

## EXPERIMENT 7

### Identifying a Substance by Acid-Base Titration

#### SAFETY WARNING

In this experiment you will be working with NaOH pellets and using 0.25 M NaOH as a titrant. Sodium hydroxide is extremely basic, caustic, and corrosive. Use of rubber gloves when preparing or titrating with it is recommended. *NEVER* pour a solution of NaOH or any other caustic substance above eye level. Place the burette stand on the floor or on one of the pull-out shelves to fill your burette. If you get any of the solution on your hands or clothes, *rinse it off immediately with copious amounts of water*. If you spill a large amount on your clothing, *head immediately for one of the showers*. *Keep your hands away from your eyes at all times* during the experiment unless you have just rinsed your hands thoroughly. Sodium hydroxide solutions feel slimy or slippery to the touch. If your fingers ever feel extra slippery or if some part of your body starts itching, *don't stop to ask a TA about this, wash the affected part with lots of water immediately*. Stay alert and work in a controlled and *very neat* manner. Keep things clean at all times.

#### USE FRESH DEIONIZED WATER THROUGHOUT THIS EXPERIMENT

Deionized water should have had most of the carbon dioxide removed from it during its preparation. Solid NaOH and its solutions absorb carbon dioxide (an acid anhydride) from the air to form carbonate. The equilibrium level of dissolved CO<sub>2</sub> in water open to the atmosphere is about  $1.5 \times 10^{-5}$  M. This reduces the titer of the base, and also makes endpoints slow and less distinct. Fine powder that doesn't dissolve quickly when you are preparing the NaOH titrant is probably sodium carbonate. If you see white particles while preparing the NaOH the solution, it should be filtered through a Buchner or fritted-glass funnel and then transferred into a 1-L plastic bottle prior to use. See the Teaching Assistant.

#### UNKNOWN

Submit a clean, labeled, and dry sample vial to the instructor so that your unknown acid can be issued. Your name, section number, and your locker number should be written legibly on this vial. Note that *the vial must be turned in at least 1 lab period before you plan to do the experiment* so that the Teaching Assistants will have time to prepare the unknown.

#### BACKGROUND

Acid-base titrations can provide valuable information about the nature and properties of an acid or a base. These titrations can be useful not only in determining the molecular mass and  $pK_a$  values, but also whether the substance is polyfunctional. *Polyfunctional* acids and bases have two or more acidic or basic functional groups; i.e., they may donate or accept more than one proton. The end point of an acid-base titration can be monitored by using colorimetric indicators or a pH meter and glass electrode.

## INSTRUMENTATION

Corning Model 430 pH meter.  
Combination pH and reference electrode.  
Magnetic stirrer and stir bar.  
Electrode holder.

## PREPARATION OF SOLUTIONS

### 0.25 M NaOH

1. To prepare 1 L, carefully pipet approximately 18 mL (about 20 g) of *highly caustic*, concentrated, carbonate-free, 50% NaOH solution into a 1-L plastic bottle containing 500 mL of fresh deionized water. The solution is somewhat viscous, so it is better to use a pipet with a large tip opening.
2. Screw the cap on the plastic bottle and swirl to mix thoroughly.
3. Add another 500 mL of deionized water and mix thoroughly.
4. Immediately rinse out the pipet thoroughly to remove all traces of NaOH, which could be hazardous to you or others and will etch the glass surface.

Keep the cap tightly screwed onto the plastic bottle except when transferring some to your burette in order to minimize absorption of atmospheric carbon dioxide. In similar manner, you should also have a burette cap on the top of the burette for the same reason.

### 0.2 M Potassium Acid Phthalate (KHP) Standard Solution.

Prepare 250 mL of 0.2 M KHP. This solution will be used to standardize the NaOH titrant that you prepared to be *approximately* 0.25 M.

1. Calculate the mass of KHP ( $\text{KHC}_8\text{H}_8\text{O}_4$ , 204.22 g/mol) needed to prepare exactly 250 mL of 0.2000 M KHP. Accurately (to 0.1 mg) weigh by difference a quantity of KHP (oven-dried at 110 °C for 1-2 hr) close to this amount into a small plastic weighing boat. It does not have to be the *exact* amount calculated, but should be reasonably near. **NOTE: NEVER transfer chemicals inside an analytical balance.**
2. Transfer the KHP quantitatively into a 250-mL volumetric flask. Rinse the last traces from the boat and the neck of the volumetric flask with a squirt bottle. Add about 150 mL of deionized water, swirl to dissolve completely, carefully dilute to volume, and mix thoroughly.

## CALIBRATION OF THE pH METER

A pH meter needs to be calibrated every time it is used for an experiment, and should be checked for accuracy periodically when doing a series of measurements. pH and reference electrodes tend to drift with time owing to changes in temperature, the surfaces of the electrodes, and other factors.

1. Obtain a pH meter, electrode, and buffer solutions from one of the laboratory instructors. Be sure to sign and print your name on the sign in sheet for the pH meter and electrode. Record the instrument numbers found on the outside of the electrode and meter into your lab book. Also, be sure that before you sign for an electrode that the plastic cap on the side of the electrode covering the inlet for the internal filling solution is securely in place. If the cap has been removed notify a TA immediately.
2. Turn on the pH meter and let it warm up for 10-15 minutes. Rinse the combination pH electrode thoroughly with deionized water and gently pat off the excess water with a kimwipe.
3. Insert the electrode into a small beaker (or vial) containing pH 4 buffer solution. Press **CALIBRATE** and wait for **OK**.
4. Rinse the pH electrode with deionized water and insert it into a small beaker with pH 10 buffer. Press **CALIBRATE** again to perform a 2-point calibration. If a high enough % value is not obtained for the slope, an **ERR** message will appear. Repeat the calibration one or two times more. If **ERR** still appears, consult a Teaching Assistant. Record the slope value in your notebook.
5. Rinse the electrode thoroughly and pat dry.
6. When not in use during the experiment, keep the pH electrode immersed in deionized water.
7. When you have completed the entire experiment, the pH electrode should be stored in pH 7 buffer solution.

## STANDARDIZATION OF 0.25 M NaOH

Standardize the 0.25 M NaOH solution you prepared by means of a conventional acid-base titration using phenolphthalein indicator.

1. Fill a 50-mL burette in proper manner with the prepared NaOH solution.
2. Pipet 25 mL of the KHP standard solution into a 250-mL Erlenmeyer flask. Add 3 drops of phenolphthalein indicator, and titrate carefully to the first permanent light pink color. (What should the endpoint volume of NaOH be, given the nominal concentrations of the two solutions?)

3. Do at least 2 more replicate titrations. The values should agree to within  $\pm 0.5\%$  RSD. If not, titrate another replicate sample or two. Recall that you can always reject data *for cause*, or *one* outlier from a full data set using the Q-test.
4. Calculate the exact molarity of the NaOH solution.

### TITRATION OF THE UNKNOWN ACID

The unknown acid can be mono-, di-, or triprotic. Once diluted to volume, the concentration of the acid should be about 0.1 M (0.15 M at the highest and 0.067 M at the lowest using the procedure below).

1. Obtain your sample of an unknown acid from the instructors. The acid may be monoprotic, diprotic, or triprotic. Weigh between 3.25 – 5.0 grams of your acid into a clean 250 mL volumetric flask. Record the exact mass, as you will need it later. Add 100-150 mL of deionized water to the flask and dissolve the acid completely with swirling. If this proves to be difficult, insert a stir bar into the flask and use a magnetic stirrer to speed complete dissolution. Once dissolution is complete, remove the stir bar carefully with a magnet, rinsing the stir bar off into the flask as you remove it. Then dilute carefully to volume.
2. Carefully pipet 50 mL of the solution of unknown acid into a 150 mL beaker.
3. Place a small stir bar into the beaker. Place the beaker on the magnetic stirrer such that the stir bar is centered in the beaker. Start the stirring and adjust the stirring rate to the stir bar is spinning moderately fast, but stable and with little or no vortex. Insert the pH electrode into the solution near, but not touching the beaker wall and bottom. Check to see that the solution is covering the electrode sensing tip.
4. Using a 50-mL burette, perform a careful titration using 1-mL additions of the titrant in the early stages but smaller additions near the endpoint(s). After each addition, wait for the pH reading to equilibrate and record the pH along with the corresponding volume of sodium hydroxide added. [HELPFUL HINT: Given the nominal molarities of the unknown acid and the NaOH titrant, where should the equivalence point(s) be for a monoprotic acid? A diprotic acid? A triprotic acid? If you think for a minute or two, this should speed your titration considerably and also result in better data.]
5. Perform a total of three “good” replicate titrations.
6. After completing the experiment, thoroughly rinse the electrode and insert it into pH 7 buffer. This will ensure that the electrode will be ready for the next group.

## REPORT

In addition to items expected in any lab report, the following should be specifically addressed or provided:

- A properly labeled plot of your best titration curve.
- Identification of whether your acid is monoprotic, diprotic, or triprotic, and the reasoning for this assertion.
- The  $pK_a$  value(s) and the equivalence point(s) for your acid. The  $pK_a$  is the pH at which the acid is exactly half neutralized. The equivalence point is at the center of the steepest increase on the sigmoidal titration curve.
- The equivalent weight of your acid, assuming the concentration of the unknown acid is  $0.10 \pm 0.02$  M. [The *equivalent weight* of an acid is its molar mass divided by the number of acidic protons.]
- Identification of your unknown acid.
- Comparison of your experimental value(s) with those in the table of possible unknown acids and bases in the Appendix below and identify your unknown acid.

*NOTE: It is probably wise to retain your standard KHP solution and the now-standardized NaOH solution until you have received your grade for the experiment. You may need to re-do the experiment, and retaining these solutions may save you time. Remember, however, that NaOH solutions can “go bad” and lose their titer with time owing to the absorption of atmospheric  $CO_2$ . You may need to check or re-standardize your NaOH solution.*

## HAZARDOUS WASTE DISPOSAL

*Solutions that have been titrated and the contents of your “waste beaker” (or “slop pot”) can simply be poured down the drain, as long as the pH is not greater than 9. Any remaining 0.25 M NaOH solution and any other solutions with  $pH > 9$  must be disposed of in the proper Hazardous Waste Bottle for this experiment. If you are unsure of the proper container, ASK.*

## TEXT REFERENCE

D.A. Skoog, D.M. West, F.J. Holler and S.R. Crouch, *Analytical Chemistry: An Introduction*, 7th ed. Chapters 12 and 13, pp. 265-324, Sections 14A-3, pp. 331-332, Section 14A-4, p. 333.

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**APPENDIX: POSSIBLE “UNKNOWN” ACIDS  
FOR THE ACID-BASE TITRATION EXPERIMENT\***

Acid	Molar Mass, g/mol	$pK_{a1}$	$pK_{a2}$	$pK_{a3}$
Acetic	60.05	4.756		
Adipic	146.14	4.418	5.412	
Ascorbic	176.12	4.10	11.79	
D-Aspartic	133.10	3.87	10.00	
Benzoic	122.12	4.202		
Butyric	88.10	4.817		
Carbonic	62.03	6.36	10.33	
Citric	192.12	3.15	4.77	6.19
Formic	46.03	3.751		
Fumaric	116.07	3.10	4.60	
L-Glutamic	147.13	4.31	9.76	
Glutaric	132.11	3.77	6.08	
Hexanoic (caproic)	116.16	4.849		
Iminodiacetic	133.10	2.98	9.89	
Indoleacetic	175.18	4.75		
Inosine	268.23	8.96	12.36	
Lactic	90.08	3.86		
Maleic	116.07	1.910	6.33	
Malic	134.09	3.46	5.10	
Malonic	104.06	2.85	5.70	
Mandelic	152.14	3.40		
Nitrilotriacetic	191.14	3.03	3.07	10.70
Oxalic	90.04	1.23	4.19	
Pentanoic (valeric)	102.13	4.842		
<i>o</i> -Phthalic	166.13	2.95	5.41	
Phosphoric	98.00	2.12	7.21	12.66
Propionic (propanoic)	74.08	4.874		
Salicylic	138.12	2.97		
Succinic	118.09	4.207	5.635	
D-Tartaric	168.10	3.036	4.366	

\*  $pK_a$  values generally at 25 °C

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