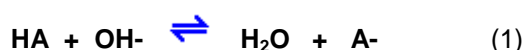
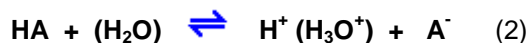

Determination of the Equivalent Weight and Ionization Constant of a Weak Acid

Introduction: The object of this experiment will be to determine the ionization constant, K_a , and the **equivalent weight** of an unknown weak acid by titration with a standard sodium hydroxide solution. The approximate equivalent weight for the compound will be given so that amount of compound needed for each titration can be estimated. The equivalent weight of an acid is defined as the molecular weight divided by the number of replaceable hydrogen ions.

The titration reaction for a weak acid reacting with sodium hydroxide is given by



The degree of ionization of the weak acid is given by the ionization constant, K_a , which is calculated from the following equilibrium relationship:



$$K_a = \frac{[\text{H}^+] \times [\text{A}^-]}{[\text{HA}]}$$

Before you come to class:

- Read sections 8-3 and 8-6 in your textbook.
- Record the molecular formula and molar mass of potassium hydrogen phthalate, KHP, in your lab notebook. List all other reagents (formulas and names) in your notebook. Also include the NFPA ratings for any compounds with a non-zero rating. Familiarity with the reagents will help you avoid costly mistakes during the experiment.
- Write reactions 1, 2, 3 in your lab notebook.

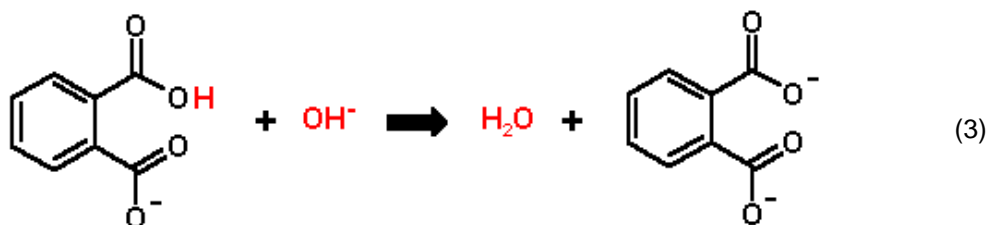
Reagents:

- pH buffers
- potassium hydrogen phthalate
- 0.1M NaOH
- phenolphthalein

Procedure:

Standardization of 0.10 M NaOH:

Fill a clean plastic 1 L bottle with approximately 500 mL of the 0.1M NaOH solution. Remember to **never store** NaOH in a glass stoppered bottle. The general standardization procedure involves the titration of known, solid, primary standard potassium hydrogen phthalate, KHP. The reaction involved is



1. Weigh enough solid KHP into a 250 mL Erlenmeyer flask to require ~35 mL of 0.1 NaOH for titration.
2. Add ~75 mL of distilled water and a few drops of phenolphthalein indicator and titrate to the end-point, the first appearance of a pink color.
3. Perform at least three standardization titrations where the results agree to $\pm 1\%$.

pH meter use:

Use your magnetic stirrer + stirbar to keep your titration mixture stirring. You can use a beaker for this titration since you won't be swirling it by hand to mix it.

Keep your pH probe tip immersed in the solution, away from the stirbar, and away from the tip of your buret. You should have room to keep all of these things away from each other.

Before beginning titration, you must calibrate the pH meter as instructed.

pH Titration of the Weak Acid Unknown (*perform two titrations of your unknown*):

1. Prepare approximately 250 mL of a ~0.1 M solution of KCl (74.5 g/mole) to serve as your constant ionic strength buffer. Use this as the diluent when you make up your unknown samples to approximately 100 mL volume for titration. Use the top-loading balance to prepare this solution.
2. Accurately weigh by difference (into a 250 mL beaker) enough unknown so that each titration will require about 35 mL of the 0.1 M NaOH using the approximate equivalent weight given to you by the instructor.
3. Dilute the samples to a total volume of about 100 mL with the ~0.1 M KCl. Make sure solid samples are completely dissolved before beginning the titration.
4. Fill your buret with the NaOH solution to titrate your acid.
5. Make sure the pH electrode is below the solution level in the beaker and is not being hit by the stirrer.
6. Add a few drops of phenolphthalein indicator to the solution and note the pH values when the indicator color changes.
7. *It is advisable to make a rough plot of the data as it is being recorded.*
8. Record the mL added versus pH data in your notebook. Readings should initially be taken approximately 2.0 mL apart until the pH starts to change significantly. Smaller volume additions should be made dropping from 1.0 to 0.5 to 0.25 mL as the titration proceeds through the equivalence point. The smaller the additions made in this range, the more accurately the equivalence point can be located. Note that you do not have to use exactly 0.50 or 0.25 mL changes.
9. After passing through the equivalence point, the volume addition size can be increased as the pH change decreases.
10. ***Continue the titration at least 10 mL beyond the equivalence point.***
11. Your titration curve should appear similar to that shown at the top of page 5.

KEEP YOUR STANDARDIZED NaOH SOLUTION FOR A FUTURE EXPERIMENT.

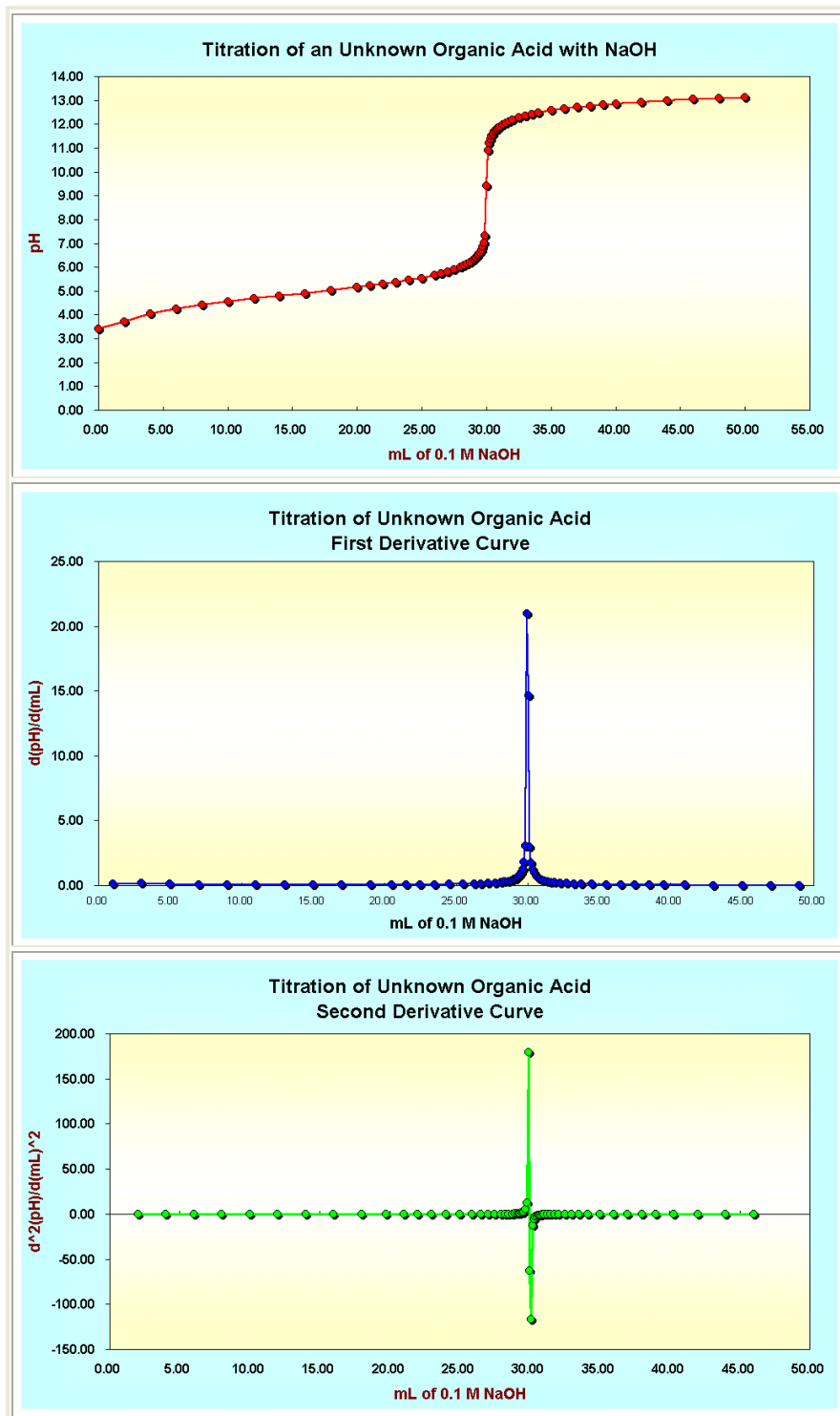
Data Analysis:

The equivalence point for your titration is defined as the **point of inflection** (where the slope changes) on the titration curve. It may be located graphically from the titration curve or, more, accurately, by **plotting the first or second derivative of the titration curve and finding the inflection points**. You will make use of a spreadsheet to calculate and plot the first and second derivative curves of your data.

The numbers from your titration data that you use for calculations should come from these Excel graphs and calculations. Although you used the phenolphthalein indicator to observe the end point visually, the numerical pH data and inflection point data will give you better accuracy.

	A	B	C	D	E	F	G	H	I	J
	mL NaOH	pH	$\Delta(\text{mL})$	$\Delta(\text{pH})$	avg. mL	$\Delta(\text{pH/mL})$	$\Delta(\text{mL})^2$	$\Delta(\Delta\text{pH/mL})$	avg. mL	$\Delta^2(\text{pH})/\Delta(\text{mL})^2$
4	0.00	3.40	---	---	---	---	---	---	---	---
5	2.24	3.55	=B4-B5	=(C5-C4)	=(B4+B5)/2	=(E5/D5)	---	---	---	---
6	4.32	4.10	2.08	0.55	3.28	0.26	=(F6-F5)	=(G6-G5)	=(F5+F6)/2	=(I6/H6)
7	5.99	4.12	1.67	0.02	5.16	0.01	1.88	-0.25	4.22	-0.13
8	7.86	4.45	1.87	0.33	6.93	0.18	1.77	0.16	6.04	0.09
9	9.98	4.48	2.12	0.03	8.92	0.01	2.00	-0.16	7.92	-0.08
10	12.25	4.72	2.27	0.24	11.12	0.11	2.20	0.09	10.02	0.04
11	15.50	4.79	3.25	0.07	13.88	0.02	2.76	-0.08	12.50	-0.03
12	18.15	5.06	2.65	0.27	16.83	0.10	2.95	0.08	15.35	0.03
13	20.22	5.12	2.07	0.06	19.19	0.03	2.36	-0.07	18.01	-0.03
14	23.77	5.72	3.55	0.60	22.00	0.17	2.81	0.14	20.59	0.05
15	26.43	5.91	2.66	0.19	25.10	0.07	3.11	-0.10	23.55	-0.03
16	28.02	6.15	1.59	0.24	27.23	0.15	2.13	0.08	26.16	0.04
17	28.80	6.45	0.78	0.30	28.41	0.38	1.19	0.23	27.82	0.20
18	29.12	7.95	0.32	1.50	28.96	4.69	0.55	4.30	28.69	7.82
19	29.93	8.33	0.81	0.38	29.53	0.47	0.56	-4.22	29.24	-7.47
20	30.03	9.35	0.10	1.02	29.98	10.20	0.46	9.73	29.75	21.39
21	30.22	10.56	0.19	1.21	30.13	6.37	0.15	-3.83	30.05	-26.42
22	30.90	10.63	0.68	0.07	30.56	0.10	0.43	-6.27	30.34	-14.40
23	31.30	11.88	0.40	1.25	31.10	3.12	0.54	3.02	30.83	5.60
24	31.46	12.00	0.16	0.12	31.38	0.75	0.28	-2.37	31.24	-8.48
25	32.05	12.04	0.59	0.04	31.76	0.07	0.37	-0.68	31.57	-1.82
26	33.55	12.08	1.50	0.04	32.80	0.03	1.05	-0.04	32.28	-0.04
27	34.12	12.49	0.57	0.41	33.84	0.71	1.04	0.69	33.32	0.66

The worksheet **ACIDPLOT.XLS**, a template for this experiment, can be downloaded from the course homepage. ACIDPLOT.XLS contains some simulated data which was calculated for an ideal titration. You can observe the graphs of the titration (NORMAL), first derivative (1DERIV), and second derivative (2DERIV) curves. Type in your data using the appropriate columns. You will be responsible for understanding how the derivatives are calculated from the data. After your data has been entered, save the file as ACID1.XLS (Note: You can reload the template ACIDPLOT.XLS and repeat the procedure for your second data set.) You should see plots (**tabs** in the Excel workbook) like the Figures below.



The equivalence points can be located from the plots but it is easier to find them from the numerical data. For the **first derivative data**, the end point should be where the derivative is a **maximum**:

18	29.12	7.95	0.32	1.50	28.96	4.69	0.55	4.30	28.69	7.82
19	29.93	8.33	0.81	0.38	29.53	0.47	0.56	-4.22	29.24	-7.47
20	30.03	9.35	0.10	1.02	29.98	10.20	0.46	9.73	29.75	21.39
21	30.22	10.56	0.19	1.21	30.13	6.37	0.15	-3.83	30.05	-26.42
22	30.90	10.63	0.68	0.07	30.56	0.10	0.43	-6.27	30.34	-14.40

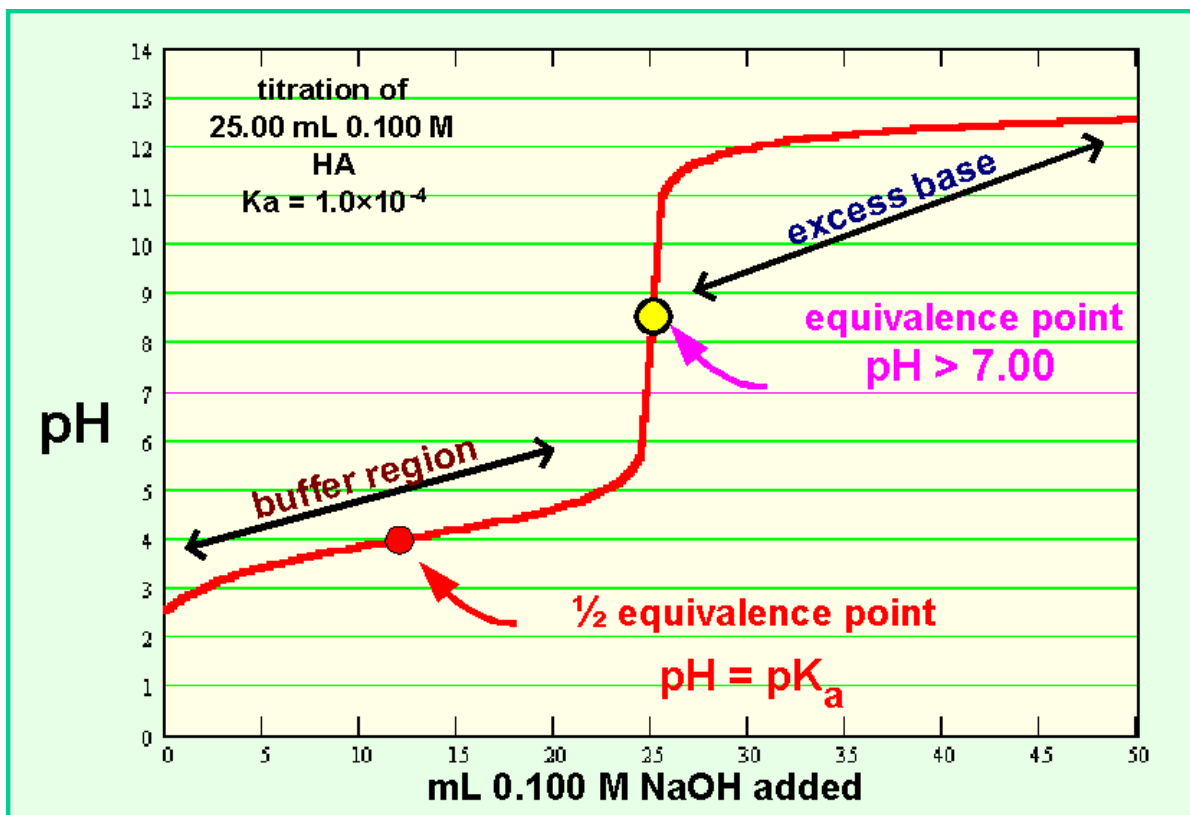
For the **second derivative data**, the equivalence point should be interpolated from the range where the second derivative **crosses from positive to negative values**:

18	29.12	7.95	0.32	1.50	28.96	4.69	0.55	4.30	28.69	7.82
19	29.93	8.33	0.81	0.38	29.53	0.47	0.56	-4.22	29.24	-7.47
20	30.03	9.35	0.10	1.02	29.98	10.20	0.46	9.73	29.75	21.39
21	30.22	10.56	0.19	1.21	30.13	6.37	0.15	-3.83	30.05	-26.42
22	30.90	10.63	0.68	0.07	30.56	0.10	0.43	-6.27	30.34	-14.40
23	31.30	11.88	0.40	1.25	31.10	3.12	0.54	3.02	30.83	5.60

Note that each plot gives a slightly different value for the equivalence point, 29.98 for the first derivative and $(29.75+30.05)/2 = 29.90$ for the second derivative. Experimental points obtained with smaller volume increments would have exhibited less variation.

- **Use the volume at the equivalence point to calculate the equivalent weight of your unknown acid.** The value should be ± 10 from the estimate given by the instructor.

The second part of the experiment is to determine the ionization constant, K_a (pK_a), for the weak acid. Remember that at the half way to the equivalence point, the concentration of the weak acid salt created in the titration is exactly equal to the concentration of the weak acid untitrated. At this point, the pH is equal to the pK_a .



Since it is impossible to know the half titration point until the titration is completed, the pK_a values must be calculated from data taken near the half titration point. The total number of moles of acid can be calculated from the equivalence point and the concentration of the NaOH solution. At any point in the buffer region, the moles of salt are equal to the moles of NaOH added and the moles of acid left can be calculated from the total number of moles of acid present minus the moles of salt formed. Since both the salt and acid are in the same beaker, the volumes divide out.

$$pH = pK_a + \log \frac{[\text{salt formed}]}{[\text{acid left}]} = pK_a + \log \frac{(V_{\text{NaOH}} \times C_{\text{NaOH}})}{(V_{\text{NaOH}_{\text{equiv pt}}} \times C_{\text{NaOH}} - V_{\text{NaOH}} \times C_{\text{NaOH}})}$$

A spreadsheet program **ORGACID.XLS** is available to assist in the calculations. It can be downloaded from the course home page. You will be asked to provide the information in dark red and the data in red will be evaluated for your grade.

NaOH Concentration	0.1045 M		
	sample weight	mL to end-point	equivalent weight
Titration 1	0.2345	30.10	74.55
Titration 2	0.2456	30.25	77.69
Best estimate of equivalent weight			80.50

Calculation of pKa

Titration 1	End-point	30.10			
Data point	ml	pH	log(A)/(HA)	pKa	
1	10.00	4.55	-0.30	4.85	
2	12.00	4.67	-0.18	4.85	
3	14.00	4.79	-0.06	4.85	
4	16.00	4.91	0.05	4.86	
5	18.00	5.03	0.17	4.86	
6	20.00	5.15	0.30	4.85	
Average				4.85	
Titration 2	End-point	30.25			
Data point	ml	pH	log(A)/(HA)	pKa	
1	11.00	4.57	-0.24	4.81	
2	13.00	4.68	-0.12	4.80	
3	15.00	4.80	-0.01	4.81	
4	17.00	4.99	0.11	4.88	
5	19.00	5.01	0.23	4.78	
6	20.00	5.15	0.29	4.86	
Average				4.82	
Best estimate of pKa		4.75			

Turn in:

- Plots of the titration curves from ACIDPLOT.xls
- ORGACID.xls worksheet with pKa clearly labeled – this is your result to be graded.