> Victory awaits those who have everything in order. People call this luck. Defeat awaits those who fail to take the necessary precautions. This is known as bad luck.
> --Roald Amundsen

Weak acids and K_a

Strong acids, such as HCl, are said to dissociate 100% in water:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

Essentially no HCl molecules remain in the mixture and it does not respond to the changes which LeChâtelier's Principle describes as relevant to equilibrium systems. In contrast, a weak acid such as acetic acid dissociates in water to only a very small extent:

$$CH_3COOH + H_2O \leftrightarrows H_3O^+ + CH_3COO^-$$

In this, as in the case of other weak acids, the equilibrium at room temperature lies far to the left. Whether an acid is strong or weak depends on factors such as the strength of the bond connecting the ionizable hydrogen to the rest of the molecule and (in the case of oxyacids) other factors such as the number of oxygens and the identity of the central atom. However all weak acids share common behaviors based on the fact that relatively few ions exist in equilibrium with the molecular form of the acid. In this experiment you will investigate some of these behaviors and use a variety of techniques to determine the value of the equilibrium constant, K_a, for the reaction shown above.

One valuable tool in the investigation of weak acid behavior is titration. You have already seen how titration can be used to determine the Molarity of a strong acid solution. This technique is also valid for weak acids. However, carefully recorded pH data for a weak acid titration yields even more information. Consider the form of K_a for acetic acid:

$$\frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = K_a$$

As the titration proceeds, CH_3COOH is gradually converted into CH_3COO^- while water is formed. At the equivalence point, all of the original acid has been converted into the acetate ion. Logically, at the point half-way to the equivalence point, exactly half of the original acetic acid must have been converted to acetate ion. In other words, the concentrations of these two species are equal half-way to the equivalence point.

Since that is true, the following would also be true:

$$\frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = K_a$$

And so at this half-way point, the pH would equal the pK_a (or -log K_a). Because most K_a values are small, careful titration technique is needed to obtain accurate results.

It is also possible to obtain an estimate of the K_a for a weak acid by careful measurement of the pH of a solution with a known concentration (the concentration could be accurately established by titration) since for a monoprotic acid like acetic acid:

$$[H_3O^+] = [CH_3COO^-]$$

A carefully calibrated pH electrode will give enough information to calculate $[H_3O^+]$. This value can be used along with the Molarity of the acid to determine K_a, recalling that

	$CH_3COOH + H_2O \leftrightarrows H_3O^+ + CH_3COO^-$		
Start	M	0	0
Δ	-x	+x	+x
Equil	M-x	x	x

Knowing the $[H_3O^+]$ also allows determination of the % dissociation for the weak acid, defined as the part which has dissociated divided by the original concentration:

$$\frac{x}{M} \times 100 = \% \text{ dissociation}$$

Preparing to experiment

You will be provided with the following materials:

1. approx. 0.5 M CH_3COOH (use 10.0 mL for titration)
2. 10-fold dilution of solution in #1
3. 0.30 M NaOH
4. a magnetic stirrer and stirring bar
5. a pH electrode
6. pH buffers: 2, 3, 4, 10
7. a buret and clamp

Design an experiment to determine the exact Molarity of the acetic acid solution by titration, using a pH electrode.

Design an experiment to determine K_a and the % dissociation of the acetic acid solution by pH. Repeat the measurements on a 10-fold dilution of the original acid solution.

BE SURE TO BRING YOUR TI-83/84 CALCULATOR TO CLASS FOR THIS EXPERIMENT. YOU WILL ALSO NEED A COPY OF THE HCHEM.83G FILES IN YOUR CALCULATOR MEMORY.

Technique

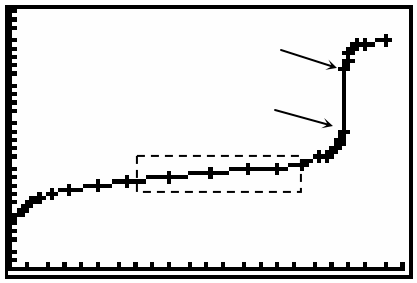
1. recording pH during titration

For this experiment you can use the GRAPHICAL option with the VS. USER X option to watch the progress of your titration if you wish. Graphing parameters would be : Ymax = 14, Ymin=0, Xmax = 20, Xmin = 0. Remember to aim for a pH change of about 0.2 units with each addition of base and to go about 2 mL beyond the equivalence point.

The rest of your measurements should be done in CONTINUOUS mode so that the titration data will not be erased from the calculator memory

Analysis

1. Use your titration data to determine the exact Molarity of the acetic acid solution. If you recorded your data carefully you might have a graph that looks something like the one below:



After reading the data into the lists (start with opening menu item 3, PROCESS DATA) the equivalence point can be readily determined by using the cursor keys on your calculator and tracing the curve to find the values indicated by the arrows. The average of the two volumes at these points should be very close to the equivalence point volume. Then you can determine the Molarity of the acid. **Be sure to include a properly labeled graph with your report.**

2. Use your titration data to determine the K_a of acetic acid. Referring to the graph shown in #1, the volume half-way to the equivalence point is in the more-or-less linear region enclosed by the dotted box. One way to get an accurate pH at the half-way volume from your graph is to erase all the data points from the lists except for those in this linear region. Then find the best-fit line equation and solve for the pH at half the equivalence point volume. Recall that at the half-way point, pH = pK_a or $[H_3O^+] = K_a$. **NOTE THAT THIS IS THE <u>ONLY</u> CONDITION UNDER WHICH THIS IS TRUE IN THIS EXPERIMENT**.

Alternative methods would be to plot a graph carefully by hand or use Excel to plot a graph with a fine scale so you can read values accurately.

3. Use your value of the pH for the original acid solution to calculate K_a and the % dissociation. **REMEMBER, THE pH ALLOWS YOU TO DETERMINE $[H_3O^+]$, NOT K_a DIRECTLY.** Compare these values with the known value for K_a (1.8×10^{-5}) and the calculated theoretical % dissociation for a solution with the Molarity you determined by titration. Comment on differences.

4. Determine K_a and the % dissociation for the <u>diluted</u> solution using the pH measurement. Compare to your results from #3. Explain the difference in % dissociation [*hint*: LeChâtelier's Principle].