# 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 <u>the molecular weight divided by the number of replaceable hydrogen ions</u>.

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

$$HA_{(aq)} + OH^-_{(aq)} \rightleftarrows H_2O_{(l)} + A^-_{(aq)} \qquad (1)$$
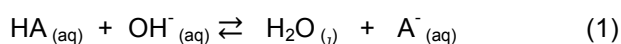
The degree of ionization of the weak acid is given by the ionization constant, K_a, which is calculated from the following equilibrium relationship:

$HA_{(aq)} + OH^-_{(aq)} \rightleftarrows H_2O_{(l)} + A^-_{(aq)}$	$K_a = \dfrac{[H^+] \times [A^-]}{[HA]}$
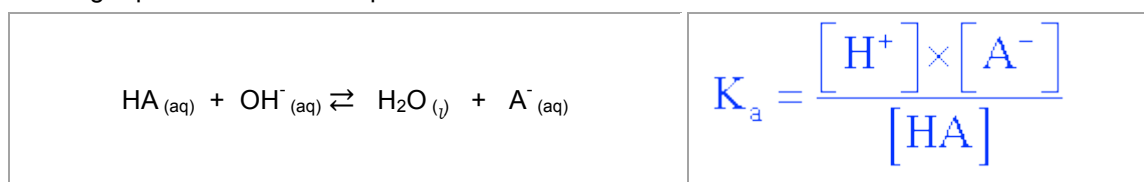
Before you come to class:
- Read sections 8-3 and 8-6 in your textbook.
- Record the molecular formula and molar mass of potassium hydrogen phthalate, KHP, in your lab notebook. List all other reagents (formulas and names) in your notebook. Also include the NFPA ratings for any compounds with a non-zero rating. <u>Familiarity with the reagents will help you avoid costly mistakes during the experiment.</u>
- Write reaction 1 and 2(see page 2) in your lab notebook.

Reagents:
- pH buffers
- potassium hydrogen phthalate
- unknown weak acid sample (salt)
- 0.1M NaOH
- phenolphthalein

Waste Disposal: All solutions in today's lab can be disposed of down the sink with running water.

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:

(2)
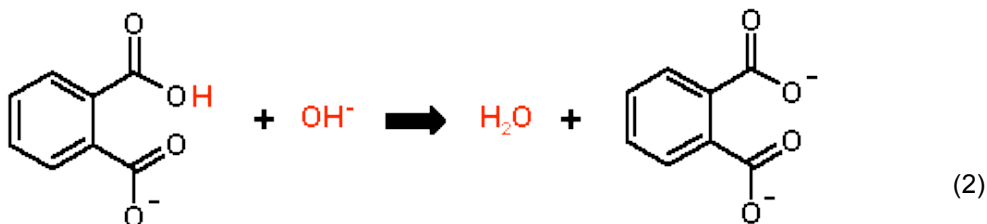
1. Weigh enough solid KHP into a 250 mL Erlenmeyer flask to require ~35 mL of 0.1 NaOH for titration.
2. Add ~75 mL of distilled water and a few drops of phenolphthalein indicator and titrate to the end-point, the first appearance of a pink color.
3. Perform at least three standardization titrations where the results agree to ±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,
unless you have already used the NaOH standard in a previous 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 **calculating 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.
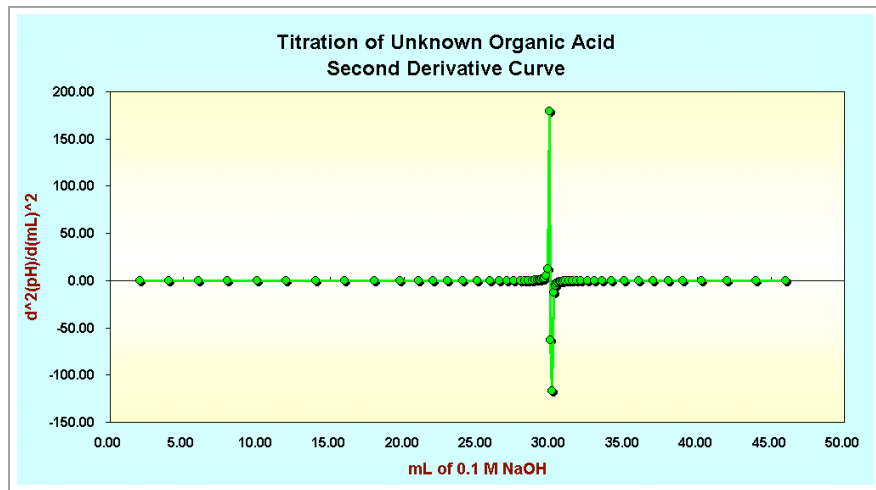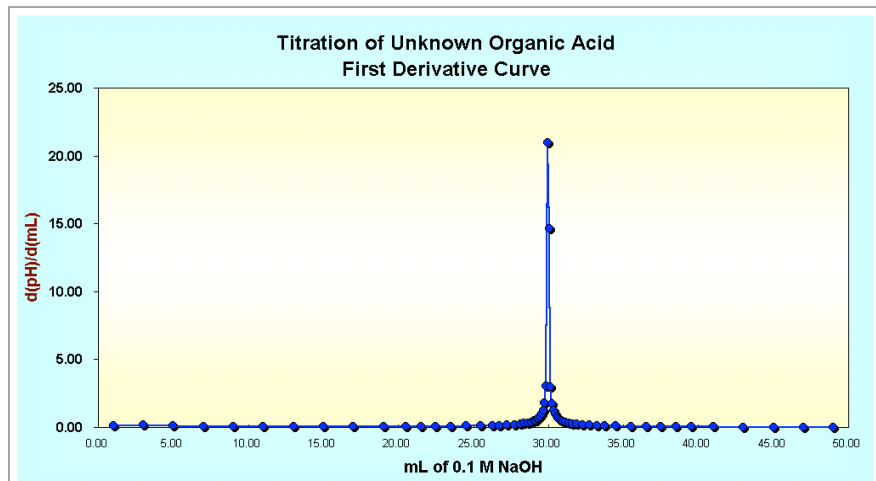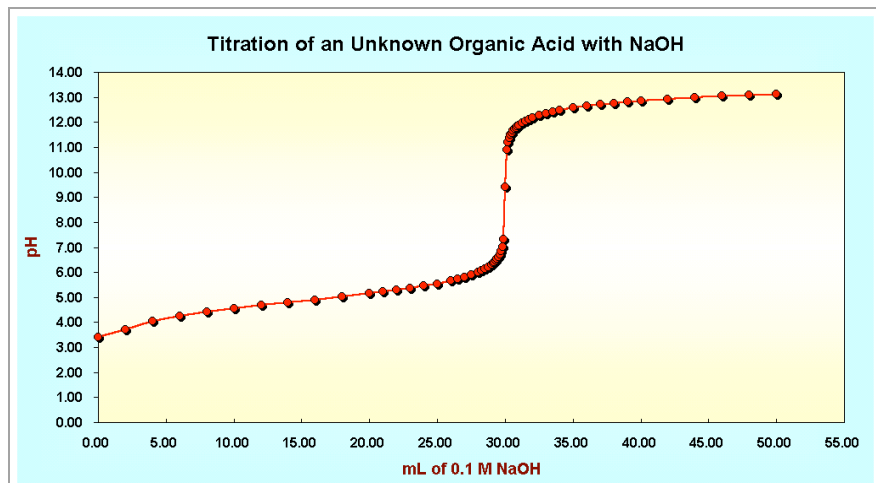
The numbers from your titration data that you use for calculations should come from these Excel graphs and calculations. Although you used the phenolphthalein indicator to observe the end point visually, the numerical pH data and inflection point data will give you better accuracy.

The worksheet **ACIDPLOT.xls**, a template for this experiment, can be downloaded from the course website. 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 under a new file name and start from a new template file to type in your second data set. Save the second titration data too. You should see plots (***tabs*** in the Excel workbook) like the figures on the following pages. These plots show the titration curve (NORMAL), first derivative (1DERIV), and second derivative (2DERIV) curves.

You will need to copy some of the data from ACIDPLOT.xls into the second template file, **ORGACID.xls** in order to calculate the equivalent weight and pKa of your unknown. This process is described in detail on the following pages.

What You Must Turn in as Your Lab Report:

•   Plots of the titration curves from ACIDPLOT.xls (the "normal" titration curve, the "1deriv" first derivative, and the "2deriv" second derivative graphs). You may choose the best titration to turn in.

•   Report sheet from ORGACID.xls with the equivalent weight and the pKa results that you are submitting for grading clearly labeled in the "best estimate" cells.

Titration of an Unknown Organic Acid with NaOH

Titration of Unknown Organic Acid
First Derivative Curve

Titration of Unknown Organic Acid
Second Derivative Curve

Look at the plots to get a rough idea of the equivalence point. The inflection point of the titration curve, the maximum peak in the plot of the first derivative, and the point at which the second derivative changes sign should all occur at the same volume of NaOH added during the titration, which is the equivalence point. Next, find that general number within your data (see below) and use the numerical data to find the exact equivalence point:

	A	B	C	D	E	F	G	H	I	J
	mL NaOH	pH	Δ(mL)	Δ (pH)	avg. mL	Δ (pH/mL)	Δ (mL)^2	Δ (ΔpH/mL)	avg. mL	Δ^2(pH)/Δ(mL)^2

For the **first derivative data**, the end point should be where the derivative is a **maximum**:

	A	B	C	D	E	F	G	H	I	J
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**:

	A	B	C	D	E	F	G	H	I	J
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. 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 the light blue boxes, and the "best estimate" cells in bright red font will be evaluated for your grade.

The second part of the experiment is to determine the ionization constant, K_a (pK_a), for the weak acid. Remember that at 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.
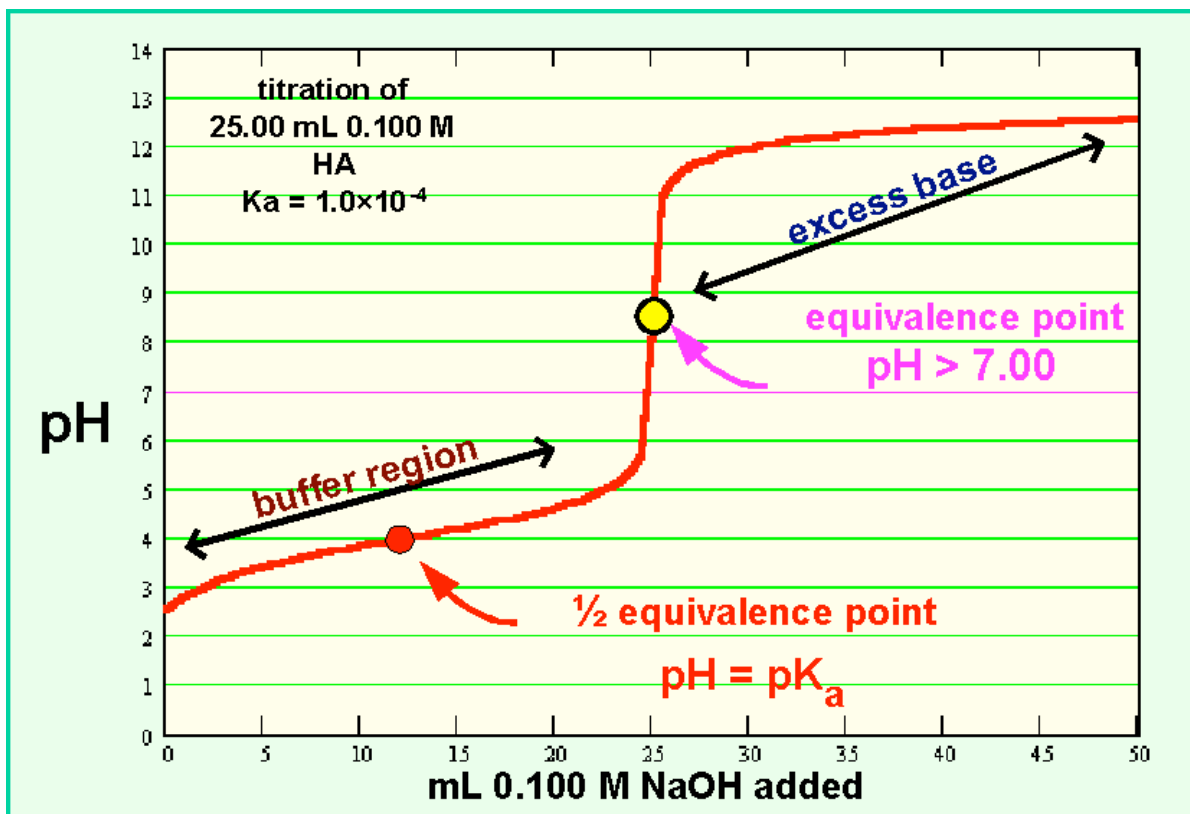
The pK_a values must be calculated from data taken near the half-equivalence point (half the value of the equivalence point you have already calculated). The total number of moles of acid can be calculated from the equivalence point and the concentration of the NaOH solution. At any point in the buffer 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.

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

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 the light blue boxes, and the "best estimate" cells in bright red font will be evaluated for your grade.

	sample weight	mL to end-point	equivalent weight
NaOH Concentration		0.1045 M	
Titration 1	0.2345	29.98	74.55
Titration 2	0.2456	30.25	77.69
Best estimate of equivalent weight			76.12

Calculation of pKa

Titration 1	End-point	29.98		
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		4.84		