

Identification of an Unknown Weak Acid by pH Titration

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(Rev 10/08, RFS)

Purpose of this Exercise: To identify an unknown weak acid by measuring its titration curve. From the titration curve, to determine the pK_a and molar mass of the acid, which will allow identification by comparison with a list of common weak acids.

Background Information

Weak acids are all around us. Earlier in this course, we determined their presence in a variety of juices and beverages. Organic weak acids are formed in many bacterial decomposition reactions of fats and oils; for example, rancid butter smells of butyric acid and unwashed sweatsocks smell of isobutyric acid. Citrus juices derive much of their tangy flavor from citric acid, and tartaric acid may form beautiful crystals on the cork of a wine bottle. Boric acid is used in eyewash, and sodium hydrogen sulfate in toilet cleaner.

Review: When a weak acid HA is dissolved in water, only a fraction of the acid molecules dissociate into $H^+(aq)$ and $A^-(aq)$ ions. Most of the acid molecules remain intact. However, the molecules and ions do not remain fixed as such; over any given time interval, some molecules will dissociate and some ions will recombine. This occurrence of forward and reverse reactions leads to a condition of balance, called equilibrium. In an equilibrium situation, the net concentrations of the species involved do not change.

The quantitative measure of the position of the equilibrium is called the equilibrium constant. For an acid dissociation, the equilibrium constant is called the acid dissociation constant, or K_a . It is defined as follows:



Equilibrium Expression: $K_a = [H^+][A^-] / [HA]$

In the equilibrium expression, the use of square brackets indicates the concentration of the chemical entity inside the brackets, expressed in moles per liter (or millimoles per milliliter), and symbolized as M. So $[H^+]$ means "concentration of H^+ in moles per liter." In the case of a weak acid, the actual value of K_a is a small number, indicating that only a small fraction of the acid is dissociated into ions at any given time. For acetic acid, for example, K_a is about 1.75×10^{-5} in water at room temperature. Since use of exponential numbers is rather clumsy, we often use the negative log of the K_a , or pK_a , instead of the K_a . The pK_a of acetic acid is 4.75.

How do we measure such a small number? A weak acid, even though it does not spontaneously dissociate to a very large extent, may react completely with a strong base such as hydroxide ion. You already know that you can determine the concentration of a weak acid by titrating with

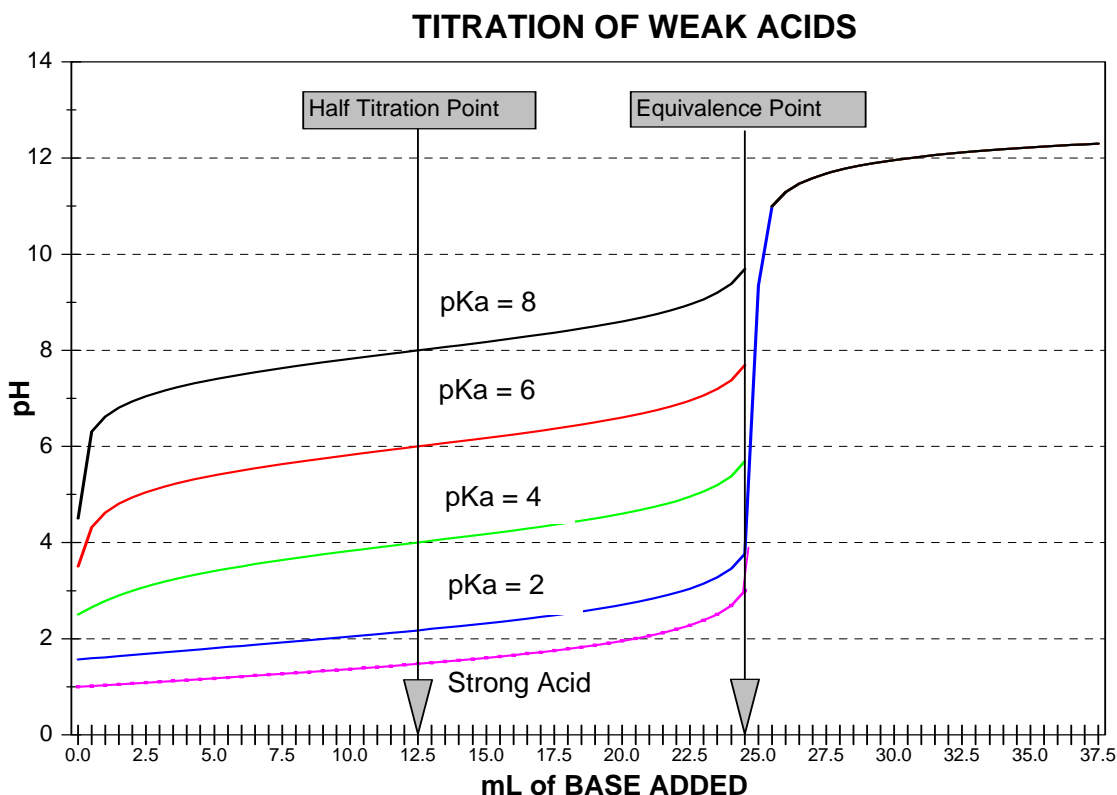
sodium hydroxide solution. When the number of moles of hydroxide added equals the number of moles of acid present, the pH ($\text{pH} = -\log [\text{H}^+]$) rises abruptly, which can be detected by use of an indicator whose color changes with pH, or by use of a pH meter.

For a sufficiently weak acid, what is the result of adding exactly half as many moles of hydroxide ion as there are moles of acid present? We might expect that half of the acid will be neutralized. The concentrations of HA and A^- in the resulting half-neutralized solution will be equal: $[\text{HA}] = [\text{A}^-]$. Let us call this concentration \mathbf{X} , so that $[\text{HA}] = [\text{A}^-] = \mathbf{X}$. Then, going back to the definition of K_a ,

$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}] = [\text{H}^+]\mathbf{X}/\mathbf{X} = [\text{H}^+].$$

This result shows that the K_a is equal to $[\text{H}^+]$, the hydrogen ion concentration, in a solution where the concentrations of un-ionized acid, HA, and acid anion, A^- , are equal. Also, $\text{pH} = \text{p}K_a$.

Therefore, to determine the K_a of an acid, all we need to do is to titrate the acid with NaOH solution, and to carefully record the pH as a function of volume of base added. We can plot the resulting data in the form of a graph, called a titration curve. When we reach the point of equivalence and the pH rises sharply, we know that the number of moles of base added equals the number of moles of acid originally present. **If we look back at the titration curve to the point where we have added exactly half as much base as was required for complete neutralization, then the $[\text{H}^+]$ at that point equals the K_a , and the pH at that point equals the** $\text{p}K_a$.*



A full discussion of this approximation is given on the web at <http://www.ic.sunysb.edu/Class/che134/lectures/phpkahalftitr.pdf>

1. Review the procedures for use of pH meters in **SUPL-006**
2. Record the sample number of your unknown acid, and transfer the identifying sticker to your data sheet. *Accurately* weigh out approximately 0.2 g. of unknown into a clean Erlenmeyer flask by difference. Record the mass in your notebook.
3. Dissolve the acid sample in about 40 mL of distilled water, warming gently, if necessary, to insure complete dissolution. Cool the solution to room temperature.
4. Bring no more than 100 mL of standardized NaOH solution to your workplace. Keep your solution covered when not in use. Rinse a buret with about 10 mL of standardized NaOH solution, and then fill it to near the top of the graduated portion. **Record the concentration of the base from the dispensing container**, and record your initial buret reading.
5. In a preliminary run, add two or three drops of phenolphthalein solution to the flask, and titrate the acid solution to the point where a faint pink phenolphthalein color just persists. Calculate a molar mass based on this preliminary titration.
6. Calculate the weight range of your unknown that will require 25 ± 3 mL of base. Weigh out, again in a *clean* 150 mL beaker, the appropriate amount of unknown acid, and record the mass in your notebook. After you have weighed the sample, compute the volume of base you should expect to use for this (actual) mass of acid. Keep this volume in mind as you perform the pH titration.
7. Again, dissolve the unknown acid in about 40 mL of distilled water, warming if necessary.
8. With the pH meter set at **STANDBY**, rinse the pH meter electrode with distilled water, using a squeeze bottle containing distilled water and a spare beaker to catch the washings. Place the electrode into your acid solution, so that the tip of the electrode is fully immersed, but not touching the bottom of the beaker. Refill your buret with standard NaOH solution, and mount it so that it will deliver solution into your beaker. Take the initial buret reading and record it. As you proceed, enter the results in the table in your notebook showing buret reading, total net volume added, and pH after each addition.
9. Turn the knob on the pH meter to the **pH** position, and record the initial pH reading.
10. Add a portion, perhaps 2-3 mL, of NaOH solution, and record the volume reading (as always read to the nearest 0.02 mL) and pH reading. **Be sure to stir the solution with a stirring rod after each addition of base but before making the pH reading.**
11. Add additional portions of NaOH solution, stir the solution and take volume and pH readings after each addition. The volume readings you record should be the actual buret readings, not the incremental ones. You will subtract the initial reading later.

12. When you are within 2 mL of the equivalence point (refer to your calculation from part 6 above), the pH will rise more rapidly, and you should now add smaller increments of NaOH solution between readings. Within ± 1 mL of the equivalence point, ***and only in that region***, you should take readings drop by drop.
13. After you have passed the equivalence point, add at least two or three additional portions of NaOH solution and continue to take readings as before, in order to define the upper region of the titration curve. *Go at least 10 mL past the equivalence point.*
14. Return the pH meter to **STANDBY** and remove the electrode from your solution. Rinse it with distilled water, and leave it standing in distilled water for the next user.
15. Using careful graphing technique (as described in SUPL-004*#), construct a titration curve, **remembering to subtract the initial buret reading from each subsequent reading to get actual volume added**. Connect your experimental points with a *smooth curve*. If you choose to plot your titration curve using a computer, be sure that the graph you produce satisfies the guidelines for graphs described in SUPL-004 – in particular, that it fills at least $2/3$ of an $8\frac{1}{2}$ by 11 inch sheet of paper in landscape mode.
16. Determine from the graph the equivalence point, which is the point of steepest ascent of the curve. Record the volume of NaOH solution added at that point, and calculate the molar mass of your unknown acid from that volume.
17. Divide this volume by 2, and mark this half-neutralization point on your volume axis. Draw a vertical line which intercepts your titration curve, then a horizontal line from the point of intersection over to the pH axis. Determine the pH at this point; this is also the pK_a of your unknown acid.
18. If the curve you obtain has significant irregularities, you probably did not stir the solution sufficiently after each addition of base. Repeat the pH titration.
19. Consult Table I to find an acid which matches yours in both molar mass and in pK_a . A reasonable match in both parameters will constitute good evidence of identity. You should use your **most reliable values** of the equivalent molar mass and pK_a in reaching your conclusion. You may wish to repeat the phenolphthalein titration if the equivalent molar mass computed from the first run differs substantially from that determined using the pH titration graph.

SUPL-004 is available on the course web site.

TABLE I: WEAK ACIDS

COMPOUND	FORMULA	MOLAR MASS	pK_a[#]
Acetic acid	HC ₂ H ₃ O ₂	60.0	4.8
Propanoic acid	HC ₃ H ₅ O ₂	74.1	4.9
Crotonic acid	HC ₄ H ₅ O ₂	86.1	4.7
dl-Lactic acid	HC ₃ H ₅ O ₃	90.1	3.9
Chloroacetic acid	HC ₂ ClH ₂ O ₂	94.5	2.9
Maleic acid	H ₂ C ₄ H ₂ O ₄	116.1	1.8, 5.9
Succinic acid	H ₂ C ₄ H ₄ O ₄	118.1	4.2, 5.6
Oxalic acid dihydrate	H ₂ C ₂ O ₄ ·2H ₂ O	126.1	1.2, 4.2
Potassium hydrogen oxalate	KHC ₂ O ₄	128.5	4.2
Glutaric acid	H ₂ C ₅ H ₆ O ₄	132.1	4.3, 5.2
dl-Malic acid	HC ₄ H ₄ O ₅	134.1	3.4, 5.0
Potassium dihydrogenphosphate	KH ₂ PO ₄	136.1	7.2, 12.7
Potassium bisulfate	KHSO ₄	136.2	1.9
Sodium bisulfate hydrate	NaHSO ₄ ·H ₂ O	137.4	1.9
Sodium dihydrogenphosphate	NaH ₂ PO ₄ ·H ₂ O	138.0	7.2, 12.7
Adipic acid	H ₂ C ₆ H ₈ O ₄	146.1	4.3, 4.4
dl-Mandelic acid	HC ₈ H ₇ O ₃	152.1	3.4
dl-Tartaric acid	H ₂ C ₄ H ₄ O ₆	168.1	3.0, 4.2
Sulfanilic acid	HC ₆ H ₆ NO ₃ S	173.2	3.2
Potassium hydrogen tartrate	KHC ₄ H ₄ O ₆	188.1	4.3
Sodium hydrogen tartrate	NaHC ₄ H ₄ O ₆ ·H ₂ O	190.1	4.3
Sulfanilic acid hydrate	HC ₆ H ₆ NO ₃ S·H ₂ O	191.2	3.2
Potassium hydrogen phthalate	KHC ₈ O ₈	204.2	5.5

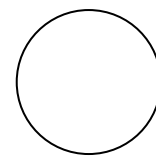
The pK_a values in the table should be viewed as approximate. Measured values may differ from the tabulated values by ± 0.5 units or more.

SUSB-014 Data Sheet

Notebook Grade: _____

Safety Grade: _____

Name	Section	Date
Conc. of NaOH solution from label	_____ M.	_____ M.
	<u>Run 1</u>	<u>Run 2 (pH titration)</u>
Initial Mass of vial	_____ g	_____ g
Final Mass of vial	_____ g	_____ g
Mass of acid sample	_____ g	_____ g
Mass of acid sample	_____ mg	_____ mg
Calculated volume of NaOH required		_____ mL
Final buret reading	_____ mL	
Initial buret reading	_____ mL	
Net Volume of NaOH sol'n. at equivalence point	_____ mL	_____ mL(graph)
Millimoles of NaOH	_____ mmol	_____ mmol
Millimoles of acid	_____ mmol	_____ mmol
Molar mass of unknown acid	_____ mg/mmol	_____ mg/mmol



Weight of acid for 25 mL of NaOH in Part 2 _____ mg

Volume of NaOH sol'n at half-equivalence point	_____ mL(graph)
pH of solution at half-equivalence point	_____ (graph)
pK _a of unknown acid	_____

Identity of unknown acid: _____

Attach your pH titration curve. Be sure the relevant points are clearly labeled.

