

Determining the Acid Dissociation Constant, K_a , for a Weak Acid

Objective: To determine the dissociation constant, K_a , for a weak acid using pH measurements to use the calculated K_a to identify the unknown acid

Materials: 0.500 M NaOH; 1.00 M unknown weak acid; pH=7.00 standard buffer solution (additional buffers at pH=4.00 and/or pH=10.00, if available)

Equipment: Two 50-mL burets; 250-mL volumetric flask; two 250-mL Erlenmeyer flask; pH stick electrode or pH meter

Safety: NaOH solutions are caustic and corrosive, and should be handled with care. Gloves may be worn if available in the lab. Weak acid solutions can be irritants. Lab goggles should be worn at all times.

Waste Disposal: Most solutions can be discarded in the sink with plenty of water, unless instructed otherwise by your lab TA/instructor.

INTRODUCTION

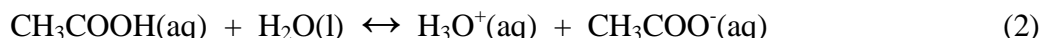
Acids and bases play a significant role in many areas of chemistry and biochemistry. We can classify substances as acids and bases based on chemical behavior. The definition of an **Arrhenius acid** is a substance that produces hydronium ions (H_3O^+) in aqueous solution, while an **Arrhenius base** is a substance that produces hydroxide ions (OH^-). A more useful definition of acids and bases is based on the Brønsted-Lowry theory. A **Brønsted-Lowry acid** is defined as a substance that acts as a proton donor, while a **Brønsted-Lowry base** acts as a proton acceptor.

Consider the behavior of hydrochloric acid illustrated in Eq. (1).



In this reaction, the acid HCl donates a proton (i.e., H^+) to a water molecule (the base) to produce the ions H_3O^+ and Cl^- . HCl is a **strong acid**, which means that ionization is essentially complete; nearly 100% of the HCl in solution has been converted to H_3O^+ and Cl^- ions.

By contrast, **weak acids** are substances that only ionize to a slight extent. Consider the ionization of acetic acid (CH_3COOH), the major component of vinegar, shown in Eq. (2).



In this case only about 1% of the acetic acid dissociates into ions. An equilibrium state, indicated by the double-headed arrow, exists between the undissociated acid on the left and the

ions on the right. The extent of dissociation is indicated by the value of the acid dissociation constant, or K_a , which is calculated as

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} \quad (3)$$

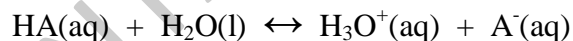
The square brackets ([]) indicate the molar concentrations of the products and reactants at equilibrium. Although water appears as a reactant, its concentration remains essentially constant at 55.5 M in dilute solutions and is not included in the expression for K_a . Acid dissociation constants for several weak acids (at 25°C) are included in Table 1.

Table 1. Acid dissociation constant (K_a) values for some weak acids at 25 °C.

Weak Acid	Formula	K_a
Acetic acid	CH ₃ COOH	1.7 x 10 ⁻⁵
Boric acid	B(OH) ₃	5.8 x 10 ⁻¹⁰
Chloroacetic acid	CH ₂ ClCOOH	1.4 x 10 ⁻³
Crotonic acid	CH ₃ (CH) ₂ COOH	2.0 x 10 ⁻⁵
Formic acid	HCOOH	1.8 x 10 ⁻⁴
Bicarbonate ion	HCO ₃ ⁻	4.8 x 10 ⁻¹¹
Dihydrogen phosphate ion	H ₂ PO ₄ ⁻	6.2 x 10 ⁻⁸
Hydrogen phosphate ion	HPO ₄ ²⁻	1.7 x 10 ⁻¹²
Hydrogen sulfide ion	HS ⁻	5.6 x 10 ⁻⁸
Propionic acid	CH ₃ CH ₂ COOH	1.4 x 10 ⁻⁵

Calculating K_a from pH Measurements

Consider the dissociation equilibrium and K_a expression for a generic weak acid:

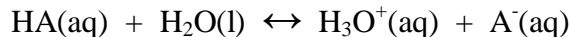


$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad (4)$$

If we know the initial concentration of the weak acid and the extent of ionization, then we can calculate the equilibrium concentrations of the acid and ions, and use Eq. (4) to calculate K_a . This approach is demonstrated in Example 1.

Example 1. A 0.12 M solution of unknown weak acid has a pH = 3.38. Calculate the value of K_a for this acid.

We can derive expressions for the equilibrium concentration by setting up a reaction table as follows:



Initial conc.:	0.12 M	---	---
Change:	- x	+x	+x
at equilibrium:	(0.12 - x)	(x)	(x)

Substituting these equilibrium expressions into the expression for K_a yields

$$K_a = \frac{[x][x]}{[0.12 - x]}$$

If we know the value of x we can calculate K_a . Since the pH of the solution is known, we can use the pH to calculate $[\text{H}_3\text{O}^+]$ using Eq. (5). Since $[\text{H}_3\text{O}^+]$ is equal to x in our reaction table, we can now calculate K_a .

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-3.38} = 4.17 \times 10^{-4} \quad (5)$$

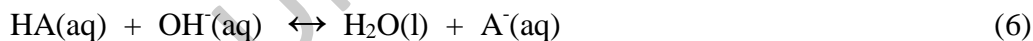
And

$$K_a = \frac{[x][x]}{[0.12 - x]} = \frac{[4.17 \times 10^{-4}]^2}{\sim(0.12)} = 1.45 \times 10^{-6}$$

Note that the value of x in Example 1 is negligible compared to the initial concentration of the weak acid, so it can be ignored in the denominator of the K_a expression without introducing significant error in the result. If the value of K_a is $>10^{-3}$ the extent of dissociation may not be negligible, however, and a more rigorous mathematical treatment may be necessary.

Calculating K_a from Partial Neutralization Data

A variation on the method described in the previous section involves performing pH measurements following the partial neutralization of the weak acid with OH^- . A general equation showing this reaction is shown in Eq. (6).



Because the reaction of OH^- with HA goes essentially to completion, the number of moles of A^- formed is equal to the number of moles of OH^- added to the solution. Likewise, the number of moles of HA remaining at equilibrium is equal to the initial number of moles of HA minus the number of moles of OH^- added. Because the concentration of A^- present in solution is now significantly larger than in Example 1, additional ionization of HA is suppressed and any unneutralized HA remains in the undissociated form.

The method for calculating K_a after partial neutralization is illustrated in Example 2.

Example 2. A 50.0 mL sample of 0.12 M weak acid is partially neutralized by addition of 20.0 mL of 0.10 M NaOH. Deionized water was added to adjust the total volume to 150.0 mL. The final solution has a pH = 5.32. Calculate K_a for this acid.

First we determine the number of moles of acid present initially, and the number of moles of OH⁻ added by Eqs. (7) and (8). With this information we can then calculate the concentrations of HA and A⁻ remaining in solution using Eqs. (9) and (10).

$$\text{Initial moles of HA} = (0.0500 \text{ L})(0.120 \text{ Mol/L}) = 0.00600 \text{ mol HA} \quad (7)$$

$$\text{Moles of OH}^- \text{ added} = (0.0200 \text{ L})(0.10 \text{ Mol/L}) = 0.00200 \text{ mol OH}^- \quad (8)$$

$$[\text{HA}] = \frac{(\text{initial moles HA} - \text{moles OH}^- \text{ added})}{\text{total volume (L)}} = \frac{0.0040 \text{ mol}}{0.1500 \text{ L}} = 0.0267 \text{ M} \quad (9)$$

$$[\text{A}^-] = \frac{(\text{moles OH}^- \text{ added})}{\text{total volume (L)}} = \frac{0.00200 \text{ mol}}{0.1500 \text{ L}} = 0.0133 \text{ M} \quad (10)$$

With these concentrations in hand, we can use the pH to obtain the $[\text{H}_3\text{O}^+]$, and substitute these concentrations into Eq. (4) to calculate the K_a .

$$[\text{H}_3\text{O}^+] = 10^{\text{pH}} = 10^{-5.32} = 4.79 \times 10^{-6}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(4.79 \times 10^{-6} \text{ M})(0.0133 \text{ M})}{(0.0267 \text{ M})} = 2.4 \times 10^{-6}$$

Determining K_a by Graphical Analysis of Neutralization Data

One advantage of graphical analysis is that we arrive at an answer by extrapolation from multiple data points. Thus, errors associated with individual measurements do not have a large influence on the final result. We can use pH data from a series of neutralization solutions to perform a graphical analysis to determine K_a .

Consider again the expression for K_a in Eq. (4). Since the equilibrium concentration of HA can be calculated as the initial concentration of HA minus the equilibrium concentration of A⁻, we can rewrite Eq. (4) as shown in Eq. (11),

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{B - [\text{A}^-]} \quad (11)$$

where B represents the initial concentration of the weak acid in the neutralization solution, as calculated in Example 2. We can rearrange Eq. (11) in several steps as outlined below:

1. Isolate the $[\text{H}_3\text{O}^+]$ by cross-multiplication:

$$[\text{H}_3\text{O}^+] = \frac{(K_a)(B - [\text{A}^-])}{[\text{A}^-]} = \frac{K_a(B)}{[\text{A}^-]} - K_a$$

2. Divide both sides by ($K_a \cdot B$):

$$\frac{[H_3O^+]}{K_a B} = \frac{1}{[A^-]} - \frac{1}{B}$$

3. Rearrange to isolate the $1/[A^-]$ term:

$$\frac{1}{[A^-]} = \frac{[H_3O^+]}{K_a B} + \frac{1}{B} \quad (12)$$

Equation (12) takes the form of a straight line equation, $y = mx + b$. When the values of $1/[A^-]$ are plotted vs $[H_3O^+]$ for a series of neutralization solutions, the slope of the resulting plot would be $m = 1/(K_a B)$, and the intercept would be equal to $1/B$. The slope can be calculated as:

$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{\text{change in } 1/[A^-]}{\text{change in } [H_3O^+]} \quad (13)$$

Once the slope is known, we can calculate K_a from Eq. (12):

$$\text{slope} = \frac{1}{K_a B} \rightarrow K_a = \frac{1}{(\text{slope})(B)} \quad (14)$$

This approach is illustrated in Example 3.

Example 3. A student determined the K_a of a weak acid using the graphing method. She prepared three different neutralization solutions using the volumes and concentrations of HA and NaOH listed in Table 2. After measuring the pH of these solutions, she calculated the initial $[HA]$ and equilibrium concentrations of HA, A^- and H_3O^+ as indicated in the table.

The student then plotted these data to produce the graph in Figure 1. Using the data for Solutions 1 and 3, she calculated the slope using Eq. (13).

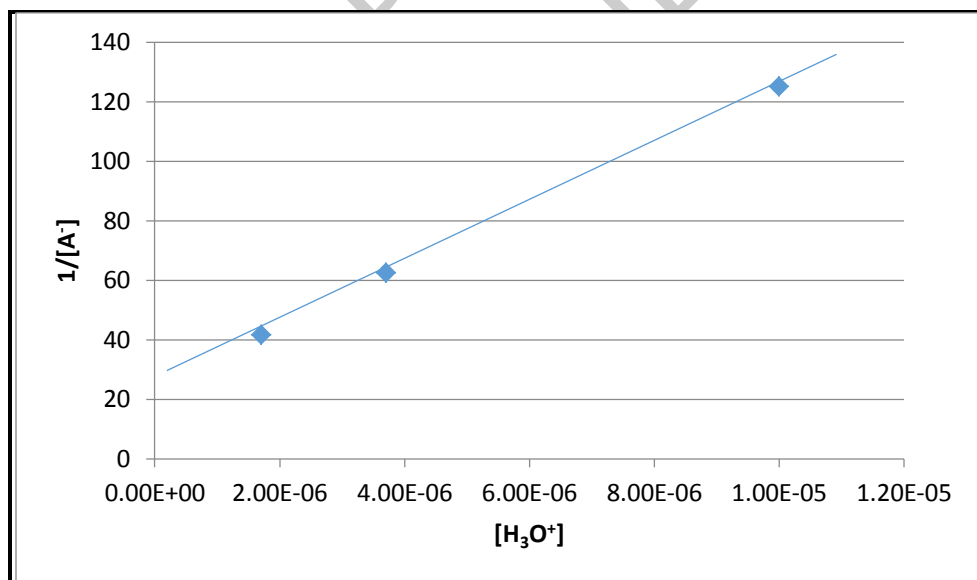
$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{\text{change in } 1/[A^-]}{\text{change in } [H_3O^+]} = \frac{(125 - 41.7)}{(1.0 \times 10^{-5} - 1.7 \times 10^{-6})} = \frac{83.3}{(8.3 \times 10^{-6})} = 1.0 \times 10^7$$

From the slope, she used Eq. (14) to calculate K_a :

$$K_a = \frac{1}{(\text{slope})(B)} = \frac{1}{(1.0 \times 10^7)(0.0400)} = 2.5 \times 10^{-6}$$

Table 2. Neutralization Solution Data and Equilibrium Concentrations

	<i>Solution 1</i>	<i>Solution 2</i>	<i>Solution 3</i>
<i>Volume of 0.500 M HA, mL</i>	20.0	20.0	20.0
<i>Volume of 0.200 M NaOH, mL</i>	10.0	20.0	30.0
<i>Final volume of solution, mL</i>	250	250	250
<i>pH =</i>	5.00	5.43	5.78
<i>Initial moles of HA, mol</i>	0.0100	0.0100	0.0100
<i>Initial moles of OH</i>	0.0020	0.0040	0.0060
<i>Initial [HA] =</i>	0.0400 M		
<i>Equilibrium values:</i>			
<i>(from Eq. (7)) [HA]=</i>	0.0320	0.0240	0.0160
<i>(from Eq. (8)) [A⁻] =</i>	0.0080	0.0160	0.0240
<i>(from Eq. (5)) [H₃O⁺] =</i>	1.0 x 10 ⁻⁵	3.7 x 10 ⁻⁶	1.7 x 10 ⁻⁶
<i>1/[A⁻] =</i>	125	62.5	41.7

Figure 1. Graphical Analysis of Neutralization Solution Data for Weak Acid

In this experiment you will prepare several neutralization solutions using known amounts of a weak acid and NaOH. From the pH data and equilibrium concentrations of HA and A⁻ you will calculate K_a using both methods: the neutralization pH data as illustrated in Example 2, and the graphing method as illustrated in Example 3.

Pre-Lab Questions

1. A student performing this experiment spilled a small amount of 0.500 M NaOH on the bench top. Describe the procedures to be followed to clean up this spill.

2. A student is trying to identify an unknown acid. The label on the acid bottle says 0.15 M, but the identity of the acid on the label has been obscured. The student prepares a solution by taking 50.0 mL of the acid, adding 20.0 mL of 0.05 M NaOH, and diluting the mixture to a final volume of 150.0 mL. The pH of the solution was 4.28. Calculate the K_a for this unknown acid. Show all work.

3. The student in Question 2 forgot to calibrate the pH meter before performing the analysis. The pH reading was 0.12 pH units higher than the actual pH.
 - (a) What was the real K_a for the unknown acid?

 - (b) Calculate the percent error that resulted from the uncalibrated pH meter.

PROCEDURE

1. Clean two 50-mL burets and a 250-mL volumetric flask. Rinse each buret and the volumetric flask with three separate 10-mL portions of de-ionized water.
2. Obtain 180 mL of a 1.00 M weak acid solution in a clean, dry 250-mL Erlenmeyer flask. Record the unknown ID and exact molarity of the solution on your Data Sheet.
3. Rinse one of the burets with a 5-mL portion of the unknown weak acid solution, making sure to coat as much of the inner surface of the buret as possible with the acid solution. Drain the solution through the tip of the buret into a waste beaker. Repeat this rinse procedure with two more 5-mL portions of the weak acid, and collect the waste in the waste beaker.
4. Close the stopcock on the buret and fill the buret above the zero calibration mark with the unknown acid. If any air bubbles are visible in the buret, tap the side of the buret gently to remove the bubbles from the wall of the buret and allow the bubbles to rise to the top. Briefly open the stopcock and allow a small amount of solution to drain from the buret to ensure that the buret tip is filled with the weak acid solution. If the solution level is above the zero calibration mark on the buret, open the stopcock slightly and allow solution to drain from the buret until the meniscus level is on or below the zero mark. Gently touch the buret tip to the side of your beaker to remove any hanging droplets. Record the buret volume reading on your Data Sheet to the nearest 0.01 mL.
5. Obtain 140 mL of the 0.500 M NaOH solution in another clean, dry 250-mL Erlenmeyer flask. Record the actual molarity of the NaOH on your Data Sheet.
6. Using the same procedure as outlined in Step 3, rinse and fill the other 50-mL buret with 0.500 M NaOH solution. Collect the rinse solutions in your waste beaker. Record the initial buret volume reading of the NaOH solution on your Data Sheet.
7. Prepare Solution 1 by adding 40.00 mL of the unknown acid from the buret to a clean, dry 250-mL volumetric flask. Record the final buret reading to the nearest 0.01 mL on your Data Sheet. Add 12.50 mL of NaOH solution from the buret to the acid solution in the 250 mL volumetric flask. Record the final buret volume to the nearest 0.01 mL on your Data Sheet.
8. Add deionized water to the solution in the 250-mL volumetric flask until the bottom of the meniscus is level with the base of the neck of the flask. Stopper the flask and mix the solution by inverting the flask several times. Be sure to firmly hold the stopper in place with your forefinger while mixing the solution.
9. Allow any air bubbles in the solution to rise to the top of the flask. Add deionized water to the flask until the bottom of the meniscus is level with the calibration mark on the neck of the volumetric flask. Stopper the flask and mix the solution again by inverting the flask several times while holding the stopper in place. Label the flask "Solution 1."
10. Turn on your pH meter or stick electrode and allow it to warm up for several minutes. Carefully rinse the glass electrode in the pH meter with deionized water from a wash bottle. Then obtain 50 mL of the pH=7.00 buffer solution in a clean, dry 100-mL beaker.

11. Use the pH=7.00 standard buffer solution to calibrate your pH meter using the following procedure or the instructions supplied by your lab instructor or TA.
 - a. Measure the temperature of your buffer solution, and set the temperature compensation knob on your pH electrode to match the solution temperature.
 - b. Carefully immerse the pH electrode in the pH=7.00 buffer solution and turn the function knob to “pH.” Allow the pH electrode reading to stabilize, then adjust the pH display until the pH reading matches the pH of your standard solution.
 - c. If available, repeat the procedure in steps 11a. and 11b. with the other standard pH buffer solutions (pH=4.00/10.00). When the pH meter reading is stable in all solutions, the calibration is complete.
 - d. Turn the function knob to “Standby.” Carefully remove the pH electrode from the buffer solution and rinse with de-ionized water from a rinse bottle.
12. Pour about 50 mL of Solution 1 into a clean, dry 100-mL beaker. Place the pH electrode in this solution and turn the function knob to “pH”. Read the pH of the solution to the nearest 0.01 pH unit and record this pH value on your Data Sheet.
13. Discard the solution in the beaker and in the volumetric flask as instructed. Wash and rinse the beaker and volumetric flask with deionized water.
14. Using the amounts of reagents indicated in Table 3, repeat Steps 7–13 to prepare and measure the pH of Solutions 2–4.

Table 3. Reagent Volumes for Neutralization Solutions

Solution Number	Volume of 1.0 M weak acid, mL	Volume of 0.500 M NaOH, mL
1	40.00	12.50
2	40.00	25.00
3	40.00	37.50
4	40.00	50.00

CALCULATIONS

Perform the following calculations for Solutions 1–4 and record your results on the Calculations sheet for Solutions 1–4.

1. Calculate the volumes of unknown acid (HA) and NaOH used in preparing Solutions 1–4.
2. Calculate the initial number of moles of HA and OH⁻ in Solutions 1–4 using Eqs. (7) and (8).
3. Record the number of moles of A⁻ ion in each solution at equilibrium. This should be equal to the number of moles of OH⁻ ion added from Eq. (8).

- Determine the number of moles of HA remaining in each solution at equilibrium as the difference between the results obtained for Eqs. (7) and (8).
- Calculate the equilibrium concentration of HA in each solution using Eq. (9).
- Calculate the $[A^-]$, using Eq. (10), and the $1/[A^-]$ values for each solution at equilibrium.
- Calculate the $[H_3O^+]$ at equilibrium for each solution from the pH readings, using Eq. (5).
- Using the equilibrium concentrations of HA, A^- , and H_3O^+ for each solution, calculate the value of K_a for your weak acid. Record the K_a for each determination, and calculate the average K_a value for your weak acid.
- To calculate K_a using the graphical method, prepare a graph by plotting $1/[A^-]$ vs. $[H_3O^+]$ for Solutions 1–4. Draw the best straight line through the data. Determine the slope of the line using Eq.(13) and calculate the value of K_a using Eq. (14). Alternatively, you can plot the data using spreadsheet software (e.g., Excel), and calculate the slope using a trend line or regression function.

Data Sheet

Unknown acid ID: _____

Molarity of unknown acid: _____

Molarity of NaOH: _____

		<i>Solution</i>			
	1	2	3	4	
<i>Unknown acid solution</i>					
Final buret reading, mL	_____	_____	_____	_____	
Initial buret reading, mL	_____	_____	_____	_____	
Volume of unknown acid, mL	_____	_____	_____	_____	
<i>NaOH solution</i>					
Final buret reading, mL	_____	_____	_____	_____	
Initial buret reading, mL	_____	_____	_____	_____	
Volume of NaOH solution, mL	_____	_____	_____	_____	
Total volume of solution, mL	_____	_____	_____	_____	
pH of solution	_____	_____	_____	_____	

Calculations

	<i>Solution</i>			
	1	2	3	4
<i>Initial number of moles</i>				
HA (aq)	_____	_____	_____	_____
OH ⁻ (aq)	_____	_____	_____	_____
<i>Number of moles at equilibrium</i>				
HA(aq)	_____	_____	_____	_____
A ⁻ (aq)	_____	_____	_____	_____
<i>Equilibrium concentrations</i>				
HA(aq)	_____	_____	_____	_____
A ⁻ (aq)	_____	_____	_____	_____
H ₃ O ⁺ (aq)	_____	_____	_____	_____
1/[A ⁻]	_____	_____	_____	_____
K _a	_____	_____	_____	_____
Average K _a =	_____			

Graphical Determination of K_a

Slope of line: _____

K_a (calculated from slope): _____

Post-Lab Questions

1. Based on your calculated value of K_a , what is the identity of your unknown acid?
2. Based on the accepted values of K_a for your unknown acid in Table 1, calculate the percent error in your graphical determination of K_a .
3. Calculate the percent error in the average K_a value obtained from the equilibrium ion concentrations for Solutions 1–4.
4. The equations used in this experiment assume that the amount of dissociation after neutralization is negligible compared to the remaining concentration of HA. These equations would have to be modified for acids having $K_a > 1.0 \times 10^{-3}$. Explain the problems that would arise (i.e., how the calculated value of K_a be affected) and the modifications that would be necessary to produce accurate results.