Experiment 8. Determination of the Molar Mass of an Unknown Acid by Acid-Base Titration

In this experiment you will:

- Prepare and standardize a solution of sodium hydroxide
- Determine the molecular weight of an unknown acid by reacting the acid with standardized sodium hydroxide solution.

BACKGROUND

Acid/Base Reaction Scheme 1

$$H_2SO_{4(aq)} + 2\ NaOH_{(aq)} \rightarrow 2\ H_2O_{(l)} + Na_2SO_{4(aq)}$$

Strong acid | Strong base | Water | Salt

An acid reacts with a base to form a salt plus water (see Scheme 1). Many acids have one proton available for reaction with a base such as sodium hydroxide. An acid with one reactive proton per molecule or formula unit is called a monoprotic acid or a monobasic acid. A diprotic acid or a dibasic acid has a maximum of two reactive protons per molecule. A triprotic acid or a tribasic acid has a maximum of three reactive protons per molecule. There are also examples of acids, which have four and even more reactive protons per molecule. In contrast, most useful bases have one or two available hydroxide ions per formula units.

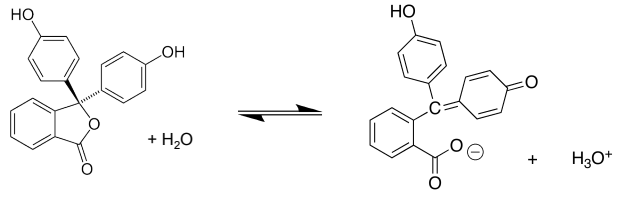
$$\underline{\mathbf{H}}A_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \qquad \text{monoprotic acid}$$

$$\underline{\mathbf{H_2}}A_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HA^-_{(aq)}$$
$$HA^-_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^{2-}_{(aq)} \qquad \text{diprotic acid}$$

$$\underline{\mathbf{H_3}}A_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + H_2A^-_{(aq)}$$
$$H_2A^-_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HA^{2-}_{(aq)}$$
$$HA^{2-}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^{3-}_{(aq)} \qquad \text{triprotic acid}$$

Titration is the process for ascertaining the exact volume of a solution that reacts stoichiometrically according to a balanced chemical equation with a given volume of a second solution. One reagent is added by means of a burette until the endpoint is reached. The endpoint occurs when stoichiometric quantities of reagents have been mixed. The endpoint of a titration for reactions of acids and bases is usually indicated by a third reagent, the indicator, which has an abrupt and distinctive color change at the hydrogen ion concentration which is present after the stoichiometric reaction has occurred. The typical indicator for titrations of strong acids and bases is phenolphthalein. Phenolphthalein is colorless in acidic solution and red (pink in dilute solutions) in basic solution. Since it is much easier and distinctive to see a color change from colorless to pink rather than from pink to colorless, sodium hydroxide is added by means of the burette to the acid, usually contained in an Erlenmeyer flask.

Phenolphthalein = **In**



HIn — *Colorless* ⇌ **In⁻** — *Fuchsia*

In this experiment, you will standardize (determine precisely the concentration) a solution of sodium hydroxide, NaOH, using oxalic acid dihydrate, $H_2C_2O_4 \bullet 2\ H_2O$, as a primary standard acid. A primary standard acid is a solid with high degree of purity and large molar mass. The solid acid whose mass is an accurate measure of the number of moles of protons the acid will furnish. Oxalic acid, $H_2C_2O_4 \bullet 2H_2O$, is a diprotic acid and provides two reactive protons per molecule according to the following net equation for the neutralization reaction.

$$H_2C_2O_4 \bullet 2H_2O_{(s)} + 2\ NaOH_{(aq)} \rightarrow Na_2C_2O_{4(aq)} + 4\ H_2O_{(l)}$$

We must standardize the NaOH solution as sodium hydroxide reacts with carbon dioxide (CO_2) from the air to produce $NaHCO_3$. The concentration of NaOH is then decreased. We must standardize it against a compound that does not easily react with air or decompose, such as oxalic acid. In the second part of the experiment you will titrate an unknown acid with your standardized NaOH solution using phenolphthalein as the indicator. Your goal will be to calculate the molecular mass of your acid. Your instructor will tell you the number of protons your acid furnishes for reaction with base.

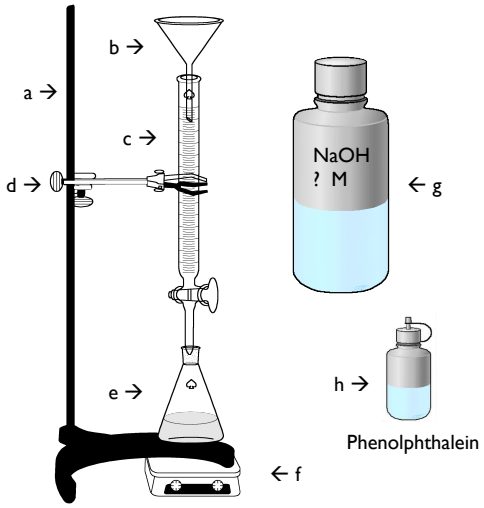
TITRATION EXPERIMENT • PRE-LAB ASSIGNMENT

Reading	☐ Lab manual pages ☐ Laboratory Handbook: Section IV – *Measuring Liquid Volumes* ☐ *Chemistry*, 6th ed. by Silberberg: sections 3.5 & 4.4 or *General Chemistry*, 5th ed. by Olmsted and Williams: section 4.6.
Pre-Lab Assignment	☐ Begin the pre-lab on a new page of your laboratory notebook. **ALL elements of the pre-lab MUST be completed before an experiment is started.** ☐ The COPY page from your notebook will be collected as you enter the lab. The original pages must stay in your notebook.
Heading	☐ Title of experiment and number ☐ Your name ☐ Dates of the experiment
Purpose	☐ Explain the purpose of the experiment.
General Strategy	☐ **Summarize and explain** the procedure of the experiment. ☐ Provide the balanced equation for the standardization reaction & a generic diprotic acid.
Data Tables	☐ On a NEW page, prepare **two** tables recording each quantity you will measure in Part A (Standardization of NaOH) and Part B (Determination of the molar mas of an unknown).
Answer to Pre-Lab Questions	☐ Answer the question #3 in your LAB NOTEBOOK. ☐ Answer the other question on the page to turn in.

PRE-LAB ASSIGNMENT

Titration Experiment **Name:** _____

1. Identify and describe the function of each piece of equipment shown below:



2. Name the primary standard (name and formula) for this experiment and define the function.

3. Write the net ionic equation for the following reaction. Please note that oxalic acid is a weak acid and is not fully dissociated when dissolved in water.

$$H_2C_2O_{4(aq)} + 2\ NaOH_{(aq)} \rightarrow Na_2C_2O_{4(aq)} + 2\ H_2O_{(l)}$$

4. Explain why it is a good technique to wash the sides of the Erlenmeyer flask during the titration.

5. If we assume that the NaOH solution that we will prepare for standardization is approximately 0.12 *M*, calculate the number of moles and the mass of oxalic acid dihydrate, $H_2C_2O_4 \bullet 2\ H_2O$, required to neutralize approximately 35 mL of the NaOH solution. Write this in your lab book.

EXPERIMENTAL PROCEDURE

Part A. Standardization of NaOH solution

1. Prepare a solution of sodium hydroxide that is approximately 0.12 *M* by adding 100 mL of the 0.8 *M* stock solution to 500 mL of deionized (DI) water in a clean 1-L plastic bottle. Cap the bottle and shake vigorously to thoroughly mix the material. You do not need to be precise, as we will be determining the precise concentration of the NaOH solution in the next steps.

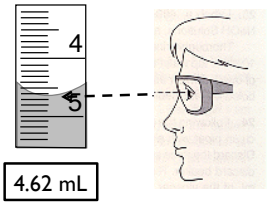
2. *Rinsing the burette with DI water*: Thoroughly clean a burette with DI water. Rinse with DI water three times. If many water spots are observed on the inside of the burette, use soap, water and a burette brush to clean the burette, followed by multiple tap water rinses, and three DI water rinses.

3. *Rinsing the burette with titrant solution*: Empty the burette, and then rinse with two 5-mL portions of the NaOH solution. Allow some of the solution to run through the stopcock, draining into a waste beaker, and pour the rest out the large top opening to coat the inside of the burette. This process will prevent dilution of your NaOH solution when you add it to the burette for titration.

4. *Filling the burette*: Set up a burette clamp on a ring stand, and put the clean burette on the clamp. Using a funnel rinsed in the same manner as the burette, fill the burette with the NaOH solution (titrant) just below the 0.00 mL mark. Remember there is no need to fill the burette exactly since you will read the difference between the ending and starting volumes to determine the amount of volume delivered. Once the burette is full, remove the funnel. If you overfill the burette, drain a small amount into an empty waste beaker. Always pour fresh solution to the burette prior to each titration.

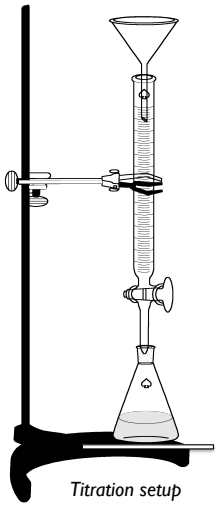
5. *Remove air bubbles*: Air bubbles will be trap in the tip of the newly filled burette. These can be difficult to remove and may alter the volume measurement. Hold the burette over an open beaker an open the stopcock fully to allow solution to flow out of the burette. Your instructor will demonstrate the technique. Refill burette if necessary.

6. *Reading the burette*: Practice reading the burette using deionized water in it. Remember to always read the volume to the nearest 0.01 mL. See figure to the left.



Reading the burette

7. Mass out three samples of oxalic acid dihydrate (this is the mass you calculated in the prelab questions) on the analytical balance. Record each mass to the full precision allowed by the balance. Dissolve each in 50 mL of DI water in a 125 or 250-mL flask, and add 2-3 drops of phenolphthalein.


Titration setup

8. Using the sample with the smallest mass of oxalic acid, prepare to carry out your titration. Place a sheet of white paper under the flask to assist in the visualization of the endpoint. Position the burette such that the glass tip is below the opening to the flask. Record the initial volume. See titration setup figure.

9. Titrate the sample. Because we calculated the mass of oxalic acid to require ~ 35 mL of solution, add 25 mL of the NaOH solution quickly. Then add more slowly, always swirling with one hand, while you control the stopcock with the other. Alternatively, you can set up a magnetic stir bar to stir the solution for you. Occasionally use DI water from your squirt bottle to wash any stray drops on the side of the flask into the solution.

10. When a pink color appears in the solution when a drop hits, but then goes away with swirling, you are near the endpoint and should begin adding the solution very slowly – one drop at a time, always swirling to see if any hint of pink color remains. At this point, wash down any drops on the side of the flask with DI water. If you are very close to the endpoint, and need less than a full drop, allow a drop to ***start*** to form on the tip, close the stopcock, then touch the flask to the tip. The partial drop will transfer to the flask; wash it down with DI water.

11. When the hint of pink remains, you have reached the endpoint. Record the final volume of the solution on the burette.

12. Repeat this procedure for the other two samples of oxalic acid. Refill the burette between samples. Because you know how much solution was required for the first sample, you can add close to that volume very quickly

for the other samples – perhaps just 2 mL less than the volume required for the first trial. Then add the additional solution slowly.

13. Calculate the concentration of NaOH in mol/L for all three trials, and then calculate the average [NaOH] and the relative range. Follow instructions as to relative range required before going on to the next step. Show your results to your instructor. The average value is the NaOH concentration you will use in part B.

14. Save the solution. You will use this same solution for the next set of titrations.

Part B. Determination of the molar mass of an unknown acid

15. Obtain an unknown acid from your instructor. Record the number of the acid, and whether it is mono-, di-, or tri- protic.

16. Precisely mass three samples of the unknown. Use the same approximate mass as you used for the oxalic acid in part A.

17. Dissolve each in 50-mL of DI water in a 125 or 250-mL flask. If it does not all dissolve, that is OK, just be sure it dissolves prior to end point.

18. Starting with the sample of smallest mass, titrate the unknown samples. Use the same method as part A. Be sure to record all necessary data. Several acids are less soluble than oxalic acid. You can start titration before all solid is dissolved but as you approach endpoint, be sure that the solid is dissolved.

19. Calculate the molar mass of your unknown for all three trials, and then calculate the average. Also, calculate the relative range. Show this result to your instructor for signoff. If the range is greater than 2%, discuss your data with your instructor. Use this average molar mass to compare to the possible unknowns, and make an identification of your unknown.

Error Analysis Questions for Acid-Base Titration Experiment

1. In standardizing the solution of aqueous sodium hydroxide, a chemist overshoots the end point and adds too much NaOH(aq). Would this error result in a calculated concentration of NaOH that was overestimated or underestimated? Explain your reasoning.

2. In the titration of the unknown diprotic acid, assume a chemist uses a standardized solution of NaOH that has been underestimated in its concentration. How would this error affect the final calculation for the molar mass of the unknown acid? Would it be overestimated, underestimated or remain unaffected? Explain your reasoning.

3. In the titration of the unknown diprotic acid with NaOH, assume a chemist overshoots the end point and adds too much NaOH. How would this error affect the final calculation for the molar mass of the unknown acid? Would it be overestimated, underestimated or remain unaffected? Explain your reasoning.

LAB REPORT GUIDELINES

The lab report section includes work recorded during the lab, your analysis and discussion of data and results, and your conclusions. ***The discussion and conclusion sections should be word-processed.*** Other parts of the report - calculations, etc. may be typed.

Heading	☐ Title of experiment and number ☐ Your name ☐ Dates of the experiment
Data/Observations/ Results	☐ ORIGINAL QUANTITATIVE DATA (signed data pages from your lab notebook)
Calculations	Show calculations for the following quantities in your report (use proper format for labeling and showing calculations in a formal report): Part A: ☐ Calculate [NaOH] based on each titration ☐ Calculate the average [NaOH] (of the good trials as described in the procedure) ☐ Calculate the relative range ☐ Provide a discussion of your choice to omit any bad trials, including any other relative range calculations you may have performed. Part B: ☐ Calculate the molar mass of the unknown acid for each trial ☐ Calculate the average molar mass (of the good trials as described in the procedure) ☐ Calculate the relative range ☐ Provide a discussion of your choice to omit any bad trials, including any other relative range calculations you may have performed. ☐ ***Determine the identity of your unknown acid.*** Your acid is one of the following: o Oxalic acid dihydrate ($H_2C_2O_4 \cdot 2\ H_2O$) (diprotic) o Succinic acid ($C_4H_6O_4$) (diprotic) o Fumaric acid ($C_4H_4O_4$) (diprotic) o Tartaric acid ($C_4H_6O_6$) (diprotic) o Citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) (triprotic) o Based on the molar masses of these compounds (calculate and provide in a table), identify the most likely identity of your unknown. If you cannot definitively determine its identity, suggest the reasonable possibilities. ☐ **Calculate the percent error** for the experimental molar mass with the value for the acid you have determined it to be. (If more than one possibility, show the percent error for each of them).
Discussion/Theory/ Results/Error Analysis	In this section, you will explain the experiment, evaluate, discuss your results, and analyze errors in paragraph form. ☐ Briefly explain *why* we standardized the sodium hydroxide

	solution and *how* we did it. ☐ Write the balanced chemical equation for the reaction of the specific acid you have determined your unknown to be with NaOH. (If more than one possibility, show one of them). ☐ Discuss your percent error. Explain how the error may have arisen and how significant each source of error might be. This error analysis should support your data. Some errors increase the molecular mass; others decrease it.
Conclusions	Your conclusions should include: ☐ Unknown number, experimental molar mass, and the likely identity of the unknown acid.
Post-Lab Questions	Answer the questions on the POST-LAB Questions Handout. Write all answers on that handout and turn in with the Lab Report. Show ALL units and work.

Acid-Base Titration
POST-LAB QUESTIONS Name: _____

1. KHP, potassium hydrogen phthalate ($KHC_8H_4O_4$), is often used to standardize basic solution used in titration. If a 0.855-g sample of KHP requires 31.44 mL of a KOH solution to fully neutralize it, what is the [KOH] in the solution?

   The reaction is $KHC_8H_4O_{4(aq)} + KOH_{(aq)} \rightarrow K_2C_8H_4O_{4(aq)} + H_2O_{(l)}$

2. The KOH solution standardized above is used to titrate a 20.00-mL sample of sulfuric acid (H_2SO_4) solution of unknown concentration. Determine [H_2SO_4] for the unknown acid solution if 41.27 mL of the NaOH solution is needed to fully react with it.

3. A 25.00 mL aliquot of a nitric acid solution of unknown concentration is pipetted into a 125 ml Erlenmeyer flask and two drops of phenolphthalein are added. The above sodium hydroxide solution (the titrant) is used to titrate the nitric acid solution (the analyte). If 16.77 mL of the titrant is dispensed from a burette in causing a color change of the phenolphthalein, what is the molar concentration of the nitric acid (a monoprotic acid) solution? Express the molar concentration of nitric acid to the correct number of significant figures.