Determining Molar Mass of an Unknown Acid by Titration

Objectives: To learn the technique of titration, and apply it to determine the molar mass of an unknown weak acid by titration with sodium hydroxide

Materials: Three 250-mL Erlenmeyer flasks, one 250-mL beaker, a sample bottle, 50-mL buret, 0.100 M NaOH solution (standardized sodium hydroxide), phenolphthalein indicator, pH meters, standard buffer solutions (pH = 4.00, 7.00, 10.00, if available), stirring plate with stirring magnet, samples of unknown acids

Safety: Sodium hydroxide solution is very caustic! It can cause skin burns and is extremely damaging if it gets in your eyes. Acid solutions are also corrosive and can cause irritation if in contact with skin, eyes, and clothing. Always wear safety glasses when working at the bench with sodium hydroxide or acid solutions.

Waste Disposal: All solutions may be washed down the sink with plenty of water at the completion of the titrations.

INTRODUCTION

The determination of **molar mass** represents an important step in the identification of an unknown substance. There are many methods to obtain this vital information that are related to physical properties (vapor pressure, osmotic pressure), while others rely on chemical behavior, such as reactions of known stoichiometry. In this lab you will determine the molar mass of an unknown acid based on its reaction with a known quantity of base.

The concept of acid-base behavior is one of the most fundamental in chemistry, with important applications in biochemistry and industry. There are many ways to define acid-base behavior, but the most common involves the behavior of a substance in aqueous solution: an acid generates hydronium ions (H_3O^+), while a base generates hydroxide ions (OH^-).

Acid: $HCl(aq) + H_2O(l) \rightarrow \mathbf{H_3O^+}(aq) + Cl^-(aq)$

Base: $NaOH(aq) \rightarrow Na^+(aq) + \mathbf{OH^-}(aq)$

Acids and bases are characterized as **strong** or **weak**, depending on the extent of ionization. In the case of strong acids, such as hydrochloric acid, the acid in solution is completely ionized. For weak acids, such as acetic acid, only a small fraction of the acid in solution forms ions.

Strong: $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$ (~100%)

Weak: $CH_3CO_2H(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + CH_3CO_2^-(aq)$ (>5%)

For weak acids, equilibrium exists between the undissociated acid (on the left) and the ionized products (on the right). The extent of ionization can be quantified by the acid dissociation constant, K_a. The expression for K_a for the acetic acid equilibrium can be represented as:

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} \qquad (1)$$

Some acids have more than one ionizable hydrogen and, hence, will exhibit more than one K_a equilibrium. Consider, for example, the two equilibria for a generic **diprotic acid** (i.e., two ionizable hydrogens).

$$H_2A(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HA^-(aq) \qquad K_{a1} = \frac{[H_3O^+][HA^-]}{[H_2A]}$$

$$HA^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + A^{2-}(aq) \qquad K_{a2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]}$$

The relative strength of acids can be determined by comparing their K_a values. For convenience, K_a values are often reported as pK_a, where $pK_a = -\log(K_a)$.The K_a expression is also useful because it allows a direct connection between the concentration of a weak acid and the **pH** of the solution, where pH is defined as pH = -log $[H_3O^+]$. When both K_a and the $[H_3O^+]$ are expressed in logarithmic form, the K_a expression can be rearranged to yield:

$$pH = pK_a + \log \frac{[CH_3CO_2^-]}{[CH_3CO_2H]} \qquad (2)$$

From Eq. (2), it is clear that the pH of the solution will depend on the K_a of the acid and the ratio of the concentrations of the ionized and unionized forms of the acid. It is also worth noting that when the concentrations of ionized and unionized forms of the acid are equal, the ratio in Eq. (2) equals unity, and $pH = pK_a$. Some typical weak acids and their corresponding pK_a values are included in Table 1.

Table 1. Weak Acids and K_a values.

Acid	Formula	Molar Mass	pK_a	Application
Acetic Acid	CH_3CO_2H	60.05	4.74	Vinegar
Benzoic Acid	$C_7H_6O_2$	122.12	4.20	Food Preservative
Potassium Hydrogen Phthalate (KHP)	$C_8H_5O_4K$	204.22	5.4	Buffering Agent
Oxalic Acid (dihydrate) (diprotic)	$C_2O_4H_2{\cdot}2H_2O$	126.07	1.25 4.14	Found in rhubarb, spinach
Ascorbic Acid (diprotic)	$C_6H_8O_6$	176.12	4.10 11.6	Vitamin C, antioxidant
Citric Acid (triprotic)	$C_6H_8O_7$	192.12	3.13 4.76 6.40	Food preservative

When acids and bases are added together, they participate in a **neutralization reaction** in which the acid and base properties of these substances are "neutralized" as the hydronium and hydroxide ions react to form water.

Acid:	$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$
Base:	$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$
Neutralization:	$H_3O^+(aq) + OH^-(aq) \rightarrow 2\ H_2O(l)$
Net Reaction:	$HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + Na^+(aq) + Cl^-(aq)$

Neutralization reactions go to completion, so that all the acid and base that are added to solution react completely to form water and salt, as indicated in the net reaction. Neutralization reactions are often used to advantage in analytical procedures known as **assays**, such as determining the amount of acetic acid in a vinegar sample, or the amount of ascorbic acid (Vitamin C) in a vitamin tablet. The most common acid-base assay is called a **titration**, in which one of the reactants is added step-wise to the reaction solution from a buret, or graduated glass tube. This reagent is called the **titrant**, and its concentration is usually known. The other reactant in solution is called the **analyte**, and its concentration is unknown. In the acid-base titration reaction between hydrochloric acid and sodium hydroxide shown, the reaction is complete when equal moles of HCl and NaOH have been added to the reaction solution.This is called the **equivalence point** in the titration because stoichiometrically equivalent amounts of the acid ion (H_3O^+) and base ion (OH^-) have reacted. In other words,

$$\#\ \text{moles acid } (H_3O^+) = \#\ \text{moles base } (OH^-) \tag{3}$$

which can also be represented as

$$M_{acid}\ (\text{mol/L}) \cdot V_{acid}\ (\text{L}) = M_{base}\ (\text{mol/L}) \cdot V_{base}\ (\text{L}) \tag{4}$$

If the molarity (M) and volume (V) of the titrant are known, the moles of the titrant added at the equivalence point can be calculated. If the stoichiometry of the neutralization reaction is not 1:1, then a stoichiometric factor must be included in the equation to reflect the stoichiometry. The stoichiometry of the neutralization reaction involving a **diprotic acid** is provided here:

$$H_2A(aq) + 2\ OH^-(aq) \rightarrow 2\ H_2O(l) + A^-(aq)$$

$$\#\ \text{moles acid} = \#\text{moles base} \times \left(\frac{1\ \text{mole acid}}{2\ \text{moles base}}\right) \tag{5}$$

The last term in Eq. (5) is the mole ratio, and represents the stoichiometric relationship between acid and base in the neutralization reaction in Eq. (4). If the stoichiometry of the neutralization reaction is known, the molar mass of the unknown acid can be calculated by modification of equation (3). The moles of base (titrant) can be determined from the molarity of the base solution multiplied by the volume of titrant required to reach the equivalence point, or

$$\#\ \text{moles base} = M_{base}\ (\text{moles/L}) \times V_{base}\ (\text{L}). \tag{6}$$

The moles of acid can be expressed as:

$$\#\ \text{moles acid} = \text{mass of acid (g)} / \text{MW (g/mol)} \tag{7}$$

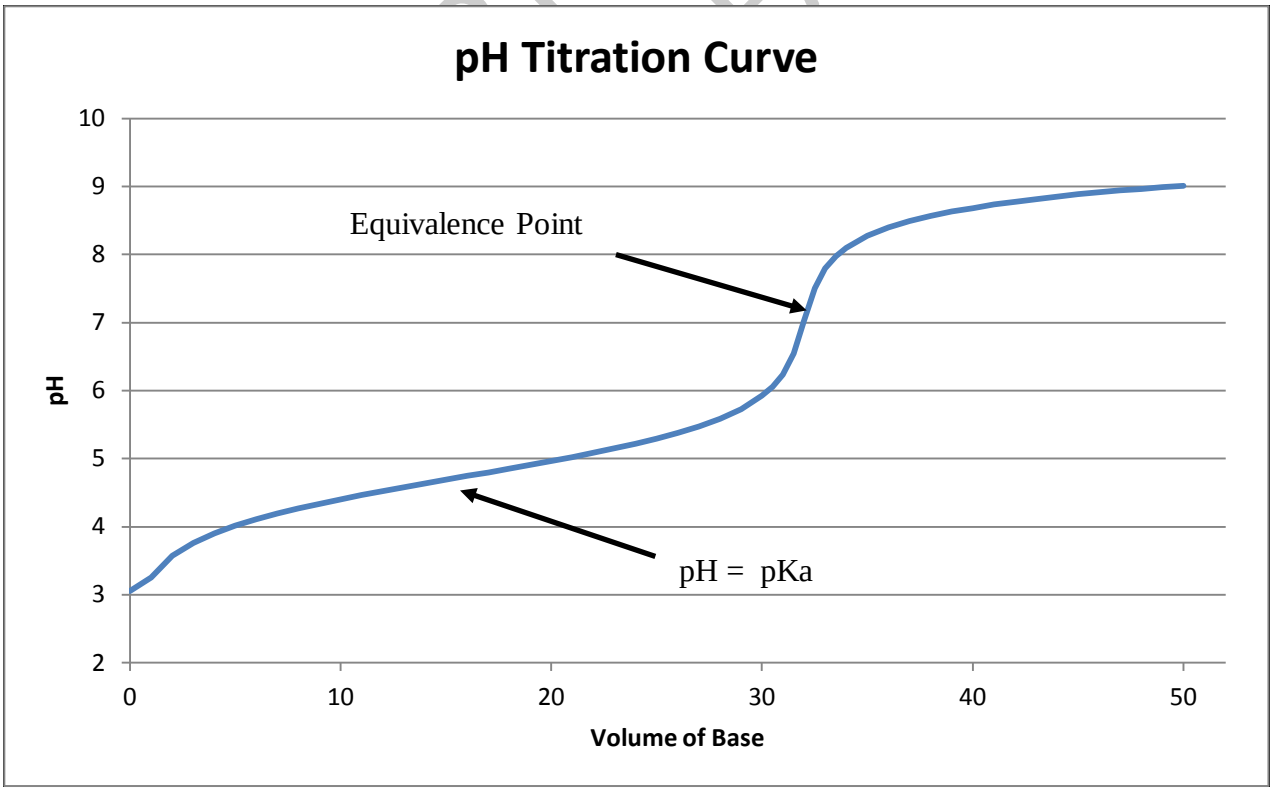
Combining Equations (5) and (6) and rearranging yields:

$$(MW)_{acid} = \frac{(mass\ of\ acid)}{(M_{base}) \times (V_{base})} \quad (8)$$

A critical component in these calculations is the volume of titrant required to reach the stoichiometric equivalence point, i.e., the point in the titration at which the neutralization reaction is complete. One method of identifying the equivalence point is to add an **indicator**, or a substance that changes color at or near the equivalence point. The point at which the indicator changes color is called the **end point** of the titration. Ideally, the end point and the equivalence point should occur as close as possible in the titration. Another method is to perform a **pH titration**, in which the pH of the solution is monitored while titrant is added. When the solution pH is plotted vs the volume of titrant added, the equivalence point is identified as the inflection point in the sigmoidal-shaped titration curve (see Figure 1.) A unique point in the titration of a weak acid is the **half-equivalence point**, when you have added enough titrant to neutralize half of the original acid, converting it to the ionized form. At this point, pH = pK_a for the weak acid.

In this lab you will perform a pH titration to determine if an unknown acid is monoprotic or diprotic, and to determine the Ka value(s) for the acid. You will then perform replicate indicator titrations and calculate the molar mass of the unknown acid using Equation (8).

Figure 1. pH Titration Curve for Acetic Acid Titration



Pre-Lab Questions

1. What does it mean to say that an acid is a *strong* acid? How is a strong acid different from a weak acid?

2. What is the difference between an **end point** and an **equivalence point** in a titration?

3. For sulfurous acid (H_2SO_3, a diprotic acid), write the equilibrium dissociation reactions and the corresponding expressions for the equilibrium constants, K_{a1} and K_{a2}.

4. Write the balanced neutralization reaction for sulfurous acid reacting with sodium hydroxide.

5. In a typical titration experiment a student titrates a 5.00 mL sample of formic acid with 26.59 mL of 0.1088 M NaOH. At this point the indicator turns pink. Calculate the # of moles of base added and the concentration of formic acid in the original sample.

PROCEDURE

Part A. pH Titation Curve

1. Obtain a pH meter and calibrate it using the standard pH buffer solutions as per directions from your instructor.

2. Using a sample bottle, obtain about 2.0 g of an unknown acid sample as assigned by your instructor.

3. Obtain a 50.0 mL buret, buret clamp and a ring stand. Set up your titration apparatus as shown in Figure 2.

4. Obtain about 200 mL of standardized sodium hydroxide (NaOH) solution. Record the concentration of the solution on your Data Sheet. Keep the solution covered until you are ready to use it in the titration.

5. Clean and rinse your buret, and fill it with NaOH solution as directed by the instructor. Fill the buret above the 0.00 mL mark. Slowly drain some of the NaOH solution from the buret until the buret reading is at or close to 0.00 mL. Be sure that the tip of the buret if filled with NaOH.

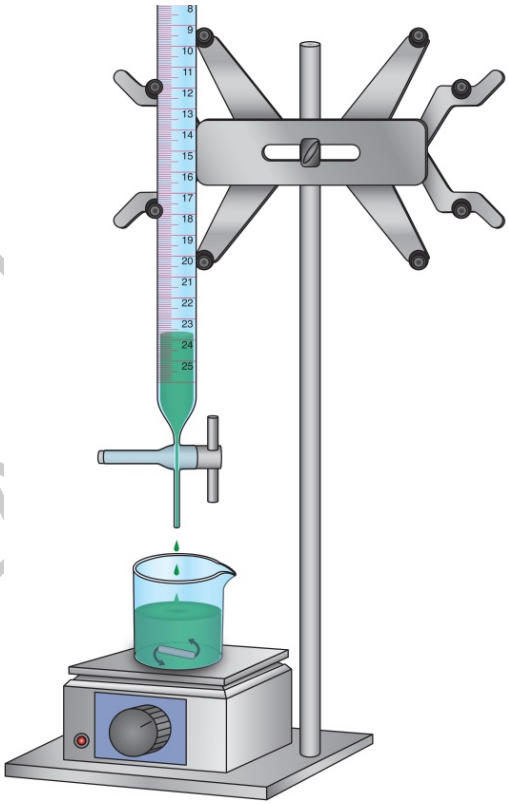


Figure 2. pH Titration apparatus, with pH meter

6. Record the initial mass of the sample vial containing your unknown acid on your Data Sheet (Part A). Carefully transfer ~ 0.40 g sample of your unknown acid to a clean 250m-mL beaker. Record the final mass of your sample vial, and calculate the actual mass of sample transferred. Record the mass of your unknown sample on the Data Sheet to the nearest 0.0001 g.

7. Add approx. 100 mL of DI water to the beaker and swirl until all the acid sample has dissolved. Add three drops of phenolphthalein indicator to the beaker and swirl well. Insert the pH meter into the solution; record the initial pH on your Data Sheet.

8. Open the stopcock on the buret and carefully add 1.0 mL of NaOH from the buret to the titration solution. Record the pH of the solution on your data sheet.

9. Repeat step 9, adding 1.0 mL of titrant and recording the pH, occasionally rinsing the sides of your beaker with DI water to wash down down any NaOH that may have splashed onto the sides of the beaker. Continue adding 1.00 mL increments until the indicator changes color. Record the volume of NaOH delivered at this point.

10. Continue adding 1.0 mL increments of NaOH and recording the pH until you have added a total of 50.00 mL of titrant.

Part B. Indicator Titrations

11. Refill the buret with NaOH, draining the excess and recording the initial NaOH buret volume on your Data Sheet Part B.

12. Using the same technique as in Step 7, transfer ~0.40 g of unknown acid from the sample vial to a 250 mL Erlenmeyer flask. Add about 100 mL DI water and dissolve.

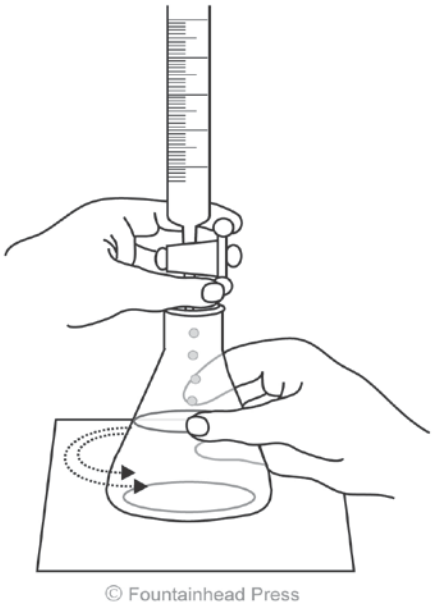


Figure 3. Proper titration technique

13. Carefully open the stopcock and allow some NaOH to drain into the flask while swirling, as illustrated in Figure 3. With practice you will be able to control the stopcock with one hand and swirl the reaction mixture with the other hand.

14. Note the color of the reaction mixture as NaOH is added from the buret. As it is added to solution it will turn pink, but the pink color will disappear as the solution is swirled. As you get nearer to the equivalence point in the titration the pink color will persist longer in solution before disappearing. When this occurs, slow down the rate at which you are adding titrant.

15. As you approach the end point, add the NaOH titrant one drop at a time and swirl to mix the solution. Occasionally, wash down the sides of your flask to be sure that all of your titrant has been mixed into the reaction solution.

16. When you are very close to the end point you can “hang a drop.” This is a technique for adding less than one drop by opening the stopcock slightly until a drop starts to form. Close the stopcock before the drop falls. Wash the half-drop into solution.

17. The end point in the titration is the first pink color that persists in solution after mixing. Record the volume of NaOH in the buret when you reach the end point.

18. Refill the buret with NaOH. Repeat steps 12–18 until you have completed three titrations.

19. Dispose of all titration solutions and excess titrant as directed by your TA.

CALCULATIONS

Part A.

1. Calculate the mass of sample by subtracting the final mass of the sample vial from the initial mass of the sample vial. Record the mass of the sample to the nearest 0.0001 g.

2. Using either the graph paper provided or appropriate spreadsheet software (e.g. Excel), plot the pH of the titration solution vs the Volume of NaOH.

3. From the plot, estimate the volume of NaOH required to reach the equivalence point, identified as the inflection point in the pH titration curve, and record this volume on the Data Sheet, Part A.

Part B.

1. For each trial, calculate the actual mass of sample used in the titration and record the mass on the data sheet to the nearest 0.0001 g.

2. For each trial, subtract the initial NaOH buret volume reading from the final buret volume reading to obtain the total NaOH volume used in each titration. These volumes should be reported to the nearest 0.01 mL.

3. Using the molarity and volume of the NaOH solution used for each trial, calculate the moles of sodium hydroxide added for each trial as indicated in Equation (6). Record this value on your Data Sheet, Part B for each trial. Be sure to convert your volume from mL to liters before calculating, and to record your results to the appropriate number of significant figures.

4. Report the number of moles of acid in each trial. If the stoichiometry of your neutralization reaction was 1:1 (based on your pH titration curve), this will be the same as the number of moles of NaOH. If your titration curve had more than one equivalence point, you will have to include the mole ratio in your calculations as indicated in Equation (5).

5. Calculate the molar mass of the unknown acid by dividing the mass of acid sample by the moles of acid determined for each trial. Calculate the average molar mass of the unknown acid and report it on your Data Sheet.

6. Estimate the pK_a for the unknown acid by referring to the pH titration curve; the pK_a will be equal to the pH of the solution at the half-way point in the titration. For polyprotic acid you will need to estimate more than one pKa.

7. From the average molar mass and the estimated pKa values, indicate the identity of your unknown acid from among the candidates in Table 1.

Data Sheet: Part A (pH Titration Curve)

ID of Unknown Acid: _____

Initial mass of sample vial + acid: _____

Mass of sample vial after transfer: _____

Mass of unknown acid sample: _____

Volume of NaOH (mL)	pH	Volume of NaOH (mL)	pH	Volume of NaOH (mL)	pH
1.0		18.0		35.0	
2.0		19.0		36.0	
3.0		20.0		37.0	
4.0		21.0		38.0	
5.0		22.0		39.0	
6.0		23.0		40.0	
7.0		24.0		41.0	
8.0		25.0		42.0	
9.0		26.0		43.0	
10.0		27.0		44.0	
11.0		28.8		45.0	
12.0		29.0		46.0	
13.0		30.0		47.0	
14.0		31.0		48.0	
15.0		32.0		49.0	
16.0		33.0		50.0	
17.0		34.0			

Volume of NaOH at end point:_____ (mL)

Volume at equivalence point:_____ (estimated from pH titration curve)

Data Sheet: Part B (Indicator Titrations)

Molarity of NaOH (M): _____

	Trial 1	Trial 2	Trial 3
Initial mass of sample vial + acid:	_____	_____	_____
Mass of sample vial after transfer:	_____	_____	_____
Mass of unknown acid sample:	_____	_____	_____
Final NaOH reading (mL):	_____	_____	_____
Initial NaOH (mL):	_____	_____	_____
Volume of NaOH (mL):	_____	_____	_____
Moles of NaOH:	_____	_____	_____
Moles of unknown acid:	_____	_____	_____
Molar Mass of acid:	_____	_____	_____

Average Molar Mass (g/mol): _____

Sample Calculations: (Show work!)

pK_a estimate: pK_{a1} = _____

pK_{a2} = _____ (if applicable)

Identity of Unknown Acid: _____

Post-Lab Questions

1. Why do you rinse the buret with the sodium hydroxide solution and not with distilled water? How would your titration results be affected if you rinsed with distilled water before filling your buret? (Hint: How would the actual molarity of NaOH in the buret be affected?)

2. In steps 8 and 13 of the Procedure you were told to add about 100 mL of distilled water, but that the actual volume was not important. Explain why the volume of water you add in this step is not important.

3. How closely did the volume of titrant at the indicator end point match the volume at the equivalence point determined from the pH titration curve? How could you improve the agreement between the two values?

4. In a typical titration a student needed 36.48 mL of 0.1067 M NaOH to reach the phenolphthalein endpoint. If the mass of the sample was 0.4206 g, calculate the molar mass of the unknown acid. Report your answer to the appropriate number of significant figures.