of  $CaY^{2-}$  is negligible.

$$\frac{50.00 \text{ mL} \times 0.0400 \text{ mol } Ca^{2+}}{L} \times \frac{10}{25} \times \frac{1 \text{ L}}{15 + 50 \text{ mL}} = 0.01231 \text{ M } Ca^{2+} \text{ or } \mathbf{pCa = 1.91}$$

**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  $Ca^{2+}$ ? (4 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. 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?

As soon as a sample is deposited on the column, a concentration gradient is created, which encourages diffusion away from the sample plug. Therefore, the plug begins to broaden. A sample peak cannot be any narrower than the width of the sample plug at the time of introduction.

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

Since diffusion coefficients are very large in the gas-phase compared to those in the liquid phase, the longitudinal diffusion term dominates band broadening in GC, regardless of whether it is in a packed column or capillary.

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

At low flow rates, analyte stays on the column for a longer time, allowing longitudinal diffusion to play a larger role in band broadening.

- d. Consider liquid chromatography with a 5 packed column. Why does plate height increase and separation efficiency decrease at very high flow rates?

At high flow rates, diffusion between the mobile and stationary phase can cause some molecules in a sample plug to lag behind, causing broadened peaks and poorer separations

Possibly Useful Information

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

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 Table of the Elements**

1A 1 <b>H</b> Hydrogen 1.008	2 IIA 2A <b>Li</b> Lithium 6.941	3 IIIB 3B <b>Be</b> Beryllium 9.012	4 IVB 4B <b>Na</b> Sodium 22.990	5 VB 5B <b>Mg</b> Magnesium 24.305	6 VIB 6B <b>Sc</b> Scandium 44.956	7 VIIB 7B <b>Ti</b> Titanium 47.867	8 VIII 8 <b>V</b> Vanadium 50.942	9 VIII 9 <b>Cr</b> Chromium 51.996	10 VIII 10 <b>Mn</b> Manganese 54.938	11 IB 11 <b>Fe</b> Iron 55.845	12 IIB 12 <b>Co</b> Cobalt 58.933	13 IIIB 13 <b>Ni</b> Nickel 58.693	14 IVB 14 <b>Cu</b> Copper 63.546	15 VB 15 <b>Zn</b> Zinc 65.38	16 VIB 16 <b>Al</b> Aluminum 26.982	17 VIIB 17 <b>Si</b> Silicon 28.086	18 VIIIB 18 <b>P</b> Phosphorus 30.974	19 VIIIB 19 <b>S</b> Sulfur 32.066	20 VIIIB 20 <b>Cl</b> Chlorine 35.453	21 VIIIB 21 <b>Ar</b> Argon 39.948	22 VIIIB 22 <b>K</b> Potassium 39.098	23 VIIIB 23 <b>Ca</b> Calcium 40.078	24 VIIIB 24 <b>Sc</b> Scandium 44.956	25 VIIIB 25 <b>Ti</b> Titanium 47.867	26 VIIIB 26 <b>V</b> Vanadium 50.942	27 VIIIB 27 <b>Cr</b> Chromium 51.996	28 VIIIB 28 <b>Mn</b> Manganese 54.938	29 VIIIB 29 <b>Fe</b> Iron 55.845	30 VIIIB 30 <b>Co</b> Cobalt 58.933	31 VIIIB 31 <b>Ni</b> Nickel 58.693	32 VIIIB 32 <b>Cu</b> Copper 63.546	33 VIIIB 33 <b>Zn</b> Zinc 65.38	34 VIIIB 34 <b>Ga</b> Gallium 69.723	35 VIIIB 35 <b>Ge</b> Germanium 72.631	36 VIIIB 36 <b>As</b> Arsenic 74.922	37 VIIIB 37 <b>Se</b> Selenium 78.971	38 VIIIB 38 <b>Br</b> Bromine 79.904	39 VIIIB 39 <b>Kr</b> Krypton 83.798	40 VIIIB 40 <b>Rb</b> Rubidium 85.468	41 VIIIB 41 <b>Sr</b> Strontium 87.62	42 VIIIB 42 <b>Y</b> Yttrium 88.906	43 VIIIB 43 <b>Zr</b> Zirconium 91.224	44 VIIIB 44 <b>Nb</b> Niobium 92.906	45 VIIIB 45 <b>Mo</b> Molybdenum 95.95	46 VIIIB 46 <b>Tc</b> Technetium 98.907	47 VIIIB 47 <b>Ru</b> Ruthenium 101.07	48 VIIIB 48 <b>Rh</b> Rhodium 102.906	49 VIIIB 49 <b>Pd</b> Palladium 106.42	50 VIIIB 50 <b>Ag</b> Silver 107.868	51 VIIIB 51 <b>Cd</b> Cadmium 112.414	52 VIIIB 52 <b>In</b> Indium 114.818	53 VIIIB 53 <b>Sn</b> Tin 118.711	54 VIIIB 54 <b>Sb</b> Antimony 121.760	55 VIIIB 55 <b>Te</b> Tellurium 127.6	56 VIIIB 56 <b>I</b> Iodine 126.904	57 VIIIB 57 <b>Xe</b> Xenon 131.294	58 VIIIB 58 <b>Cs</b> Cesium 132.905	59 VIIIB 59 <b>Ba</b> Barium 137.328	60 VIIIB 60 <b>La</b> Lanthanum 138.905	61 VIIIB 61 <b>Ce</b> Cerium 140.116	62 VIIIB 62 <b>Pr</b> Praseodymium 140.908	63 VIIIB 63 <b>Nd</b> Neodymium 144.243	64 VIIIB 64 <b>Pm</b> Promethium 144.913	65 VIIIB 65 <b>Sm</b> Samarium 150.36	66 VIIIB 66 <b>Eu</b> Europium 151.964	67 VIIIB 67 <b>Gd</b> Gadolinium 157.25	68 VIIIB 68 <b>Tb</b> Terbium 158.925	69 VIIIB 69 <b>Dy</b> Dysprosium 162.500	70 VIIIB 70 <b>Ho</b> Holmium 164.930	71 VIIIB 71 <b>Er</b> Erbium 167.259	72 VIIIB 72 <b>Tm</b> Thulium 168.934	73 VIIIB 73 <b>Yb</b> Ytterbium 173.055	74 VIIIB 74 <b>Lu</b> Lutetium 174.967	75 VIIIB 75 <b>Ac</b> Actinium 227.028	76 VIIIB 76 <b>Th</b> Thorium 232.038	77 VIIIB 77 <b>Pa</b> Protactinium 231.036	78 VIIIB 78 <b>U</b> Uranium 238.029	79 VIIIB 79 <b>Np</b> Neptunium 237.048	80 VIIIB 80 <b>Pu</b> Plutonium 244.064	81 VIIIB 81 <b>Am</b> Americium 243.061	82 VIIIB 82 <b>Cm</b> Curium 247.070	83 VIIIB 83 <b>Bk</b> Berkelium 247.070	84 VIIIB 84 <b>Cf</b> Californium 251.080	85 VIIIB 85 <b>Es</b> Einsteinium [254]	86 VIIIB 86 <b>Fm</b> Fermium 257.095	87 VIIIB 87 <b>Md</b> Mendelevium 258.1	88 VIIIB 88 <b>No</b> Nobelium 259.101	89 VIIIB 89 <b>Lr</b> Lawrencium [262]
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