

# Chem 303 Exam 1. March 8, 2007. In-Class Test

Name Key

Useful Information: FW of iron(II) chloride = 126.9 g/mol,  $\text{pH} = -\log[\text{H}_3\text{O}^+]$ ,

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}. \text{K}_a \cdot \text{K}_b = \text{K}_w, \text{ See problem 5 for color indicator information.}$$

(1) (30 pts) Little Suzy Perfect carefully measured 50.00 mL of 0.100 M (standardized)  $\text{H}_2\text{SO}_4$  into a clean 250 mL beaker. She filled a buret to the 0.00 mL mark with standardized  $\text{KMnO}_4$  solution that she had diluted so that it was 0.01000 M. She weighed 0.0500 g of a  $\text{FeCl}_2$ -containing powder into a weigh boat and poured in into the beaker with  $\text{H}_2\text{SO}_4$ . She titrated dropwise to the endpoint which was carefully measured to be at 6.55 mL of  $\text{KMnO}_4$ .

She took the volume of  $\text{KMnO}_4$  and multiplied by the molarity to find the moles of iron.

$$0.01000 \frac{\text{moles}}{\text{L}} \times 0.00655 \text{L} = 6.55 \times 10^{-5} \text{ moles} \quad (1)$$

Then, she converted the moles of iron to mg of  $\text{FeCl}_2$

$$\rightarrow (6.55 \times 10^{-5} \text{ moles Fe}) \times 126.8 \text{ g / mole} = 8.42 \times 10^{-3} \text{ g} \quad (2)$$

and then to mg  
= 8.42 mg.

The percentage of  $\text{FeCl}_2$  was found to be

$$\rightarrow \frac{8.42 \text{ mg}}{50.0 \text{ mg}} \times 100\% = 19.6\%$$

Then, Big Joe Sloppy put ~50 mL of roughly 0.100 M  $\text{H}_2\text{SO}_4$  into a clean 250 mL beaker. He filled a buret to the 0.56 mL mark with 0.01223 M  $\text{KMnO}_4$ . He weighed 0.0577 g of a  $\text{FeCl}_2$ -containing powder into a weigh boat and poured in into the beaker with  $\text{H}_2\text{SO}_4$ . He reweighed the used weigh boat and subtracted the extra mass (0.0041 g) from his mass (for a final mass of 0.0536 g powder). He used 7.80 mL of  $\text{KMnO}_4$  to titrate the sample.

He found that he used  $9.53 \times 10^{-5}$  mole of  $\text{KMnO}_4$  and that is equal to  $1.91 \times 10^{-5}$  moles of  $\text{Fe}^{2+}$ .

$$0.00780 \text{L} \times 0.01223 \text{M} = 9.53 \times 10^{-5} \text{ moles}$$

He converted the moles of  $\text{Fe}^{2+}$  into mass of  $\text{FeCl}_2$ .

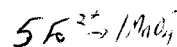
$$(1.91 \times 10^{-5} \text{ moles Fe}) \times 126.8 \text{ g / mole} = 2.42 \times 10^{-3} \text{ g}$$

and this into mg (2.42 mg). The percentage of  $\text{FeCl}_2$  in the powder was found to be 4.51%.

(a) List all of the determinant errors in the above procedures.

*Little Suzy Perfect: Didn't reweigh weigh boat to account for powder sticking to the boat. Wrote  $6.65 \times 10^{-5}$  moles of iron instead of  $6.55 \times 10^{-5}$  moles*

*The final % should be 16.9%, not 19.6%*



*Little Suzy forgot to convert that mols  $\text{MnO}_4^- \neq$  moles  $\text{Fe}^{2+}$*

*Joe used  $5 \text{MnO}_4^- / 1 \text{Fe}^{2+}$*

(b) List 3 instances with indeterminate error in the above procedure and state what the indeterminate error is.

When they read the buret, there is an uncertainty in the measurement.  
When they weigh the powder, there is an uncertainty in the measurement.  
When Suzy Perfect diluted her sample of  $\text{KMnO}_4$ , there was an uncertainty in the diluted volume.

(c) Explain how you could correct two of the determinant errors above.

recheck the math for Suzy Perfect.  
to find the transposed #'s  
and the stoichiometry error.

(d) Who's value for the purity of the powder was most correct?

Big Ice Sluggo, or Little Suzy Perfect, your choice

(2)(20 points) Analyses are often reported to the 95% confidence limit. What does that mean? In problem 1, if the two students listed their values at the 95% CL as  $\pm 0.2\%$ , could they both be right? Why or why not

If means that barring any determinant error,  
the 'true' value has a 95% ~~chance~~ chance of being in  
the given range. They both can't be  
right because they have very different answers.

(3)(20 points) When is the "activity" of an ion significant (what are some of the factors or some situations)? When can the activity be accurately predicted and when can't it?

The activity becomes significant when it is significantly different from concentration. This happens when there are charged particles present.

The activity can be accurately predicted with the Debye-Hückel eqn for ionic strengths below 0.1. Above that the effect of activity become unpredictable.

(4)(a) (15 points) If you wanted to make a pH 5.5 buffer, which of the following systems would be the best to use? Why?

Buffer System	$K_a$ of the acid
$\text{NH}_3/\text{NH}_4^+$	$5.6 \times 10^{-10}$
$\text{CH}_3\text{CO}_2\text{H}/\text{CH}_3\text{CO}_2^-$	$1.8 \times 10^{-5}$
$\text{HONH}_2/\text{HONH}_3^+$	$1.1 \times 10^{-6}$
$\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$	$6.32 \times 10^{-8}$

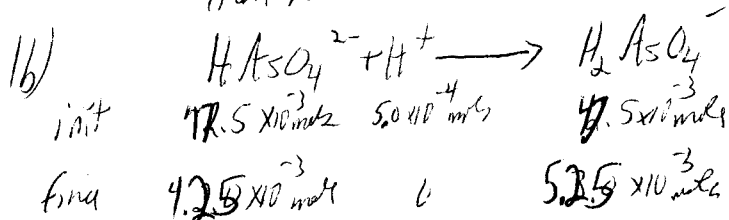
$pK_a$   
 9.25  
 4.74  
 5.96  
 7.20

The  $\text{HONH}_2/\text{HONH}_3^+$  system has a  $pK_a$  close to 5.5.  
 If the  $pK_a$  is not close to the  $pH$ , the  $\frac{[\text{base}]}{[\text{acid}]}$  ratio must be very large or very small, resulting in a low buffer capacity.

(b)(15 pts) If 5.0 mL of 0.100 M HCl is added to 95.0 mL of distilled water ( $pH = 7.00$ ), what is the change in pH? If 5.0 mL of 0.100 M HCl is added to 95.0 mL of a  $pH = 7.0$  buffer (0.0500 M  $\text{KH}_2\text{AsO}_4/0.0500$  M  $\text{K}_2\text{HAsO}_4$   $K_{a2}$  for  $\text{H}_3\text{AsO}_4 = 1.0 \times 10^{-7}$ ), what is the change in pH?

1a)  $(0.0050\text{L})(0.100\text{M}) = 5.0 \times 10^{-4} \text{ mol H}^+$   
 $\frac{5.0 \times 10^{-4} \text{ mol}}{0.100\text{L}} = 5.0 \times 10^{-3} \text{ M } [\text{H}^+]$   $pH = -\log 5.0 \times 10^{-3} = 2.3$

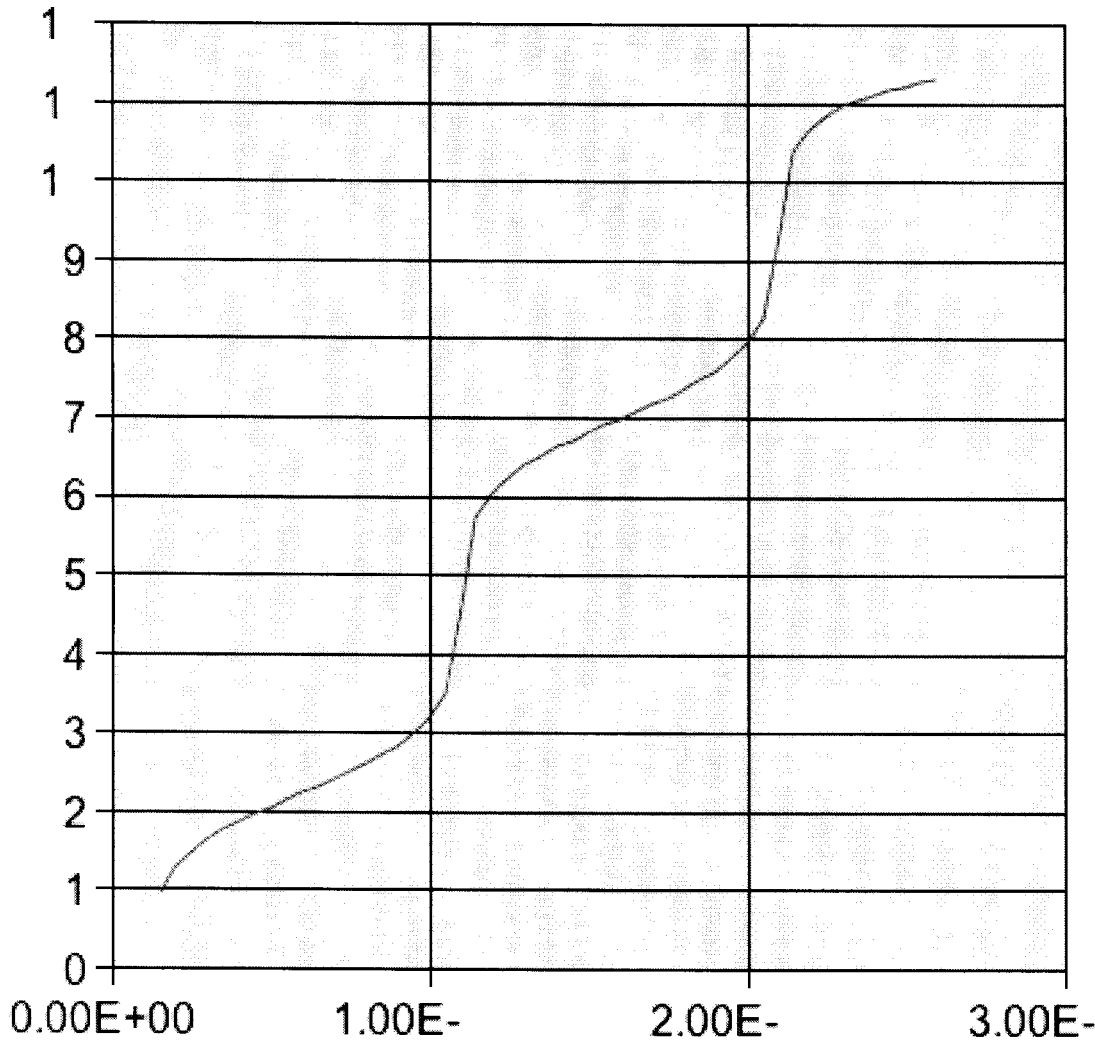
from 7.0  $\rightarrow$  2.3  $\Delta pH = -4.7$



$pH = 7.00 + \log \frac{4.25 \times 10^{-3}}{5.25 \times 10^{-3}}$   
 $pH = 7.00 - 0.092 = 6.91$

$\Delta pH = -0.1$

(5)(15 points) A pH monitored titration is shown below (pH on y-axis)



Indicator	pH of Transition
Crystal Violet	0.1-2.0
Congo Red	3.0-5.0
Bromcresol Green	3.8-5.3
Methyl Red	4.8-6.0
Phenol Red	6.4-8.0
Thymolphthalein	8.3-10.5
Alizarin Yellow	10.1-12.0

*Bromcresol green is best for the 1<sup>st</sup> transition & thymol phthalen for the second.*

*Procedure: perform titration with Bromcresol green & / with thymol phthalen*

Given the data above, choose a set of color indicators that will let you determine the two endpoints for the titration. Explain why these are the best indicators and how you would use them (how would you find the endpoints).

# Chem 3034 Exam 1. February 26, 2007. Take-Home Test

Name Key

You may use your textbook, and notes on this part of the exam. You may not work with other people on this part of the exam. You may use a spreadsheet to determine the activity coefficients, but you must include the spreadsheet (an understandable version) with your exam. Show ALL work for credit. This portion is due by 4:00 PM Friday, February 26.

## (1) Statistics

Student Group 1 tests jars of Brand X peanut butter for  $Pb^{2+}$  level using Atomic Absorption Spectroscopy. Their results from their trials are: 95 ppb, 120 ppb, 124 ppb, 121 ppb, and 123 ppb

Student Group 2 tests a different brand (Brand Y) of peanut butter with the following result: 126 ppb, 126 ppb, 126 ppb, and 127 ppb.

(a)(5 points) Can a point be discarded by the Q test for either of the two samples above (if yes, show the work and discard the point for all other parts of this question)?

$$Q \text{ test for point } 95 \quad \frac{120-95}{124-95} = \frac{25}{29} = 0.86 \text{ for } Q_{observed} \text{ is larger than } 0.64 \therefore 95 \text{ can be rejected}$$

(b)(15 points) Calculate the means, standard deviations, and the error at 95% CL for the two samples

$$\text{Group 1: } \bar{X} = \frac{120 + 124 + 121 + 123 \text{ ppb}}{4} = 122$$

$$S = \sqrt{\frac{(120-122)^2 + (124-122)^2 + (121-122)^2 + (123-122)^2}{3}} = 1.8$$

$$\bar{X} \pm \frac{t_s}{\sqrt{N}} = 122 \pm \frac{3.182(1.8)}{\sqrt{4}} = 122 \pm 2.9 = 122 \pm 3$$

$$\text{Group 2 } \bar{X} = \frac{126 + 126 + 126 + 127 \text{ ppb}}{4} = 126.25$$

$$S = \sqrt{\frac{(126-126.25)^2 + (126-126.25)^2 + (126-126.25)^2 + (127-126.25)^2}{3}} = 0.50$$

$$\bar{X} \pm \frac{t_s}{\sqrt{N}} = 126.25 \pm \frac{3.182(0.50)}{\sqrt{4}} = 126.2 \pm 0.8$$

(c) (10 points) Can you say that one peanut butter brand is lower in lead than the other based on the data?

$$S_{pooled} = \sqrt{\frac{S_1^2(n_1-1) + S_2^2(n_2-1)}{n_1+n_2-2}} = \sqrt{\frac{(1.8)^2(3) + (0.5)^2(3)}{6}} = 1.32$$

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{S_{pooled} \sqrt{\frac{16}{8}}} = 4.49$$

$$t_{table} = 2.447 \quad \therefore \text{yes, you can say brand X is lower in } P_{b^{2+}}$$

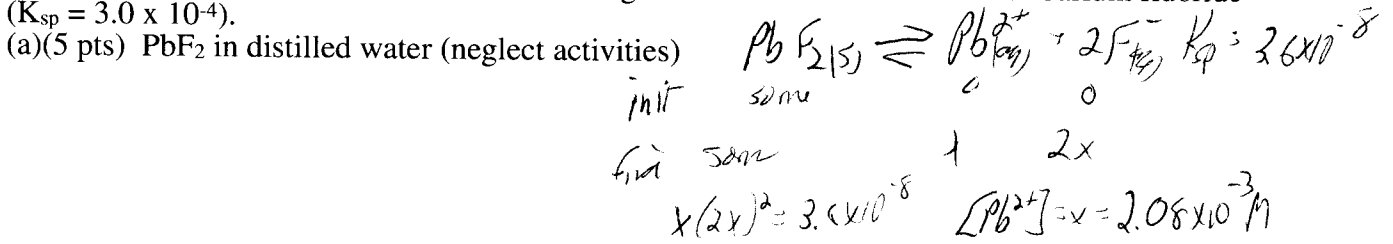
(d) (10 points) Use the F test to determine if there is a significant difference in the precision of the two tests (at the 95% CL).

$$F = \frac{S_1^2}{S_2^2} = \frac{\frac{1.8}{122}}{\frac{0.5}{126.2}} = \frac{16.0148}{0.00396} = 3.72^2 = 13.8$$

$F_{table} = 9.28$   $\therefore$  there is a significant difference in the precision of the 2 groups

-2.6 SS were wrong

(2) Calculate the  $[Pb^{2+}]$  in each of the following solutions when saturated with barium fluoride ( $K_{sp} = 3.0 \times 10^{-4}$ ).



(b) (15 pts)  $PbF_2$  in distilled water (do NOT neglect activities). Use the Debye-Hückel equation for activities.

1<sup>st</sup> guess  $M = \frac{1}{2} (2^2 (2 \times 10^{-3}) + 1(4 \times 10^{-3})) = 6.0 \times 10^{-3} M$

$$\log \gamma = \frac{-0.51 z^2 \sqrt{M}}{1 + \frac{a}{305} \sqrt{M}}$$

for  $Pb^{2+}$   $a = 450 \text{ pm}$   $\log \gamma_{Pb^{2+}} = \frac{-0.51(2^2) \sqrt{6 \times 10^{-3}}}{1 + \frac{450}{305} \sqrt{6 \times 10^{-3}}} = -0.142$

$$\gamma_{Pb^{2+}} = 0.867$$

for  $F^{-}$   $a = 350 \text{ pm}$   $\log \gamma_{F^{-}} = \frac{-0.51(1)^2 \sqrt{6 \times 10^{-3}}}{1 + \frac{350}{305} \sqrt{6 \times 10^{-3}}} = -0.036$

$$\gamma_{F^{-}} = 0.964$$

$$3.6 \times 10^{-8} = x(0.867)(2x)^2(0.964)^2$$

$$4.47 \times 10^{-8} = 4x^3$$

$$\Rightarrow x = 2.24 \times 10^{-3} M$$

2<sup>nd</sup> iteration  $M = \frac{1}{2} (4(2.24 \times 10^{-3}) + 1(4.48 \times 10^{-3})) = 6.6 \times 10^{-3} M$

$Pb^{2+}$   $\log \gamma_{Pb^{2+}} = \frac{-0.51(2)^2 \sqrt{6.6 \times 10^{-3}}}{1 + \frac{450}{305} \sqrt{6.6 \times 10^{-3}}} = -0.148 \quad \gamma_{Pb^{2+}} = 0.862$

$\log \gamma_{F^{-}} = \frac{-0.51(1)^2 \sqrt{6.6 \times 10^{-3}}}{1 + \frac{350}{305} \sqrt{6.6 \times 10^{-3}}} = -0.038 \quad \gamma_{F^{-}} = 0.963$

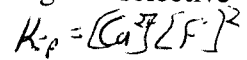
$$3.6 \times 10^{-8} = x(0.862)(2x)^2(0.963)^2$$

$$4.50 \times 10^{-8} = 4x^3$$

$$\boxed{x = 2.24 \times 10^{-3} M} \quad \text{end}$$



(3)(20 points) (Note: You may neglect activity for this problem) The students are trying to analyze tap water for  $\text{Ca}^{2+}$  content by adding  $\text{NaF}$  to precipitate  $\text{CaF}_2$ . Using a  $\text{F}^-$  selective electrode, they can monitor the fluoride concentration in the solution.



(a) At what  $[\text{F}^-]$  should they stop the addition of  $\text{NaF}$  if they wish to precipitate at least 99% of the  $\text{Ca}^{2+}$  and the  $[\text{Ca}^{2+}]$  in the water is expected to be between  $1 \times 10^{-5}$  and  $1 \times 10^{-3}$ ?

$$K_{sp} = 3.9 \times 10^{-11} \quad \text{AVOID to reduce } [\text{Ca}^{2+}] \text{ to at least } 1 \times 10^{-7} \text{ M}$$

$$3.9 \times 10^{-11} = (1 \times 10^{-7})[\text{F}^-]^2$$

$$3.9 \times 10^{-4} = [\text{F}^-]^2$$

$$2.0 \times 10^{-2} = [\text{F}^-]$$

(b) If the water samples also contain  $0.001 \text{ M Mg}^{2+}$ , would this cause a problem?

$$\text{MgF}_2 \quad K_{sp} = 6.6 \times 10^{-9} = [\text{Mg}^{2+}][\text{F}^-]^2$$

$$6.6 \times 10^{-9} = (0.001)(2.0 \times 10^{-2})^2$$

$$1.72 \times 10^{-5} = [\text{Mg}^{2+}]$$

$\text{MgF}_2$  begins to ppt at  
 $1.7 \times 10^{-5} \text{ M Mg}^{2+}$  so yes,  
 it would cause a problem

(4) (10 points) How would you prepare a 1.00 L solution of pH = 10.00 buffer from  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  with an ionic strength of 0.200?

$$pK_{a_1} = 10.329$$

$$\text{pH} = pK_a + \log \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$10.00 = 10.329 + \log \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$-0.329 = \log \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$0.469 = \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$[\text{CO}_3^{2-}] = 0.469 [\text{HCO}_3^-]$$

$$M = \frac{1}{2} \left\{ 2^2 [\text{CO}_3^{2-}] + 1^2 [\text{HCO}_3^-] + 1^2 [\text{Na}^+] \right\}$$

substitute  $[\text{Na}^+] = 2 [\text{CO}_3^{2-}] + [\text{HCO}_3^-]$

$$[\text{CO}_3^{2-}] = 0.469 [\text{HCO}_3^-]$$

$$M = \frac{1}{2} \left( 2^2 (0.469 [\text{HCO}_3^-]) + 1^2 [\text{HCO}_3^-] + 1^2 (2(0.469 [\text{HCO}_3^-]) + [\text{HCO}_3^-]) \right)$$

$$\left( \frac{1}{2} \right) (1.878 [\text{HCO}_3^-] + 1 [\text{HCO}_3^-] + 1.938 [\text{HCO}_3^-])$$

$$M = 2.41 [\text{HCO}_3^-] = 0.200$$

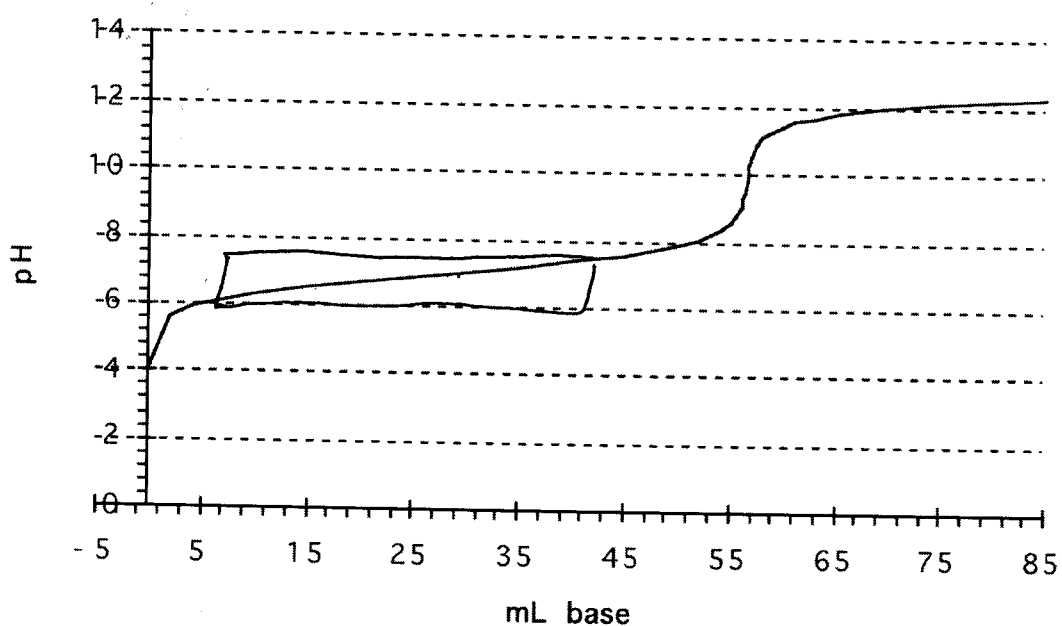
$$[\text{HCO}_3^-] = 0.083 \text{ M}$$

$$[\text{CO}_3^{2-}] = 0.469 (0.083 \text{ M}) = 0.0389 \text{ M}$$

$\therefore$  0.083 moles  $\text{NaHCO}_3$  + 0.0389 moles  $\text{Na}_2\text{CO}_3$

(5) A 50.0 mL sample of a 0.100 M weak acid was titrated with NaOH.

### Weak Acid/Strong Base Titration



pH	Volume
9.14	56.10
9.21	56.15
9.93	56.60
10.22	56.70
10.49	56.87
11.09	58.00

Indicator	pH of Transition
Congo Red	3.0-5.0
Methyl Red	4.8-6.0
Cresol Purple	7.6-9.2
Thymolphthalein	8.3-10.5
Alizarin yellow	10.1-12.0

(a)(5 points) What is the  $K_a$  of this acid (1 sig fig)?

$$pK_a = 7 \quad K_a = 1 \times 10^{-7}$$

(b)(5 points) If an indicator whose transition (blue to yellow) is between pH 6 and 7.5 was used, what problem would this cause? What would be observed in the titration as the transition was approached?

The color would change very slowly, there would not be a sharp endpoint and the endpoint will not be close to the equivalence point.

Mistake  
↓

(c)(10 points) If one group used Cresol purple as an indicator and noticed the endpoint at 9.21 mL and the second group used thymolphthalein as the indicator and the endpoint was noted at pH = 10.49 what is the difference (in mL of NaOH) between the two groups? If their precision in titrating multiple samples was  $\pm 2\%$ , would the difference be statistically significant (why or why not)?

$$\begin{aligned} 9.21 \text{ pH} &= 56.15 \text{ mL} \\ 10.49 \text{ pH} &= 56.87 \text{ mL} \end{aligned}$$

$$0.72 \text{ mL}$$

$$\frac{0.72 \text{ mL}}{56.15 \text{ mL}} \times 100\% = 1.3\%$$

The difference would not be statistically significant

(b)(5 points) If an indicator whose transition (blue to yellow) is between pH 6 and 7.5 was used, what problem would this cause? What would be observed in the titration as the transition was approached?

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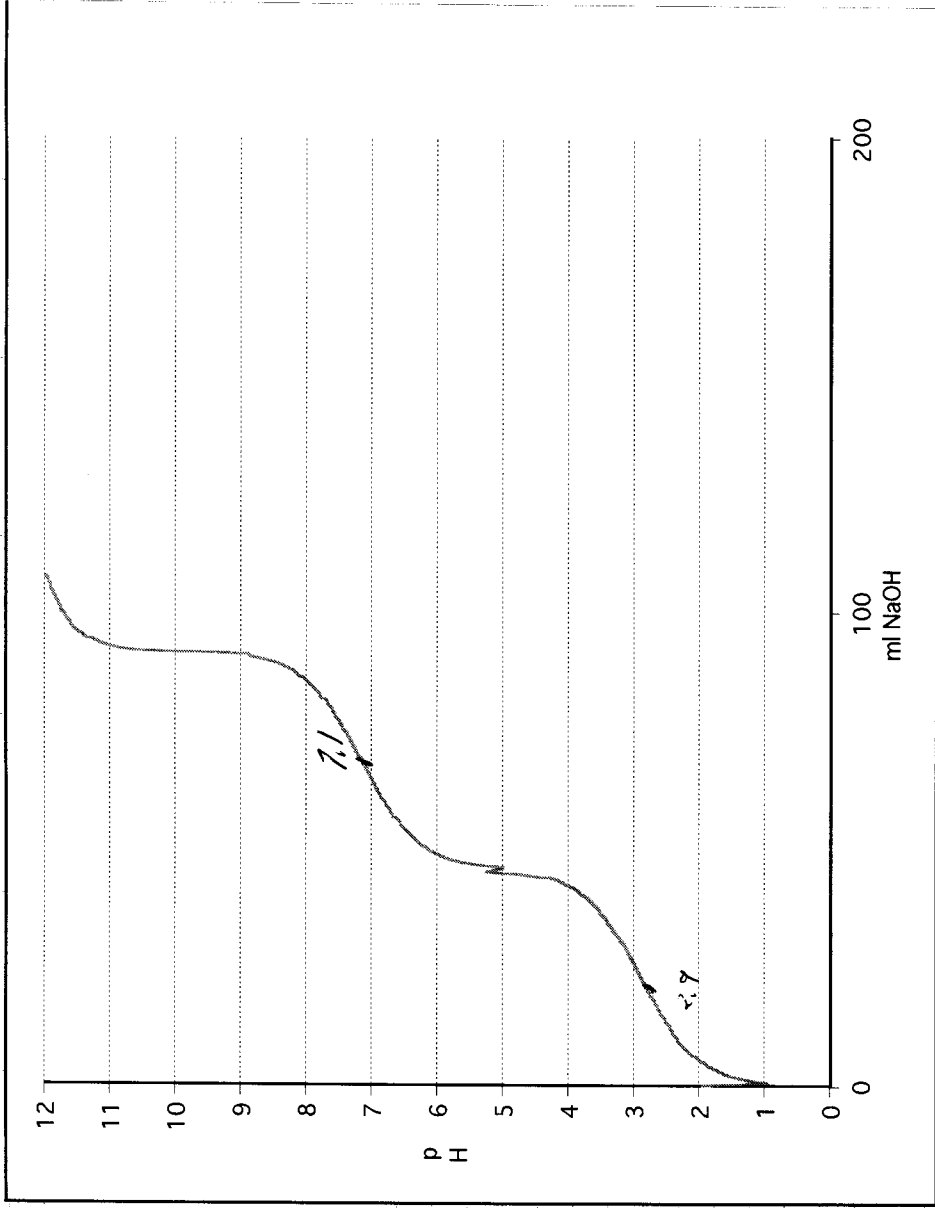
$$0.72 \text{ mL}$$

$$\frac{0.72 \text{ mL}}{56.15 \text{ mL}} \times 100\% = 1.3\%$$

The difference would not be statistically significant

**(6)**(25 points) Construct the titration curve for a weak acid  $\text{H}_2\text{SO}_3$  with a  $K_{a1} = 1.2 \times 10^{-3}$  and  $K_{a2} = 6.6 \times 10^{-8}$ . Use a spreadsheet and plot the curve as in Problem 5 above. Use a 40.0 mL sample of the 0.100 M acid to start with and titrate it with 0.0885 M NaOH. List explicitly the initial pH and the equivalence point and its pH. Calculate the point for every 0.5 mL (on the mL). Include the worksheet as well as the graph (please explain it so it is easy to understand). Do you think a color indicator would work well with this titration?

	A	B	C	D	E	F	G	H	I
1	0	1.96							
2	0.5	0.95							
3	1	1.25							
4	1.5	1.44							
5	2	1.57							
6	2.5	1.67							
7	3	1.75							
8	3.5	1.82							
9	4	1.89							
10	4.5	1.94							
11	5	1.99							
12	5.5	2.04							
13	6	2.08							
14	6.5	2.13							
15	7	2.16							
16	7.5	2.2							
17	8	2.23							
18	8.5	2.26							
19	9	2.3							
20	9.5	2.33							
21	10	2.35							
22	10.5	2.38							
23	11	2.41							
24	11.5	2.43							
25	12	2.46							
26	12.5	2.48							
27	13	2.51							
28	13.5	2.53							
29	14	2.55							
30	14.5	2.57							
31	15	2.6							
32	15.5	2.62							
33	16	2.64							
34	16.5	2.66							
35	17	2.68							
36	17.5	2.7							
37	18	2.72							



(7)(10 points) Find the fractional composition of all species for a sample of phthalic acid in a pH = 8.00 buffer. See pages 216-217 in your textbook for some ideas.

phthalic acid  $K_{a1} = 1.12 \times 10^{-3}$

$K_{a2} = 3.90 \times 10^{-6}$

$[H^+] = 1 \times 10^{-8}$

$$D = [H^+]^2 + [H^+][K_{a1} + K_{a1}K_{a2}] = (1 \times 10^{-8})^2 + (1 \times 10^{-8})(1.12 \times 10^{-3}) + (1.12 \times 10^{-3})(3.9 \times 10^{-6})$$

$$= 4.37 \times 10^{-9}$$

$$\alpha_{H_2A} = \frac{[H^+]^2}{D} = \frac{(1 \times 10^{-8})^2}{4.37 \times 10^{-9}} = 2.3 \times 10^{-8}$$

$$\alpha_{HA^-} = \frac{[H^+][K_{a1}]}{D} = \frac{(1 \times 10^{-8})(1.12 \times 10^{-3})}{4.37 \times 10^{-9}} = 0.026$$

$$\alpha_{A^{2-}} = \frac{K_{a1}K_{a2}}{D} = \frac{(1.12 \times 10^{-3})(3.90 \times 10^{-6})}{4.37 \times 10^{-9}} = 0.99$$