

Name Ken

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 5:00 PM Monday March 20.

(I) Statistics

Student Group 1 tests an unknown for Ca^{2+} content by EDTA titration with the following results: 121.4 ppm, 124.8 ppm, 120.7 ppm, and 124.9 ppm

Student Group 2 tests the same sample as group 1, but uses Atomic Absorption Spectroscopy with the following result: 125 ppm, 126 ppm, 126 ppm, and 124 ppm.

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

Group 1

$$\bar{x} = \frac{121.4 + 124.8 + 120.7 + 124.9}{4}$$
$$\bar{x} = 122.95 \text{ ppm}$$

$$s = \sqrt{\frac{(121.4 - 122.95)^2 + (124.8 - 122.95)^2 + (120.7 - 122.95)^2 + (124.9 - 122.95)^2}{3}}$$

$$s = 2.2 \text{ ppm}$$

$$\frac{ts}{\sqrt{N}} = \frac{(3.18)(2.2 \text{ ppm})}{2}$$

$$95\% \text{ CL} = \pm 3.5 \text{ ppm}$$

Group 2

$$\bar{x} = \frac{125 + 126 + 126 + 124}{4}$$
$$\bar{x} = 125.25 \text{ ppm}$$

$$s = \sqrt{\frac{(125 - 125.25)^2 + (126 - 125.25)^2 + (126 - 125.25)^2 + (124 - 125.25)^2}{3}}$$

$$s = 0.96 \text{ ppm}$$

$$\frac{ts}{\sqrt{N}} = \frac{(3.18)(0.96 \text{ ppm})}{4} = \pm 1.5 \text{ ppm}$$

$$t = \frac{\bar{x}_1 - \bar{x}_2}{s_{pooled} \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

$$s_{pooled} = \sqrt{\frac{(121.4 - 122.5)^2 + (124.8 - 122.5)^2 + (102.7 - 122.5)^2 + (127.9 - 122.5)^2 + (125 - 122.5)^2 + (126 - 122.5)^2 + (127 - 122.5)^2}{6}}$$

$$s_{pooled} = \sqrt{\frac{15.2}{6}} = 1.59$$

$$t = \frac{125.25 - 122.5}{1.59 \sqrt{\frac{4+4}{16}}}$$

$= 2.45$ for 6 degrees of freedom
 $t_{table} = 2.45$ so we can't say they are different

(c)(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).

$$\frac{s_{x1}^2}{s_{x2}^2} = \frac{(2.2)^2}{(0.95)^2} = 5.36$$

$F_{table} = 9.28$ for 3 degrees of freedom

\therefore no significant difference in precision

(d)(5 points) Can a point be discarded by the Q test for either of the two samples above (if yes, show the work)?

(b)(20pts) $\text{Ba}(\text{OH})_2$ in distilled water (do NOT neglect activities). Use the Debye-Hückel equation for activities.

1st guess $[\text{Ba}^{2+}] = 0.04 \text{ M}$ $[\text{OH}^-] = 0.080 \text{ M}$

$$\mu = \frac{1}{2} \{ (0.04)(4)^2 + (0.080)(1)^2 \} = 0.12$$

$$\gamma_{\text{Ba}^{2+}} = 0.30 \quad \gamma_{\text{OH}^-} = 0.75$$

$$3 \times 10^{-4} = (0.35)(x) [(2x)(0.75)]^2$$

$$3 \times 10^{-4} = 0.788 x^3$$

$$3.8 \times 10^{-4} = x^3$$

$$0.072 = x$$

2nd iteration $[\text{Ba}^{2+}] = 0.072 \text{ M}$ $[\text{OH}^-] = 0.144 \text{ M}$ $\mu = \frac{1}{2} \{ (0.072)(2)^2 + (0.144)(1)^2 \} = 0.216 = \mu$

$$\gamma_{\text{Ba}^{2+}} = 0.29 \quad \gamma_{\text{OH}^-} = 0.70$$

$$3 \times 10^{-4} = (0.29)(x) [(2x)(0.70)]^2$$

$$3 \times 10^{-4} = 0.568 x^3$$

$$5.3 \times 10^{-4} = x^3$$

$$0.081 = x$$

3rd iteration $[\text{Ba}^{2+}] = 0.81$ $[\text{OH}^-] = 0.162$ $\mu = \frac{1}{2} \{ (0.081)(2)^2 + (0.162)(1)^2 \} = 0.243$

$$\gamma_{\text{Ba}^{2+}} = 0.28 \quad \gamma_{\text{OH}^-} = 0.69$$

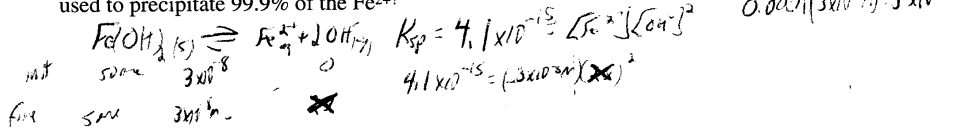
$$3 \times 10^{-4} = (0.28)(x) [(2x)(0.69)]^2$$

$$\boxed{[\text{Ba}^{2+}] = 0.083 \text{ M}}$$

7/2

(3)(35 points) (Note: You may neglect activity for this problem) A student wants to test water for Fe^{2+} content by precipitation with NaOH .

(a) If the lowest concentration of Fe^{2+} expected is $3 \times 10^{-5} \text{ M}$, what is the lowest pH that can be used to precipitate 99.9% of the Fe^{2+} ?

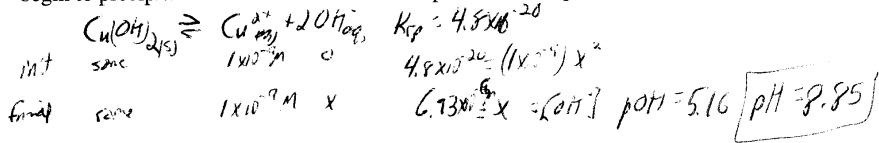


$$4.1 \times 10^{-15} = (3 \times 10^{-5})(x)^2$$

$$x = 3.69 \times 10^{-4} \text{ M} \quad \text{pOH} = 3.43$$

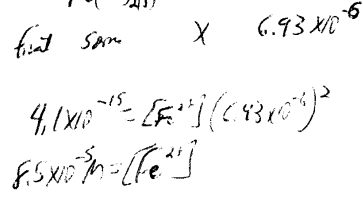
$$\text{pH} = 10.6$$

(b) If Cu^{2+} is present in the water sample with $[\text{Cu}^{2+}] = 1 \times 10^{-9} \text{ M}$. At what pH will $\text{Cu}(\text{OH})_2$ begin to precipitate? How much Fe^{2+} will be present at this point?

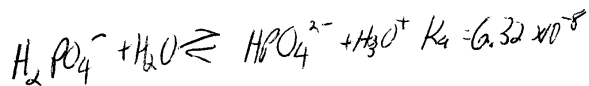


(c) Will the presence of the Cu^{2+} cause a problem? $\text{Fe}(\text{OH})_2(s) \rightleftharpoons \text{Fe}^{2+} + 2\text{OH}^- \quad K_{sp} = 4.1 \times 10^{-15}$

The $\text{Cu}(\text{OH})_2$ will start to precipitate before the Fe^{2+} does!



(4) (15 points) How would you prepare a 1.00 L solution of pH = 7.00 buffer from Na_2HPO_4 and NaH_2PO_4 with an ionic strength of 0.300?



$$\text{pH} = \text{p}K_a + \frac{\log\{\text{base}\}}{\log\{\text{acid}\}}$$

$$7.00 = 7.20 + \frac{\log\{\text{base}\}}{\log\{\text{acid}\}}$$

$$-0.20 = \log\left\{\frac{[\text{base}]}{[\text{acid}]}\right\}$$

$$0.632 = \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

$$0.632[\text{H}_2\text{PO}_4^-] = [\text{HPO}_4^{2-}]$$

$$0.300 = \frac{1}{2} \left\{ [\text{Na}^+] + [\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] \right\}$$

$$[\text{Na}^+] = 2[\text{HPO}_4^{2-}] + 2[\text{H}_2\text{PO}_4^-]$$

$$[\text{Na}^+] = 2(0.632[\text{H}_2\text{PO}_4^-]) + 2[\text{H}_2\text{PO}_4^-] = 2.26[\text{H}_2\text{PO}_4^-]$$

"

$$0.300 = \frac{1}{2} \left\{ 2.26[\text{H}_2\text{PO}_4^-] + 0.632[\text{H}_2\text{PO}_4^-] + [\text{H}_2\text{PO}_4^-] \right\}$$

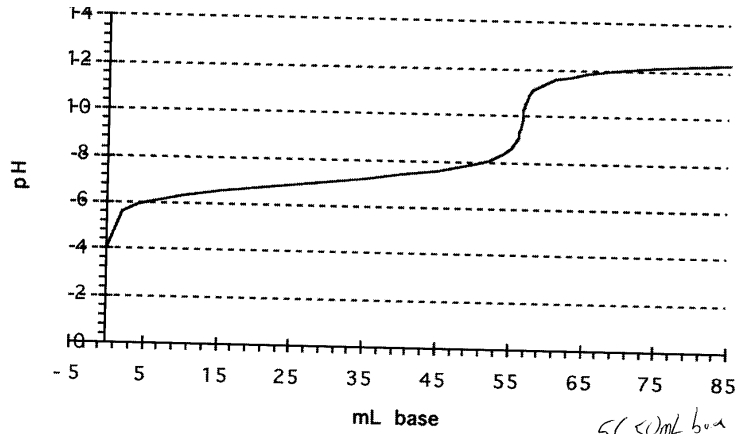
$$0.300 = \frac{1}{2} \{ 5.79[\text{H}_2\text{PO}_4^-] \}$$

$$2.59[\text{H}_2\text{PO}_4^-] = 0.3$$

$$[\text{H}_2\text{PO}_4^-] = 0.104 \text{ M}$$

$$0.632(0.104) \\ = 0.0656 \text{ M HPO}_4^{2-}$$

\therefore add 0.104 mol of NaH_2PO_4 and 0.0656 mol of Na_2HPO_4 and dilute to 1.00 L

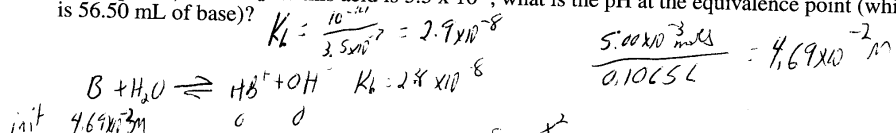


56.50 mL base = 5.00×10^{-3} moles
 $[NaOH] = 0.0885 M$

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)(10 points) If the K_a for this acid is 3.5×10^{-7} , what is the pH at the equivalence point (which is 56.50 mL of base)?



Problem 6 solution

Sheet1

ML acid	Moles acid	Moles base left	Moles conj acid	PH		
0	0.00E+000	5.00E-003	0.00E+000		9.32	Explicitly
0.5	4.43E-005	4.96E-003	4.43E-005		7.7	Calculated
1	8.85E-005	4.91E-003	8.85E-005		7.39	
1.5	1.33E-004	4.87E-003	1.33E-004		7.21	
2	1.77E-004	4.82E-003	1.77E-004		7.09	
2.5	2.21E-004	4.78E-003	2.21E-004		6.98	
3	2.66E-004	4.73E-003	2.66E-004		6.9	
3.5	3.10E-004	4.69E-003	3.10E-004		6.83	
4	3.54E-004	4.65E-003	3.54E-004		6.77	
4.5	3.98E-004	4.60E-003	3.98E-004		6.71	
5	4.43E-004	4.56E-003	4.43E-004		6.66	
5.5	4.87E-004	4.51E-003	4.87E-004		6.62	
6	5.31E-004	4.47E-003	5.31E-004		6.58	
6.5	5.75E-004	4.42E-003	5.75E-004		6.54	
7	6.20E-004	4.38E-003	6.20E-004		6.5	
7.5	6.64E-004	4.34E-003	6.64E-004		6.47	
8	7.08E-004	4.29E-003	7.08E-004		6.43	
8.5	7.52E-004	4.25E-003	7.52E-004		6.4	
9	7.97E-004	4.20E-003	7.97E-004		6.37	
9.5	8.41E-004	4.16E-003	8.41E-004		6.34	
10	8.85E-004	4.12E-003	8.85E-004		6.32	
10.5	9.29E-004	4.07E-003	9.29E-004		6.29	
11	9.74E-004	4.03E-003	9.74E-004		6.27	
11.5	1.02E-003	3.98E-003	1.02E-003		6.24	
12	1.06E-003	3.94E-003	1.06E-003		6.22	
12.5	1.11E-003	3.89E-003	1.11E-003		6.2	
13	1.15E-003	3.85E-003	1.15E-003		6.17	
13.5	1.19E-003	3.81E-003	1.19E-003		6.15	
14	1.24E-003	3.76E-003	1.24E-003		6.13	
14.5	1.28E-003	3.72E-003	1.28E-003		6.11	
15	1.33E-003	3.67E-003	1.33E-003		6.09	
15.5	1.37E-003	3.63E-003	1.37E-003		6.07	
16	1.42E-003	3.58E-003	1.42E-003		6.05	
16.5	1.46E-003	3.54E-003	1.46E-003		6.03	

Page 1

Sheet1

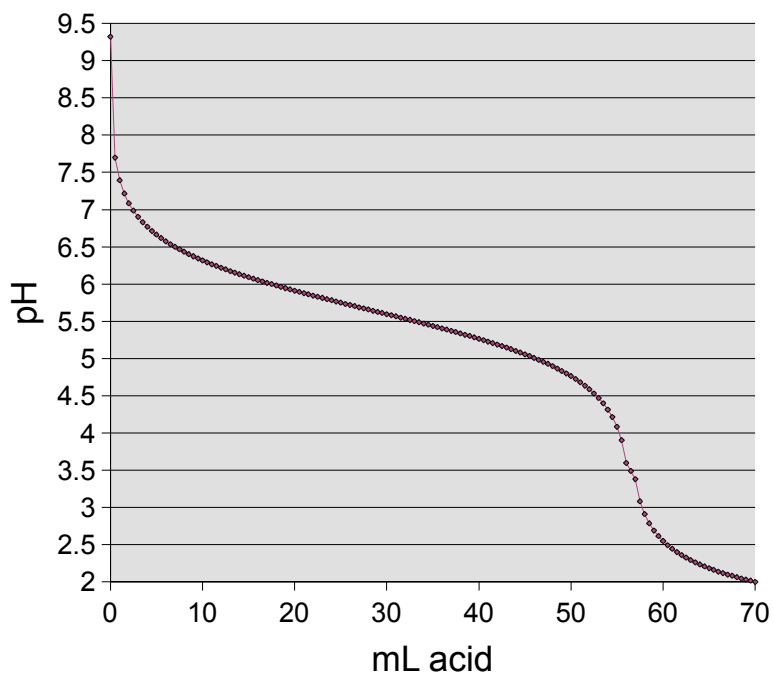
34.5	3.05E-003	1.95E-003	3.05E-003	5.45
35	3.10E-003	1.90E-003	3.10E-003	5.44
35.5	3.14E-003	1.86E-003	3.14E-003	5.42
36	3.19E-003	1.81E-003	3.19E-003	5.41
36.5	3.23E-003	1.77E-003	3.23E-003	5.39
37	3.27E-003	1.73E-003	3.27E-003	5.37
37.5	3.32E-003	1.68E-003	3.32E-003	5.35
38	3.36E-003	1.64E-003	3.36E-003	5.34
38.5	3.41E-003	1.59E-003	3.41E-003	5.32
39	3.45E-003	1.55E-003	3.45E-003	5.3
39.5	3.50E-003	1.50E-003	3.50E-003	5.28
40	3.54E-003	1.46E-003	3.54E-003	5.27
40.5	3.58E-003	1.42E-003	3.58E-003	5.25
41	3.63E-003	1.37E-003	3.63E-003	5.23
41.5	3.67E-003	1.33E-003	3.67E-003	5.21
42	3.72E-003	1.28E-003	3.72E-003	5.19
42.5	3.76E-003	1.24E-003	3.76E-003	5.17
43	3.81E-003	1.19E-003	3.81E-003	5.15
43.5	3.85E-003	1.15E-003	3.85E-003	5.13
44	3.89E-003	1.11E-003	3.89E-003	5.1
44.5	3.94E-003	1.06E-003	3.94E-003	5.08
45	3.98E-003	1.02E-003	3.98E-003	5.06
45.5	4.03E-003	9.73E-004	4.03E-003	5.03
46	4.07E-003	9.29E-004	4.07E-003	5.01
46.5	4.12E-003	8.85E-004	4.12E-003	4.98
47	4.16E-003	8.41E-004	4.16E-003	4.96
47.5	4.20E-003	7.96E-004	4.20E-003	4.93
48	4.25E-003	7.52E-004	4.25E-003	4.9
48.5	4.29E-003	7.08E-004	4.29E-003	4.87
49	4.34E-003	6.63E-004	4.34E-003	4.83
49.5	4.38E-003	6.19E-004	4.38E-003	4.8
50	4.43E-003	5.75E-004	4.43E-003	4.76
50.5	4.47E-003	5.31E-004	4.47E-003	4.72
51	4.51E-003	4.87E-004	4.51E-003	4.68
51.5	4.56E-003	4.42E-004	4.56E-003	4.64

Sheet1

69.5 6.15E-003
70 6.20E-003
70.5
71
71.5

2.02 1.15E-003
2 1.20E-003

Base Titration with HNO₃



Sheet1

52	4.60E-003	3.98E-004	4.60E-003	4.59
52.5	4.65E-003	3.54E-004	4.65E-003	4.53
53	4.69E-003	3.10E-004	4.69E-003	4.47
53.5	4.73E-003	2.65E-004	4.73E-003	4.4
54	4.78E-003	2.21E-004	4.78E-003	4.32
54.5	4.82E-003	1.77E-004	4.82E-003	4.21
55	4.87E-003	1.33E-004	4.87E-003	4.08
55.5	4.91E-003	8.82E-005	4.91E-003	3.9
56	4.96E-003	4.40E-005	4.96E-003	3.6
56.5	5.00E-003	-2.50E-007	5.00E-003	3.49 EXCESS ACID
57	5.04E-003			3.38 4.45E-005
57.5	5.09E-003			3.08 8.88E-005
58	5.13E-003			2.91 1.33E-004
58.5	5.18E-003			2.79 1.77E-004
59	5.22E-003			2.69 2.22E-004
59.5	5.27E-003			2.61 2.66E-004
60	5.31E-003			2.55 3.10E-004
60.5	5.35E-003			2.49 3.54E-004
61	5.40E-003			2.44 3.99E-004
61.5	5.44E-003			2.4 4.43E-004
62	5.49E-003			2.36 4.87E-004
62.5	5.53E-003			2.33 5.31E-004
63	5.58E-003			2.29 5.76E-004
63.5	5.62E-003			2.26 6.20E-004
64	5.66E-003			2.23 6.64E-004
64.5	5.71E-003			2.21 7.08E-004
65	5.75E-003			2.18 7.53E-004
65.5	5.80E-003			2.16 7.97E-004
66	5.84E-003			2.14 8.41E-004
66.5	5.89E-003			2.12 8.85E-004
67	5.93E-003			2.1 9.30E-004
67.5	5.97E-003			2.08 9.74E-004
68	6.02E-003			2.06 1.02E-003
68.5	6.06E-003			2.05 1.06E-003
69	6.11E-003			2.03 1.11E-003

Sheet1

17	1.50E-003	3.50E-003	1.50E-003	6.02
17.5	1.55E-003	3.45E-003	1.55E-003	6
18	1.59E-003	3.41E-003	1.59E-003	5.98
18.5	1.64E-003	3.36E-003	1.64E-003	5.96
19	1.68E-003	3.32E-003	1.68E-003	5.95
19.5	1.73E-003	3.27E-003	1.73E-003	5.93
20	1.77E-003	3.23E-003	1.77E-003	5.91
20.5	1.81E-003	3.19E-003	1.81E-003	5.89
21	1.86E-003	3.14E-003	1.86E-003	5.88
21.5	1.90E-003	3.10E-003	1.90E-003	5.86
22	1.95E-003	3.05E-003	1.95E-003	5.85
22.5	1.99E-003	3.01E-003	1.99E-003	5.83
23	2.04E-003	2.96E-003	2.04E-003	5.81
23.5	2.08E-003	2.92E-003	2.08E-003	5.8
24	2.12E-003	2.88E-003	2.12E-003	5.78
24.5	2.17E-003	2.83E-003	2.17E-003	5.77
25	2.21E-003	2.79E-003	2.21E-003	5.75
25.5	2.26E-003	2.74E-003	2.26E-003	5.73
26	2.30E-003	2.70E-003	2.30E-003	5.72
26.5	2.35E-003	2.65E-003	2.35E-003	5.7
27	2.39E-003	2.61E-003	2.39E-003	5.69
27.5	2.43E-003	2.57E-003	2.43E-003	5.67
28	2.48E-003	2.52E-003	2.48E-003	5.66
28.5	2.52E-003	2.48E-003	2.52E-003	5.64
29	2.57E-003	2.43E-003	2.57E-003	5.63
29.5	2.61E-003	2.39E-003	2.61E-003	5.61
30	2.66E-003	2.35E-003	2.66E-003	5.6
30.5	2.70E-003	2.30E-003	2.70E-003	5.58
31	2.74E-003	2.26E-003	2.74E-003	5.57
31.5	2.79E-003	2.21E-003	2.79E-003	5.55
32	2.83E-003	2.17E-003	2.83E-003	5.53
32.5	2.88E-003	2.12E-003	2.88E-003	5.52
33	2.92E-003	2.08E-003	2.92E-003	5.5
33.5	2.96E-003	2.04E-003	2.96E-003	5.49
34	3.01E-003	1.99E-003	3.01E-003	5.47

What is the difference (in mL of NaOH) between the endpoint and the equivalence point? What % error is this?

9.2) before the endpoint, in the buffer region

$$\text{pH} = 6.45 + \log \frac{[\text{base}]}{[\text{acid}]} = 9.21$$

$$\log \frac{[\text{base}]}{[\text{acid}]} = 2.75$$

$$576 = \frac{[\text{base}]}{[\text{acid}]}$$

$$\% \text{ error} = \frac{0.098 \text{ mL}}{56.5 \text{ mL}} \times 100\% = 0.173\%$$

$$[\text{acid}] - [\text{base}] = 576$$

$$\text{molar acid left} = 8.79 \times 10^{-6} \text{ moles acid}$$

$$8.79 \times 10^{-6} \text{ mol} \div 0.0885 \text{ M} = 0.098 \text{ mL difference}$$

(e) (5 points) If thymolphthalein is used as the indicator and the endpoint is noted at pH = 10.49 what is the difference (in mL of NaOH) between the endpoint and the equivalence point? What is the % error caused by the indicator?

$$\text{pH} = 10.49 \quad \text{excess } \text{NaOH} \quad \text{pOH} = 3.51$$

$$[\text{OH}^-] = 3.09 \times 10^{-4} \text{ M}$$

$$3.09 \times 10^{-4} \text{ M} = \frac{(0.0885 \text{ M})(x)}{(0.0565 \text{ L} + x)}$$

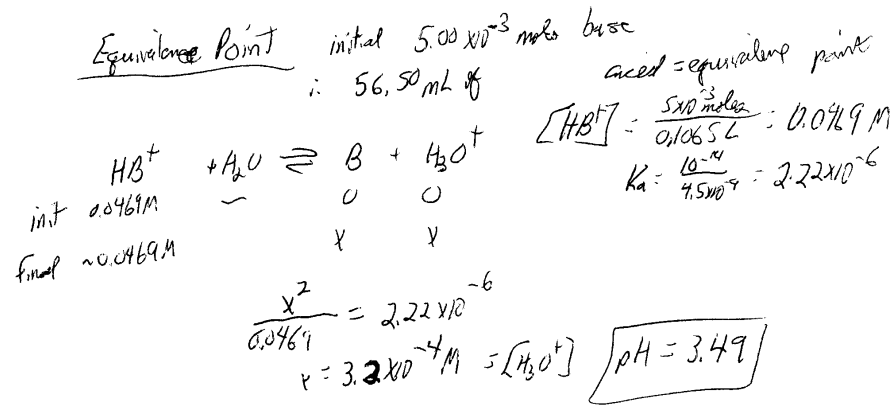
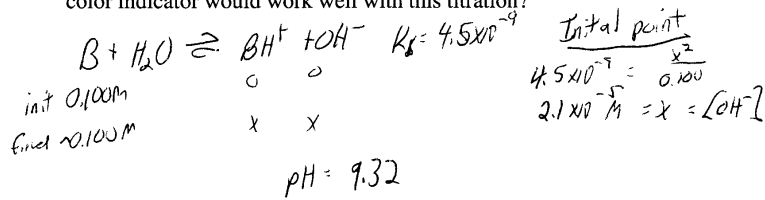
$$1.75 \times 10^{-5} + (3.09 \times 10^{-4})x = (0.0885 \text{ M} x)$$

$$1.75 \times 10^{-5} = 0.0881 \text{ M} x$$

$$2.16 \times 10^{-4} \text{ L} = x = 0.216 \text{ mL}$$

$$\% \text{ error} = \frac{0.216 \text{ mL}}{56.5 \text{ mL}} \times 100\% = 0.38\%$$

base to start with and titrate it with 0.0885 M HNO₃. 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 color indicator would be hard to see for this titration. pK_a = 5.65

(7)(20 points) For phosphoric acid, calculate the fractional composition (alpha values) for all species in solution as a function of pH. See pages 420-421 in your books for some ideas. Do this in a spreadsheet and graph it.

TABLE 3.10

1	1.00E-001	0.93	0.07	0	0
1.2	6.31E-002	0.9	0.1	0	0
1.4	3.98E-002	0.85	0.15	0	0
1.6	2.51E-002	0.78	0.22	0	0
1.8	1.58E-002	0.69	0.31	0	0
2	1.00E-002	0.58	0.42	0	0
2.2	6.31E-003	0.47	0.53	0	0
2.4	3.98E-003	0.36	0.64	0	0
2.6	2.51E-003	0.26	0.74	0	0
2.8	1.58E-003	0.18	0.82	0	0
3	1.00E-003	0.12	0.88	0	0
3.2	6.31E-004	0.08	0.92	0	0
3.4	3.98E-004	0.05	0.95	0	0
3.6	2.51E-004	0.03	0.97	0	0
3.8	1.58E-004	0.02	0.98	0	0
4	1.00E-004	0.01	0.99	0	0
4.2	6.31E-005	0.01	0.99	0	0
4.4	3.98E-005	0.01	0.99	0	0
4.6	2.51E-005	0	0.99	0	0
4.8	1.58E-005	0	0.99	0	0
5	1.00E-005	0	0.99	0.01	0
5.2	6.31E-006	0	0.99	0.01	0
5.4	3.98E-006	0	0.98	0.02	0
5.6	2.51E-006	0	0.98	0.02	0
5.8	1.58E-006	0	0.96	0.04	0
6	1.00E-006	0	0.94	0.06	0
6.2	6.31E-007	0	0.91	0.09	0
6.4	3.98E-007	0	0.86	0.14	0
6.6	2.51E-007	0	0.8	0.2	0
6.8	1.58E-007	0	0.71	0.29	0
7	1.00E-007	0	0.61	0.39	0
7.2	6.31E-008	0	0.5	0.5	0
7.4	3.98E-008	0	0.39	0.61	0
7.6	2.51E-008	0	0.28	0.72	0
7.8	1.58E-008	0	0.2	0.8	0
8	1.00E-008	0	0.14	0.86	0
8.2	6.31E-009	0	0.09	0.91	0
8.4	3.98E-009	0	0.06	0.94	0
8.6	2.51E-009	0	0.04	0.96	0

Sheet1

9.6	2.51E-010	0	0	0.99	0
9.8	1.58E-010	0	0	0.99	0
10	1.00E-010	0	0	0.99	0
10.2	6.31E-011	0	0	0.99	0.01
10.4	3.98E-011	0	0	0.99	0.01
10.6	2.51E-011	0	0	0.98	0.02
10.8	1.58E-011	0	0	0.97	0.03
11	1.00E-011	0	0	0.96	0.04
11.2	6.31E-012	0	0	0.94	0.06
11.4	3.98E-012	0	0	0.9	0.1
11.6	2.51E-012	0	0	0.86	0.14
11.8	1.58E-012	0	0	0.79	0.21
12	1.00E-012	0	0	0.7	0.3
12.2	6.31E-013	0	0	0.6	0.4
12.4	3.98E-013	0	0	0.49	0.51
12.6	2.51E-013	0	0	0.37	0.63
12.8	1.58E-013	0	0	0.27	0.73
13	1.00E-013	0	0	0.19	0.81
13.2	6.31E-014	0	0	0.13	0.87
13.4	3.98E-014	0	0	0.09	0.91
13.6	2.51E-014	0	0	0.06	0.94
13.8	1.58E-014	0	0	0.04	0.96
14	1.00E-014	0	0	0.02	0.98
14.2					
14.4					

Fractional Composition of Phosphoric Acid

