# Experiments

## EXPERIMENT 7
## Acid/Base Titration

### 7.1. Safety

Acids and bases can cause skin burns. Following skin contact with either an acid or basic solution, wash the area thoroughly with water. Acidic and basic solutions are extremely hazardous to the eyes and can cause serious vision impairment or even blindness. If the acid or base gets into your eyes, rinse them thoroughly with copious amounts of water and seek medical attention. Phenolphthalein is a strong laxative. Wash your hands after handling the phenolphthalein bottle.

### 7.2. Introduction

The Arrhenius definition of an acid is a compound that, when dissolved in water, increases the hydronium ion ($H^+$ $(aq)$ or $H_3O^+$ $(aq)$) concentration. The most common modern definition is that of a Brønsted-Lowry acid. A Brønsted-Lowry acid is a more general term for a compound that can donate a hydrogen ion to another compound. Thus a Brønsted-Lowry acid is considered to be a proton donor, while the base is a proton acceptor. The acid and its corresponding base are known as a conjugate acid/base pair. For example, when formic acid $HCHO_2$ dissolves in water, we obtain

$$HCHO_2\ (aq)\ +\ H_2O\ (l)\ \rightarrow\ CHO_2^-\ (aq)\ +\ H_3O^+\ (aq)\ .$$

Formic acid acts as the proton donor and, therefore, is a Brønsted-Lowry acid. The water acts as a proton acceptor and is a Brønsted-Lowry base. The reverse reaction is

$$CHO_2^-\ (aq)\ +\ H_3O^+\ (aq)\ \rightarrow\ HCHO_2\ (aq)\ +\ H_2O\ .$$

In this case, the formate anion ($CHO_2^-$) acts as a proton acceptor and, therefore, is a Brønsted-Lowry base, while the hydronium ion acts as a proton donor and is the Brønsted-Lowry acid. Thus, formic acid/formate anion form a conjugate acid/base pair, and water/hydronium ion form a conjugate base/acid pair. *Amphoteric* substances, such as water, can act as either a Brønsted-Lowry acid or a Brønsted-Lowry base. The advantage of the Brønsted-Lowry definition of acids and bases is the fact that this definition is independent of the acid (or base) being in aqueous solution. The final definition of an acid/base is a Lewis acid or Lewis base. A Lewis acid is an electron pair acceptor, while a Lewis base is an electron pair donor. Since Lewis acids and bases are defined by the donation or acceptance of electron pairs, compounds without protons can be defined as an acid within the Lewis definition. In this experiment, the study of Brønsted-Lowry acids and bases will

be performed by titration using standard indicators and potentiometric analysis. For the sake of convenience in this experiment, the terms acid and base will imply Brønsted-Lowry acids and bases.

**Before Laboratory Questions – Week 1**

*These questions should be used to help you write your notebook and should be answered in some form before you go to the laboratory.*

(1) What is the purpose of Week 1 of this experiment?
(2) What is your hypothesis for the Week 1 experiment? Answer in if/then statements.
(3) What materials are required for this experiment? Are any chemicals needed? If so, what are they? Which materials must be obtained from the stockroom, which must be obtained from the instructor, and which are in your laboratory drawer?
(4) Create a space to record the initial mass of KHP and the volume of the solution to the appropriate precision.
(5) Create a space for the molarity of the sodium hydroxide solution provided, the volume of the sodium hydroxide solution and the volume of water needed to create your basic solution.
(6) Create a space to write the initial KHP burette reading, the final KHP burette reading, the initial volume of KHP used, the initial NaOH burette reading, the burette reading for NaOH at the equivalence point, and the volume of NaOH required for acid neutralization. You will need to record this information for each trial.

**Before Laboratory Questions – Week 2**

*These questions should be used to help you write your notebook and should be answered in some form before you go to the laboratory.*

(1) What is the purpose of Week 2 of this experiment?
(2) What is your hypothesis for the Week 2 experiment? Answer in if/then statements.
(3) What materials are required for this experiment? Are any chemicals needed? If so, what are they? Which materials must be obtained from the stockroom, which must be obtained from the instructor, and which are in your laboratory drawer?
(4) What unknown acid were you assigned?
(5) What difference should be observed during the titration using an indicator if the acid is monoprotic or diprotic? Explain.
(6) What difference should be observed during the titration for a potentiometric titration if the acid is monoprotic or diprotic? Explain.
(7) Create a space to input the mass of acid used for the trial, the initial NaOH burette reading, the final NaOH burette reading, and the volume of NaOH needed to reach the equivalence point based on the indicator for each trial.
(8) Create a table to record the volume of NaOH and the pH for each trial.
(9) Create a grid so that you can quickly graph the first trial for each unknown acid. The y-axis should be pH and range from 0 to 14. The x-axis should be volume of NaOH and should range from 0 to 100 mL.

## 7.3. Week 1

### 7.3.1. Acid/base nomenclature

7.3.1.1. *Acids.* Acids are covalent compounds formed from the hydrogen ion and an anion (cf. Table 3.3, for example anions). Although these compounds are covalent, the hydrogen ion can be removed when the acid is in aqueous solution. Thus, acids also have some properties of ionic compounds. An acid that possesses a single hydrogen that can form $H^+$ $(aq)$ in solution is a *monoprotic acid*. In general, a *polyprotic acid* has multiple hydrogen atoms that can form $H^+$ $(aq)$ in solution with the number of possible $H^+$ $(aq)$ ions being indicated by the prefixes given in Section 3.4.1. Thus, phosphoric acid is a triprotic acid, because it has three hydrogen atoms available to form $H^+$ $(aq)$ in aqueous solution. The general rules for aqueous acid nomenclature are:

(1) Aqueous acids formed with *-ide* anions are named using a ***hydro-*** prefix and an ***-ic acid*** suffix. Thus, HCl (which contains a chloride anion) is hydrochloric acid.
(2) Aqueous acids formed with *-ate* anions (including *per-ates*) are named using an ***-ic acid*** suffix. As an example, $H_2SO_4$ is sulfuric acid and $HClO_4$ is perchloric acid.
(3) Aqueous acids formed with *-ite* anions (including *hypo-ites*) are named using an ***-ous acid*** suffix. Thus, $HNO_2$ is nitrous acid, while HClO is hypochlorous acid.

Acids having the general from $H_XA$ which completely dissociate in aqueous solution to $A^{X-}$ $(aq)$ and form X moles of $H^+$ $(aq)$ are strong acids. The general chemical reaction equation for this dissociation is

$$H_XA\ (aq)\ +\ X\ H_2O\ (aq)\ \rightarrow\ X\ H_3O^+\ (aq)\ +\ A^{X-}\ (aq)\ . \tag{7.1}$$

However, some acids do not completely dissociate in aqueous solution, and instead exist in equilibrium with the dissociation products in solution. When an equilibrium is established, the acid is known as a weak acid and has a general chemical reaction equation of

$$H_XA\ (aq)\ +\ X\ H_2O\ (aq)\ \rightleftharpoons\ X\ H_3O^+\ (aq)\ +\ A^{X-}\ (aq)\ . \tag{7.2}$$

Notice that the formation of a equilibrium condition in eq. (7.2) is indicated by $\rightleftharpoons$; whereas eq. (7.1) uses $\rightarrow$ to indicate complete dissociation. When a reaction occurs that uses $H_3O^+$ $(aq)$ from a strong acid, the concentration of $H_3O^+$ $(aq)$ decreases in solution in a simple stoichiometric ratio. For weak acids, on the other hand, the initial depletion of $H_3O^+$ $(aq)$ due to a chemical reaction causes an increase in the dissociation of the weak acid. Therefore, the concentration of $H_3O^+$ $(aq)$ remains constant during the reaction until the amount of weak acid is depleted. Once the concentration of the weak acid is depleted, then the concentration of $H_3O^+$ $(aq)$ decreases in solution in a simple stoichiometric ratio, similar to the behavior of a strong acid.

7.3.1.2. *Bases.* Arrhenius bases are either hydroxides or molecular compounds that can except $H^+$ and, therefore, form $OH^-$ when dissolved in water. Metal hydroxides are strong bases, since these compounds always completely dissociate, when dissolved in water. Molecular bases, such as $(CH_3)_3N$ $(aq)$, are usually weak bases because only a fraction of the solute is ionized to form $(CH_3)_3NH^+$ $(aq)$. Ammonia is an exception to this, since $NH_3$ $(aq)$ is a strong base.

### 7.3.2. Acid/base titrations

Acid/base reactions are neutralization reactions that generate a salt and (sometimes) water. For instance, the reaction of the insoluble base $Mg(OH)_2$ $(s)$ with the strong aqueous acid HCl $(aq)$ gives water and the aqueous salt magnesium chloride. On the other hand, the reaction of aqueous ammonia with hydrochloric acid (notice that the name hydrochloric acid

implies aqueous, since gaseous HCl would be named hydrogen chloride) gives the aqueous salt ammonium chloride. One method to accurately investigate acid/base neutralization reactions is a titration.

Titrations are the precise measurement of the volume of one reactant (of known molarity) required to completely react with another reactant in a chemical reaction. When the reaction is complete, the titration is said to have reached the **end point**, or equivalence point, of the titration. Thus, titrations can be used to determine accurate concentrations of a reactant in solution for any chemical reaction. In an acid/base titration, either a base of known molarity is added to an acid of unknown concentration or an acid of known molarity is added to a base of unknown concentration. The end point occurs when complete neutralization has occurred, where neutralization implies that the acid has reacted with the base to generate water and a salt. For example, the neutralization reaction of potassium hydroxide with hydrochloric acid yields the salt potassium chloride and water, or

$$\mathrm{KOH}\,(aq)\ +\ \mathrm{HCl}\,(aq)\ \rightarrow\ \mathrm{KCl}\,(aq)\ +\mathrm{H_2O}\,(l)\ . \tag{7.3}$$

One way of determining the end point of an acid/base titration is to use the weak acid phenolphthalein as an indicator, since phenolphthalein is colorless in acidic, a very pale pink in nearly neutral solutions, and fuchsia in basic solutions. In this experiment, you will first use an acid/base titration with phenolphthalein as an indicator to standardize a basic solution (i.e., determine the molarity of the basic solution). This basic solution will be used in next week's experiment.

As an example, if 28.50 mL of a freshly prepared aqueous solution of potassium hydroxide is required to titrate 50.00 mL of 0.0922 M hydrochloric acid, the molarity of the potassium hydroxide is easily determined using the balanced chemical equation in eq. (7.3) by

$$\begin{aligned}[\mathrm{KOH}]\ =\ 50.00\ \mathrm{mL\ HCl}\ &\left(\frac{1\ \mathrm{L}}{1000\ \mathrm{mL}}\right)\left(\frac{0.0922\ \mathrm{mole\ HCl}}{1\ \mathrm{L\ HCl}}\right)\left(\frac{1\ \mathrm{mole\ KOH}}{1\ \mathrm{mole\ HCl}}\right)\\ &\times\left(\frac{1}{28.50\ \mathrm{mL\ KOH}}\right)\left(\frac{1000\ \mathrm{mL}}{1\ \mathrm{L}}\right)\ =\ 0.162\ \mathrm{M\ KOH}\ .\end{aligned} \tag{7.4}$$

Next week this basic standardized solution will be used to titrate an unknown acid in order to determine the molar mass of an acid. For example, if it requires 25.62 mL of 0.235 M NaOH $(aq)$ to reach the end point (indicating the complete neutralization of all $\mathrm{H^+}\ (aq)$ in solution) of a titration of 0.351 g of an unknown diprotic acid (dissolved in 30 mL of water), then the stoichiometric equation is

$$\mathrm{H_2A}\,(aq)\ +\ 2\ \mathrm{NaOH}\,(aq)\ \rightleftharpoons\ \mathrm{Na_2A}\,(aq)\ +\ 2\ \mathrm{H_2O}\,(l)\ . \tag{7.5}$$

Using this equation, we determine that the moles $n$ $(\mathrm{H_2A})$ of acid titrated were

$$\begin{aligned}n\ (\mathrm{H_2A})\ &=\ 25.62\ \mathrm{mL\ NaOH}\left(\frac{1\ \mathrm{L}}{1000\ \mathrm{mL}}\right)\left(\frac{0.235\ \mathrm{mole\ NaOH}}{1\ \mathrm{L\ NaOH}}\right)\left(\frac{1\ \mathrm{mole\ H_2A}}{2\ \mathrm{mole\ NaOH}}\right)\\ &=\ 3.01\times10^{-3}\ \mathrm{mole\ H_2A}\ .\end{aligned} \tag{7.6}$$

Finally, the molar mass $M$ $(\mathrm{H_2A})$ of the unknown diprotic acid is

$$M\ (\mathrm{H_2A})\ =\ \frac{m\ (\mathrm{H_2A})}{n\ (\mathrm{H_2A})}\ =\ \frac{0.351\ \mathrm{g\ H_2A}}{3.01\times10^{-3}\ \mathrm{mole\ H_2A}}\ =\ 117\ \mathrm{g/mol\ H_2A}\ . \tag{7.7}$$

### 7.3.3. Experiment 7A. Preparation of a standard acid solution

In order to experimentally measure the molarity of a basic solution, one must first prepare a acidic solution of known molarity, or a standard acidic solution. (A standard solution is any solution of known molarity.) Potassium hydrogen phthalate (KHP, $\mathrm{KHC_8H_4O_4}$, cf.

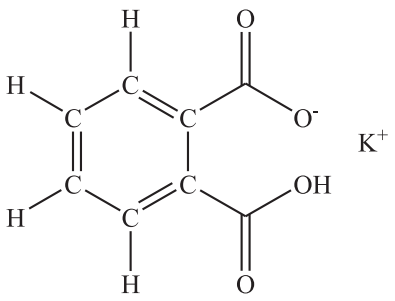

Fig. 7.1: Structure of potassium hydrogen phthalate (KHP).

Fig. 7.1) is a monoprotic acid that is inexpensive, is available in high purity, and is easily dried. The high molar mass of this compound allows for high precision when determining the number of moles in a solution of low volume (i.e., $< 100$ mL). Thus, KHP is commonly used to create standard acidic solutions.

(1) Obtain a 250 mL volumetric flask from the stockroom. A volumetric flask has been standardized and gives a volume that is accurate to four significant figures if the flask is used at room temperature. The flask contains the stated volume (i.e., 250.0 mL) when it is filled so that the bottom of the meniscus coincides with the line etched around the neck of the flask. Rinse the flask with 25 mL of distilled water. If droplets form on the inner surfaces, wash the flask with liquid detergent, rinse thoroughly with tap water, and then rinse with three 25 mL aliqouts of distilled water.
(2) Weigh 5 grams of KHP, using a tared, clean dry beaker. Record the exact weight of KHP on the Report Sheet.
(3) Add 50 mL of water to the beaker to begin to dissolve the KHP. Then transfer the KHP to the volumetric flask, being careful not to spill any of the solution.
(4) Rinse the beaker with three aliquots of 10 mL of distilled water. Add these washings to the volumetric flask (again being careful not to spill any of the solution.) This ensures that any KHP adhering to the walls of the beaker is transferred to the volumetric flask.
(5) Approximately 150 mL of distilled water should be placed in the volumetric flask (i.e., the water level should be about 3/4 of the way up the bulb of the volumetric flask). Close the flask with the lid (or a rubber stopper or parafilm) and invert several times to mix the contents. Continue this process until such time as the KHP is completely dissolved.
(6) Remove the lid (or rubber stopper or parafilm) and rinse with a small amount of distilled water, again making sure that the water drops into the volumetric flask.
(7) Add enough distilled water to nearly fill the flask to the etched line, cover, and invert several times to mix the contents. Remove the flask cover, again rinsing to ensure that all of the solution remains in the volumetric flask.
(8) Add water with a clean medicine dropper (or pipette) to bring the bottom of the meniscus to the etched line. Show your laboratory instructor your volumetric flask once you have completed the preparation of the solution. *Note: If you have overfilled your flask, your laboratory instructor will make you repeat this procedure.*

### 7.3.4. Experiment 7B. Preparing the basic solution for standardization

The determination of the molar mass of a unknown acid requires a basic solution with a concentration of approximately 0.1 M. A 2 M or 3 M stock sodium hydroxide solution is provided in the fume hood. Using this stock solution, prepare 400 mL of 0.1 M sodium hydroxide solution and store this dilute basic solution in your clean dry storage bottle. Since the actual molarity of the dilute sodium hydroxide solution will be determined using titration, volumetric flasks do not need to be used in this dilution. Thus, the volume of the stock solution can be measured using a graduate cylinder and the volume of the final solution can be measured using a graduated beaker. Be sure to note the molarity of the stock solution on the Report Sheet and show your dilution calculation to the laboratory instructor before performing the dilution.

### 7.3.5. Experiment 7C. Standardization of the basic solution

(1) Obtain two burettes from the Stockroom. Record the graduations of the burettes on the Report Sheet and determine the precision of volume measurements that can be made with these burettes. Show this information to your laboratory instructor.
(2) Put a few mL of water in each of the burettes, clamp them in a vertical position using a ring stand and burette clamp and test the stopcock (i.e., the valve at the bottom of the burette. You should be able to control the liquid flow to one drop at a time with practice. If not, return the burette to the Stockroom and obtain another burette.
(3) Put a few mL of distilled water into the burette and roll around to wet the inside walls of the burette. If droplets form inside the burette, wash it with liquid detergent and a burette brush (obtained from the Stockroom). Rinse with tap water (three 10 mL portions allowing some of each portion to run through the tip) and then with three 10 mL aliquots of distilled water.
(4) Once the burette is clean, rinse the burette with three 10 mL portions of the solution that the burette will hold (one burette will hold the sodium hydroxide solution and one will hold the standard KHP solution), again allowing some of the solution to run through the tip. Discard the rinsings in the appropriate waste bottle.
(5) Make sure that the stopcock is closed. Hold the buret with its top below eye level and fill it with solution to somewhere near the top mark. Run a little solution out of the bottom and watch for air bubbles in the tip. (To remove a bubble, hold the partly filled burette in a nearly horizontal position, open the stopcock part way and allow the slow flow of liquid to push the bubble out of the tip.)
(6) Clamp the filled burette in a vertical position and record the initial volume of liquid in each burette. Always wait at least 15 seconds before taking a volume reading to ensure that the liquid has drained down the inner surface of the burette.
(7) Use the burette containing the standard KHP to place approximately 25 mL of the KHP solution into a clean Erlenmeyer flask. Add approximately 25 mL of distilled water and 2 drops of phenolphthalein solution to the flask. Record the actual volume of KHP solution used on the Report Sheet.
(8) Place the Erlenmeyer flask on a sheet of white paper under the burette containing the sodium hydroxide solution. (The white paper will help in seeing the end point.)
(9) Begin adding sodium hydroxide to the KHP solution, Swirling the flask gently and steadily to mix the acid and base solutions thoroughly. One can begin to add sodium hydroxide in 1 - 2 mL portions. Initially, a transient pink color will appear as sodium hydroxide is added. As the titration continues, the pink color

will persist for longer intervals, but continue to disappear. As this happens, begin to add sodium hydroxide in small portions. The longer the pink color persists, the smaller the amount of sodium hydroxide should be added. As you get closer to the equivalence point, sodium hydroxide should be added dropwise.

(10) The equivalence point is marked by the first permanent faint pink color in the KHP solution. (Permanent is a color change that persists for at least 30 seconds. The pink color may ultimately fade due to the absorption of $CO_2$ from air.) If sodium hydroxide has splashed onto the walls of the Erlenmeyer flask or any drop hangs from the burette tip, when you are near the equivalence point, wash these down into solution using distilled water from your wash bottle. Show your end point to your instructor before continuing.

(11) If your instructor indicates that you have overshot the equivalence point (i.e., the color of the solution is dark pink or red/purple), add KHP solution from the acid burette dropwise until the color disappears. Then add sodium hydroxide from the base burette dropwise until you have reached the equivalence point. Be sure to record both the volume of KHP added and the volume of base added.

(12) Obtain a new clean Erlenmeyer. Refill the burettes and repeat the titration with an additional volume of KHP.

**Once the two titrations have been completed, the remaining sodium hydroxide solution should be stored in a labeled, sealed container for use in Experiment 7E.** The KHP solution can be discarded in the appropriate waste container. The volumetric flask should be cleaned and returned to the Stockroom. The burette containing KHP can also be emptied and rinsed with three 10 mL portions of distilled water. Return this burette to the Stockroom.

## 7.4. Week 2

### 7.4.1. Potentiometric titrations

In a potentiometric titration, one measures the difference in potential (in volts) caused by a difference in ion concentration on two sides of a barrier. The measured voltage $E_{cell}$ is dependent on the ion concentration and on the cell constant $E'$, which is an internal parameter that is characteristic of the voltage meter and electrode. Potentiometric titrations can be used to determine ion concentrations for various cations and anions. However, before any potentiometric measurement, the electrode must be calibrated. This calibration sets $E'$ by using solutions of known concentrations. In this experiment, a pH electrode (cf. Fig. 7.2 for a schematic) will be used to determine the equivalence point of an acid/base reaction. In a pH electrode,

$$E_{cell} \;=\; E' \;+\; 0.0592\ \text{pH}\,, \tag{7.8}$$

which shows that $E_{cell}$ is directly proportional to the pH. Thus, pH meters, when calibrated appropriately using buffer solutions of known pH, directly output pH instead of voltage.

### 7.4.2. The pH scale

As introduced in Experiment 6, a Brønsted-Lowry acid is a proton donor, while the base is a proton acceptor. Water is amphoteric and, therefore, can act as both a Lowry acid and a Lowry base. The dissociation reaction for water is

$$\text{H}_2\text{O}\ (l) + \text{H}_2\text{O}\ (l) \rightleftharpoons \text{H}_3\text{O}^+\ (aq) + \text{OH}^-\ (aq)\ .$$

As an acid, water has the conjugate acid/base pair of $H_3O^+/H_2O$; whereas when acting as a base, the conjugate acid/base pair is $H_2O/OH^-$. The $\rightleftharpoons$ indicates that the reaction reaches an equilibrium state between products and reactants, instead of a 100% conversion

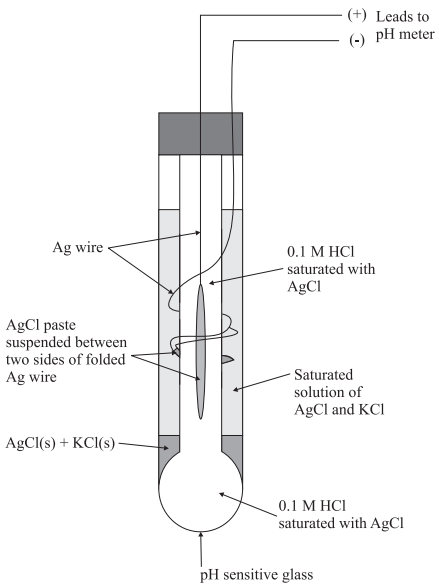


Fig. 7.2: Schematic of a pH electrode.

of reactants to products. Equilibrium reactions are defined by a temperature dependent constant $K$ called the equilibrium constant. For the general reaction,

$$\alpha\ \mathrm{A} + \beta\ \mathrm{B} \rightleftharpoons \gamma\ \mathrm{C} + \delta\ \mathrm{D}\ ,$$

the equilibrium constant is given by

$$K\ =\ \frac{a_C^{\gamma}\ a_D^{\delta}}{a_A^{\alpha}\ a_B^{\beta}}\ \approx\ \frac{[C]^{\gamma}\ [D]^{\delta}}{[A]^{\alpha}\ [B]^{\beta}}\ , \tag{7.9}$$

where $a_X$ is the activity of moiety X and [X] is the molar concentration of moiety X. Thus, the equilibrium constant $K_W$ of water at low acid concentrations is given by

$$K_W = \frac{[\mathrm{H_3O^+}][\mathrm{OH^-}]}{[\mathrm{H_2O}]^2}\ \approx\ [\mathrm{H_3O^+}]\ [\mathrm{OH^-}] = 1.0 \times 10^{-14} \tag{7.10}$$

since $a_{H_2O} = 1$ at standard ambient temperature and pressure (i.e., 25°C and 1 bar). *(Notice that $K$ and $K_W$ have no units.)*

In neat water, we obtain

$$[\mathrm{H_3O^+}]\ =\ [\mathrm{OH^-}]\ =\ \sqrt{K_W}\ =\ 1 \times 10^{-7}\ ,$$

which is the definition of a neutral water solution. When an acid is added to water, the hydronium ion concentration increases, whereas the addition of a base increases the hydroxide ion concentration. Because the concentration of hydronium (or hydroxide) ion in solution can vary from 10 M to $10^{-14}$ M, a logarithmic scale was developed to allow for ease of graphing. This scale is called the **pH scale** and is defined by

$$\mathrm{pH}\ =\ -\log\left(\frac{[\mathrm{H_3O^+}]}{\mathrm{M}}\right)\ , \tag{7.11}$$

with the inverse relation

$$[\mathrm{H_3O^+}]\ =\ 10^{-\mathrm{pH}}\ \times\ \mathrm{M}\ . \tag{7.12}$$

Thus, if cranberry juice has a pH of 2.46, then the concentration of hydronium ion is

$$[\mathrm{H_3O^+}]\ =\ 10^{-2.46}\ \times\ \mathrm{M}\ =\ 3.47 \times 10^{-3}\ \mathrm{M}\ .$$

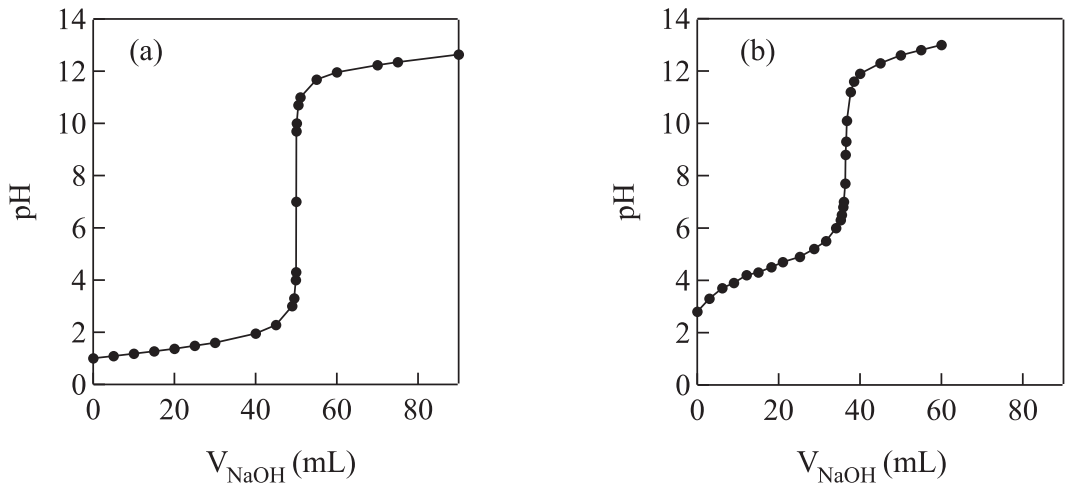


Fig. 7.3: pH plotted as a function of sodium hydroxide volume for a (a) strong monoprotic acid [1] and (b) a weak monoprotic acid [2].

Since the dissociation of pure water into hydronium and hydroxide ions defines a neutral water solution at room temperature, the pH of a neutral solution is pH $= -\log 1 \times 10^{-7} =$ 7.00. (We should note here that at temperatures other than 25°C in water or for other solvents, the pH of a neutral solution can differ from 7.00.) A pH of $< 7.00$ in an aqueous solution indicates a larger hydronium ion concentration than that of neutral water and, therefore, a more acidic solution. Similarly, a pH of $> 7.00$ in an aqueous solution at 25°C is indicative of a larger hydroxide ion concentration in water, or a more basic solution. Fig. 7.3a shows an example pH curve, plotted as a function of the volume of the titrating base, for the titration of a monoprotic strong acid by a strong base. Near the equivalence point (i.e., the point were $[H_3O^+] = [OH^-]$), the amount of acid becomes progressively smaller, so that successive increments of base neutralize a greater fraction of the acid. Thus at the equivalence point, there is a steep increase in pH which produces an inflection point in the pH curve. For a polyprotic acid, the acid can possess multiple equivalence points if each proton reacts stepwise with the base. Thus, a triprotic acid $H_3A$ would have the following set of neutralization reactions:

$$\begin{aligned} H_3A\,(aq) + OH^-\,(aq) &\rightleftharpoons H_2A^-\,aq) + H_3O^+\,(aq) \\ H_2A^-\,(aq) + OH^-\,(aq) &\rightleftharpoons HA^{2-}\,(aq) + H_3O^+\,(aq) \\ HA^{2-}\,(aq) + OH^-\,(aq) &\rightleftharpoons A^{3-}\,(aq) + H_3O^+\,(aq), \end{aligned} \tag{7.13}$$

each of which has its own equivalence point (cf. Fig. 7.4). In this experiment, you will use both an indicator titration and a potentiometric titration to determine the molar mass of a unknown acid.

Unlike strong acids that completely dissociate in aqueous solution, weak acids form an equilibrium that consists of the acid HA $(aq)$, the acid anion $A^-$ $(aq)$, and the hydronium ion $H_3O^+$ $(aq)$. Because of this equilibrium, the titration curve of a weak acid and a strong base (cf. Fig. 7.3b) has a region where the change is pH is small in comparison to the change in the amount of strong base added to the system. This region, known as the buffering region, is caused by the fact that only a small amount of the acid is neutralized since the acid is only partially dissociated. Because of this buffering region, the equivalence point pH is greater than that of neutral water (i.e., pH $> 7$) since the conjugate base of a weak acid is a fairly strong base that can remove a proton from water to generate $OH^-$ $(aq)$ and the

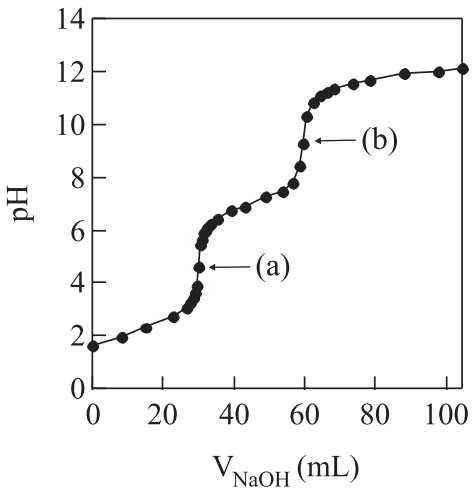


Fig. 7.4: pH plotted as a function of sodium hydroxide volume for phosphoric acid. (a) is the equivalence point of the reaction of $H_3PO_4$ with a single mole of NaOH to give $H_2PO_4^-$. (b) is the equivalence point of the reaction of $H_2PO_4^-$ with a single mole of NaOH to give $HPO_4^{2-}$. The final step requires a large volume of NaOH because $HPO_4^{2-}$ behaves more like a weak acid. Therefore, this final step is not shown.

weak acid. The molar mass of a solid acid or base can be determined from the volume of base (or acid) need to reach the final equivalence point of a titration. In this experiment, you will use titration with an indicator and potentiometric titration to determine the molar mass of an unknown acid.

### 7.4.3. Experiment 7D. Calibration of pH electrode

(1) You should obtain from the Stockroom a pH electrode and Pasco meter. Fig. 7.5 shows a picture of the Xplorer unit (Pasco meter) with all buttons labeled.
(2) Turn on the Xplorer unit by holding the power button until the Xplorer beeps once (should take approximately one second).
(3) Press the Display button until the Battery life is shown and verify that the battery life is close to F and not to E. If the battery life is low, return to the Stockroom and obtain two AA batteries or an AC adapter.
(4) Orient the pins on the mini DIN connector of the pH probe sensor to the holes on the Xplorer, then plug the sensor into the receptacle on the top of the Xplorer. The Xplorer unit should automatically recognize the pH probe.
(5) To calibrate the pH electrode, get two clean 50 mL beakers. Place 10 mL of a pH buffer with low pH and one with high pH into each beaker, respectively. Label each beaker with the pH of the buffer.
(6) Fill your wash bottle with distilled water and prepare a 100 mL (or 150 mL) beaker with approximately 50 mL of distilled water and label this beaker.
(7) Remove the pH electrode from its storage container and rinse the electrode with the wash bottle over a large beaker. Then place the electrode into the distilled water beaker and wait for 5 minutes. **When you are not using the electrode, keep the electrode moist by returning it to the distilled water beaker.**
(8) Press the Display button on the Xplorer unit until the Calibrate screen appears. Then, press the Check button.


1. **Tab button**
   Moves the edit cursors to the next field
2. **Power button:**
   Turns Xplorer on and off
3/4. **Minus/Plus buttons:**
   Changes the value in the edit filed (1 pt. for each button press).
   Chooses an alternate sensor measurement.
   Changes the sampling mode.
5. **Display button:**
   Changes the display mode.
   Ends editing – discards changes.
   Wakes up Xplorer if sleeping.
6. **LED light:**
   Flashes when Xplorer is storing data.
7. **Start/Stop button**
   Starts measuring and creates a new data set.
   Stops measuring and ends a data set.
8. **Check button**
   Begins editing (shows the edit cursors).
   Ends editing – accepts changes.
   Keeps a single value when manual sampling.

Fig. 7.5: Illustration of Pasco Xplorer unit with labels.

(9) Press the Tab button to move through the digits and use the - or + buttons to decrease or increase each digit until the display reads the pH of the low pH buffer.
(10) Place the pH Sensor into the low pH buffer, wait five minutes and press the Check button. The Pasco unit performs the low pH calibration and then automatically advances to the next calibration step.
(11) Remove the pH sensor, rinse with the wash bottle, and then return to the distilled water beaker for five minutes.
(12) Press the Tab button on the Xplorer to move through the digits and use the - or + buttons to decrease or increase each digit until the display reads the pH of the high pH buffer.
(13) Place the pH Sensor into the high pH buffer, wait five minutes, and press the Check button.
(14) Rinse the pH probe with water from the wash bottle and return the pH Sensor to the distilled water beaker.
(15) Press the display button until the screen reads pH and a value.
(16) Return the pH sensor to the low pH buffer solution, wait 2 - 5 minutes, and check the pH. Rinse the electrode and place the electrode in distilled water for 5 minutes. Then place the electrode in the high pH buffer solution and wait 2 - 5 minutes. Check the pH. If the pH being reported by the Xplorer unit does not agree with the pH of the buffers, then recalibrate the unit. Until such time as the observed pH is within 0.1 of the reported buffer pH, the unit is not appropriately calibrated. If you cannot get a stable and accurate reading after a third calibration, ask your instructor for help.

Table 7.1: The names, chemical formula, and molar masses of various mono- and diprotic acids.

| Name | Formula | (g/mol) Molar mass |
|---|---|---|
| benzoic acid | $C_6H_5$-COOH | 122.1 |
| disodium hydrogen citrate sesquihydrate | $C_6H_6Na_2O_7 \bullet 1.5\ H_2O$ | 263.11 |
| lactic acid | $CH_3$-CH(OH)-COOH | 90.08 |
| maleic acid | HOOC-CH=CH-COOH | 116.04 |
| malic acid | HOOC-$CH_2$-CH(OH)-COOH | 134.09 |
| malonic acid | HOOC-$CH_2$-COOH | 104.06 |
| nicotinic acid | $C_6H_5NO_2$ | 123.11 |
| oxalic acid dihydrate | HOOC-COOH $\bullet$ 2 $H_2O$ | 126.07 |
| potassium hydrogen phthalate | $KHC_8H_4O_4$ | 204.23 |
| potassium hydrogen tartrate | $KC_4H_5O_6$ | 188.18 |
| sulfamic acid | HO-$SO_2$-$NH_2$ | 97.10 |
| tartaric acid | HOOC-CH(OH)-CH(OH)-COOH | 150.09 |

### 7.4.4. Experiment 7E. Indicator and pH titration of unknown acid

(1) During the pre-laboratory, your laboratory instructor will assign you two different unknown acids. Obtain approximately 3 grams of one of the unknown solid acids.
(2) Place the weighed acid into a 150 or 200 mL beaker.
(3) Add 25 - 50 mL of water to the beaker to dissolve the acid. Then add two drops of phenolphtalein to serve as a visual indicator.
(4) Place the pH electrode into the beaker. Make sure that the screen on the Xplorer unit is set to display the current pH. Record the pH before the addition of base.
(5) Titrate with the sodium hydroxide solution that you standardized in Experiment 6. Record the pH for each addition of base. As the equivalence point is approached, the pH will need to be recorded at closer intervals for a smoother curve. **For the first titration, plot your data during the data aquisition.** Show these data to the instructor for advice before proceeding to other titrations. Also record the volume of the equivalence point based upon your observations. For the pH titration, you should aim for points that are separated by a pH of 0.3 units. This will require more base at the beginning and increasingly less base toward the equivalence points. You should also note that diprotic acids will give two different steps in a pH titration, but only a single equivalence point with phenolphthalein. You should continue the titration until the pH of the solution is between 11 and 12. Depending on the acid, your data should resemble Fig. 7.2 or 7.3.
(6) Repeat the titration at least once. Then perform the same steps using your second solid acid.
(7) Use the information obtained from the titrations to determine the molar mass of each acid. With the molar masses, identify the unknown acid using Table 7.1.

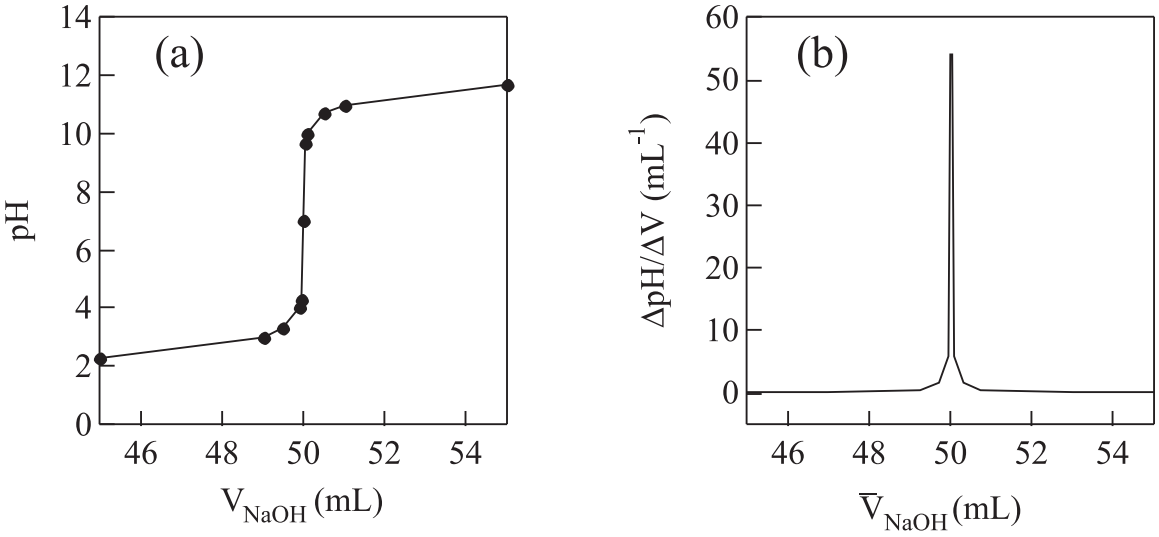


Fig. 7.6: (a) The pH of a monoprotic acid as a function of the volume $V_{\rm NaOH}$ of base added for a titration near the equivalence point. (b) Eq. (7.14) plotted as a function of eq. (7.15) for the same set of data as that in (a). See text for discussion.

### 7.4.5. Potentiometric data analysis

The large increase in pH for small changes in base volume near the equivalence point (cf. Fig. 7.6a, for example) makes it difficult to determine the volume of base at the end point of the titration. However, the volume of base at the equivalence point can be determined by graphing the change $\Delta$pH in pH divided by the change $\Delta V$ in base volume as a function of average volume $\overline{V}$. If $\mathrm{pH}_1$ and $V_1$ are the pH and volume at point 1 and $\mathrm{pH}_2$ and $V_2$ are the pH and volume at point 2, then

$$\left(\frac{\Delta \mathrm{pH}}{\Delta V}\right)_1 \;=\; \frac{\mathrm{pH}_2 - \mathrm{pH}_1}{V_2 - V_1}$$

and

$$\overline{V}_1 \;=\; V_1 \;+\; 0.5 \times (V_2 - V_1)\;.$$

Thus, for a general set of data points $\{\mathrm{pH}_i,\ V_i\}$ and $\{\mathrm{pH}_j,\ V_j\}$, where $j = i + 1$, we obtain

$$\left(\frac{\Delta \mathrm{pH}}{\Delta V}\right)_{j-i} \;=\; \frac{\mathrm{pH}_j - \mathrm{pH}_i}{V_j - V_i} \tag{7.14}$$

and

$$\overline{V}_{j-i} \;=\; V_i \;+\; 0.5 \times (V_j - V_i)\;, \tag{7.15}$$

for $j < n$, where $n$ is the total number of data points. A graph of eq. (7.14) plotted as a function of eq. (7.15) is shown in Fig. 7.6b for the data set in Fig. 7.6a. The peak in Fig. 7.6b represents the inflection point in the data of Fig. 7.6a. This inflection point is the equivalence point.

## 7.5. References

(1) S. R. Marsden, *A Laboratory Text: An exploration of the science of chemistry*, 6th ed. (2006), p. 171. From http://www.chemtopics.com/aplab/contents.htm (accessed November 30, 2008).

(2) Data provided by Ms. Xhesika Shanja, Chemistry 113 laboratory, Queens College – CUNY, Fall 2008.

**After Laboratory Questions – Week 1**

*These questions should be used to help you write your notebook and should be answered in some form after completion of the laboratory.*

(1) What is the molarity of the standard KHP solution?
(2) What is the balanced chemical reaction for the neutralization of KHP with sodium hydroxide?
(3) What is the molarity of sodium hydroxide from the data in Trial 1? in Trail 2?
(4) What is the average molarity and uncertainty?

**After Laboratory Questions – Week 2**

*These questions should be used to help you write your notebook and should be answered in some form after completion of the laboratory.*

(1) Include in your notebook graphs of pH versus volume and a graph of eq. (7.14) versus eq. (7.15) for each trial.
(2) Use the procedure provided to determine the pH at the equivalence point (or at both equivalence points).
(3) From your graphs, what is the volume of NaOH required to reach the final equivalence point?
(4) What is the molar mass of the acid (including uncertainty) as calculated from the volume of NaOH obtained graphically for each acid?
(5) What is the molar mass of the acid (including uncertainty) as calculated from the volume of NaOH obtained using the visual indicator for each acid?
(6) Given the molar masses, what are the identities of the unknown acids? A table of possible acids is given in Appendix II.
(7) Include in your report a discussion of which set of data is more precise and why for each acid investigated.