## ACIDS & BASES AND TITRATIONS & BUFFERS

Introduction

In an acid–base titration, the concentration of an **analyte** (acid or base) is quantitatively determined by the addition of a known volume of **titrant** (base or acid, respectively) in the presence of a good **indicator**. *What is an indicator and what makes it good? How does the strength and number of protons on the acid affect the titration? What is the equivalence point and how is it determined?*

In this experiment, a strong base, ~0.10 M NaOH will be used to titrate ~0.10 M solution of acetic acid, $C_2H_4O_2$. What is the balanced chemical equation for this neutralization reaction?

A **titration curve** is a plot of pH versus *volume* of titrant. The titrant, ~0.1 M NaOH, will be slowly dripped from a buret (solvent reservoir) into the acid solution which contains a computer-interfaced pH electrode. Volume will be recorded by arranging a drop counter beneath the buret and allowing the drops to fall through the "optical path slot." Each drop interrupts an infrared beam, sending a digital signal to the LabPro interface. Following calibration of the drop counter, the data collection program records the number of drops of titrant and converts that number to volume in milliliters.

A gradual change in pH occurs as the base is initially added to the acidic solution. For a weak acid, such as acetic acid, this section of the titration curve is referred to as the **buffering region**. As base is added it reacts with the acid and forms a buffer solution (a solution of an acid (HA) and its conjugate base (A^-)), which explains the gradual change in pH because the buffer resists the change in pH. At the midway point of this region, the concentration of HA equals the concentration of A^-. Derivation of the Henderson–Hasselbalch equation demonstrates that when [HA] = [A^-] the pH is the **pK_a** of the weak acid.

A weak acid (HA) dissociates in water according to the equation:
$$(1) \quad HA \ (aq) \ + \ H_2O \ (l) \ \rightleftarrows \ H_3O^+ \ (aq) \ + \ A^- \ (aq) \qquad K_a = [H_3O^+] \ [A^-] \ / \ [HA]$$
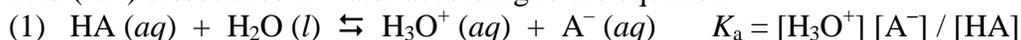
The acid dissociation constant is algebraically rearranged to the following:
$$(2) \quad [H_3O^+] = K_a \ [HA] \ / \ [A^-]$$

Taking the negative log of both sides of equation (2) results in the Henderson–Hasselbalch equation for a weak acid:
$$(3) \quad pH = pK_a + \log ([A^-] \ / \ [HA])$$

If [HA] = [A^-], the ratio [A^-] / [HA] = 1 and the logarithmic term becomes log(1) which is equal to zero, simplifying equation (2) to the following:
$$(4) \quad pH = pK_a \ \text{(half-way to the equivalence point)}$$

At some point most of the weak acid has reacted away, exhausting the buffer and the pH begins to change rapidly. The **equivalence point**, or stoichiometric point, is the titrant volume and solution pH when enough titrant has been added to react with all of the analyte present. At this

point the reaction has gone to completion; in other words, only reaction products (A⁻) are present in the flask below the buret. The concentration and volume of the titrant at the equivalence point can be used to determine the moles of titrant needed to stoichiometrically react with the analyte. Therefore, the moles of analyte can be determined by using the mole ratio from the balanced chemical equation for the reaction between the titrant and analyte. *Where is the equivalence point on a titration curve?*

The equivalence point is the **inflection point** of a titration curve. As a sigmoidal shaped curve, the inflection point is where the curvature changes sign (or direction) on a titration curve. *Note:* (1) The pH of the inflection point can be used to pick an indicator for a titration (then a pH probe would no longer be necessary). Also, an indicator can be chosen by calculating the theoretical pH at the equivalence point. (2) Half the volume of base required to reach the equivalence point is needed to reach the point where $[HA] = [A^-]$ and the $pH = pK_a$.

An **endpoint** is the titrant volume and solution pH at which the *indicator changes color.* Endpoints are a property of the indicator being used, *not* a function of the titrant or analyte. An indicator is a weak acid that when deprotonated (forming its conjugate base) changes color. The pH range of the color change is around the pK_a of the indicator. If the indicator's color change occurs at a pH near a titration's equivalence point, the indicator can be used in place of the pH probe for a titration. Continuing beyond the equivalence point, when more base has been added than acid present in the solution, another buffering region with more gradual changes in pH is observed.

The indicator used in this experiment is bromothymol blue ($pK_a = 7.10$). The removal of the "H" from the acidic form (HIn) results in a change in the conjugation, and, therefore, color in the basic form (In⁻).

Yellow, HIn   Blue, In⁻
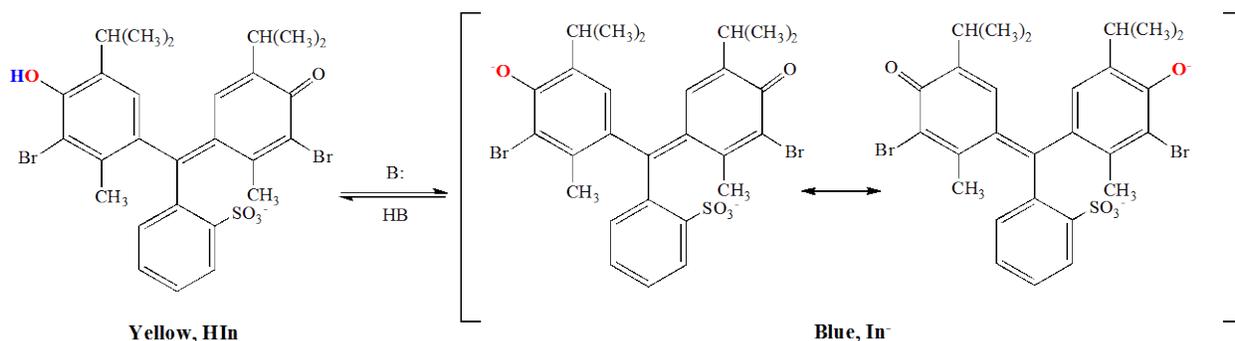
Bromothymol blue will also be used to show how pH can control **speciation**. Five buffer solutions ranging from pH 1 to 13 will be created. Because bromothymol blue is a weak acid that changes color when deprotonated, the amount of each species (HIn or In⁻) in solution can be quantified by visible spectroscopy.

In this experiment, you will determine how electrolytic strength and number of acid protons affect the shape of the titration curve and the pH of the equivalence point. A strong base (NaOH) will be used to titrate a weak acid ($C_2H_4O_2$) in the presence of bromothymol blue

indicator. The K_a of acetic acid will be determined. Bromothymol blue's speciation between acid and base form will be investigated by combining it with buffers of differing pH values.
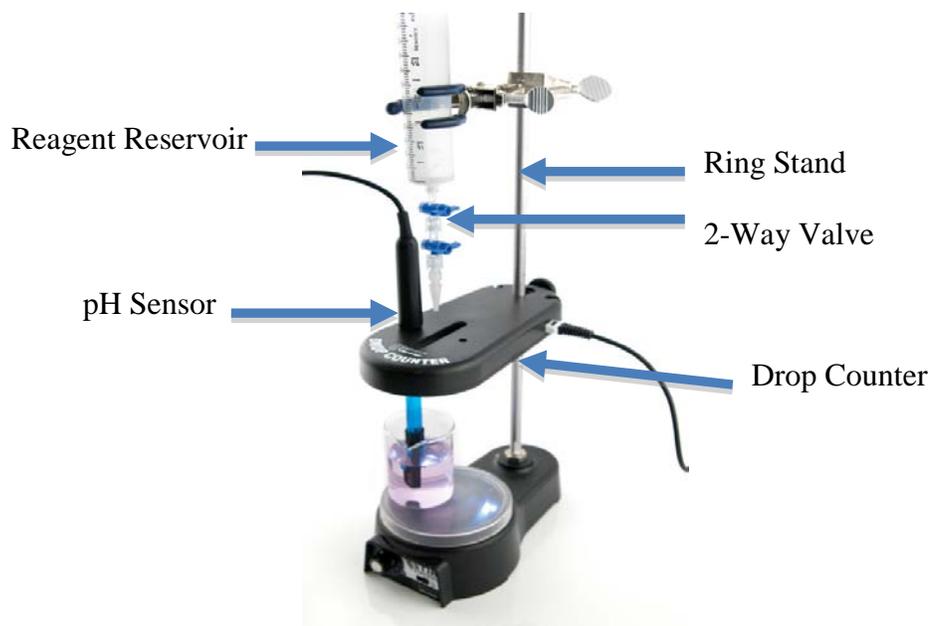
Safety

Acids and bases are caustic solutions and should be handled with care. If spills occur, wash affected areas immediately and inform your TA or course instructor.

Procedures

Part A. Standardization & Titration Curves
1. <u>Work in pairs.</u> Set up the Vernier pH meter and drop counter as follows:

- Connect the pH sensor to CH 1 and connect the drop counter to the Dig/Sonic 1 channel of the LabPro interface. Start Logger Pro on your computer. Select "File"→ "Open"→ "Experiments"→ "Chemistry with Vernier"→ "24b Acid-Base (Drop Count)."

- Go to the "Experiment" menu, select "Set Up Sensor" → "Show All Interface." Select "pH Sensor" in the drop down menu for CH 1, and select Drop Counter for Dig/Sonic 1. Close this window after the probes have been recognized.

- **Calibrate the pH probe**: Go to the "Experiment" menu and under "Calibrate" choose the channel with the pH probe (ex: "CH1:pH"). In the window that appears choose the Calibration tab. Click on "Calibrate Now." Rinse the pH meter with copious amounts of deionized water. Carefully blot dry. Dip the pH meter in less than 10 mL of pH 4 buffer. When the voltage reading stabilizes enter the pH value of the buffer in the field beneath "Enter Value." Repeat the process with pH 10 buffer. To check the calibration, measure

the pH of pH 7 buffer. Click "Done" to complete the calibration process. This new calibration becomes the current calibration for the sensor. Rinse the electrode with deionized water and then place it in a beaker with deionized water.

- **Adjust the flow rate of the reagent reservoir:** Fill the reservoir with titrant (0.10 M NaOH). Temporarily, place an empty beaker below the spout of the reagent reservoir. Completely open the bottom 2-way valve; then slowly open the top valve until a very slow drip rate is achieved – one drop every two seconds or slower. Make sure the drops are falling through the opening where the sensor is on the drop counter. Now close the bottom valve. *Take care not to move the position of the valve or the reservoir after these adjustments have been completed.*

- **Calibrate the Drop Counter**: Go to the "Experiment" menu and under "Calibrate" choose the channel with the drop counter (ex: "DIG1:Drop Counter"). Select "Automatic" in the menu that appears. Place a 10 mL graduated cylinder below the slot of the drop counter. Make sure the reservoir has at least 10 mL of titrant. Click "Start." Open the bottom 2-way valve to begin releasing drops from the reservoir to the Drop Counter. Continue to release drops until between 4 and 5 mL of liquid are in the graduated cylinder. Close the bottom 2-way valve to stop the drops. Enter the precise volume of liquid in the graduated cylinder in the Volume (mL) box on the screen. Click "OK." You are now ready to perform your titration.

2. **Standardization.** Mass 0.25 g of KHP and record the mass to the nearest milligram. (KHP is kept in a desiccator to keep it dry, be careful sliding the desiccator lid off and make sure that you put the lid back on as soon as possible.) In a 100 mL beaker, dissolve the KHP in ~20 mL of DI water and add 5 – 7 drops of bromothymol blue indicator. Place the beaker on the stir plate underneath the spout of the reagent reservoir, add a stir bar, and adjust the stirrer to a slow stirring speed. (The magnetic stirrer may cause the computer monitor to flicker.)

3. Refill the reagent reservoir with 0.10 M NaOH solution.

4. Experiment "24b Acid-Base (Drop Count)" should still be open on your computer. To start the titration click "Collect" → "Erase and Continue." Click "Start." Open the bottom 2-way valve to begin releasing drops from the reservoir through the drop counter.

5. When the solution changes color, record in your ELN the volume and pH. The titration is complete once the horizontal region of your titration curve at higher pH values appears similar in length to the one at lower pH values (i.e. the curve appears somewhat symmetrical). Click "Stop." Pour the titrated solutions into a 1 L beaker and set it aside.

6. Create a first derivative plot in Logger Pro or Excel to get a better estimate of the volume of titrant needed to reach the equivalence point. To do so in Logger Pro:
   a. Under "Data", select "New Calculated Column…"
   b. Give a name and short name to your calculated column.
   c. Click the "Functions" button, highlight "calculus" and select "derivative".

    d. Click "Variables", select your "pH", and click "Done". You can then choose to plot your calculated column on the y-axis.

7. Save this file on your computer and/or memory stick (the data is needed for answering the postlab questions).

8. Share standardization data with at least 5 other students so that you can calculate an average concentration.

Trials #1, 2, 3 (perform steps 8-14 three times):
9. Place *exactly* 100 mL of DI water into a 400 mL beaker. Add 8.0 mL of 0.10 M acetic acid solution and 5-7 drops of bromothymol blue.

10. Place the beaker on the stir plate underneath the spout of the reagent reservoir, add a stir bar, and adjust the stirrer to a slow stirring speed. (The magnetic stirrer may cause the computer monitor to flicker.)

11. Refill the reagent reservoir with 0.10 M NaOH solution. *(Note: All trials (#1 – 3) will use NaOH in the reagent reservoir.)*

12. Experiment "24b Acid-Base (Drop Count)" should still be open on your computer. To start the titration click "Collect" → "Erase and Continue." Click "Start." Open the bottom 2-way valve to begin releasing drops from the reservoir through the drop counter.

13. When the solution changes color, record in your ELN the volume and pH. The titration is complete once the horizontal region of your titration curve at higher pH values appears similar in length to the one at lower pH values (i.e. the curve appears somewhat symmetrical). Click "Stop." Pour the titrated solutions into a 1 L beaker and set it aside.

14. After determining the volume to reach the equivalence point, divide that number by two for the volume for "half-way" to equivalence point. Move the cursor across the graph, and determine the pH value at the half-way point by clicking the "Examine" button. Record this value as the pK_a of the acid.

15. Save this file on your computer and/or memory stick (the data is needed for answering the postlab questions).

16. Drain the remaining NaOH from the buret into the 1 L beaker containing the used titrated solutions. Add 1 M HCl, until the solution is neutral according to pH paper. *If you accidently make the solution acidic, add $NaHCO_3$ while stirring the solution, until the solution is neutral (pH ~7).* Once the solution is neutralized, pour it down the drain.

Part B. Spectrophotometric Determination of the pK_a of Bromothymol Blue

Logger Pro does not allow you to have both the pH probe and spectrometer plugged in on one computer at the same time. Whichever partner's computer is not in use should be used to take pH measurements.

1. Use a pipet to deliver 1.00 mL of the bromothymol blue solution to each of two, labeled 25 mL volumetric flasks. Fill to the line with 0.1 M HCl in the first flask. The resulting solution should have a pH between 1 and 2. Fill the second flask to the line with 0.1 M NaOH. The resulting solution should have a pH between 12 and 13.

2. **Create buffered solutions with different pH values in this step**. Label five 25 mL volumetric flasks with numbers 1 through 5. Use a pipet to deliver 1.00 mL of the bromothymol blue solution to each of the flasks. Add volumes of the 0.10 M Na_2HPO_4 solution and 0.10 M NaH_2PO_4 solution to each flask indicated in the table below. Dilute each solution to volume with deionized water.

Flask Number	Volume NaH_2PO_4 (mL)	Volume Na_2HPO_4 (mL)
1	5.0	0.0
2	5.0	1.0
3	10.0	5.0
4	1.0	5.0
5	1.0	10.0

3. Use the pH meter to measure the pH of the solutions prepared in step 1 & 2.

4. Using the spectrometer, record the absorption spectra of the bromothymol blue solutions prepared in step 1. From the recorded spectra choose one wavelength (λ_1) at which the pH 1 – 2 solution absorbs strongly but the pH 12 – 13 solution absorbs weakly, and a second wavelength (λ_2) at which the pH 12 – 13 solution absorbs strongly but the pH 1 – 2 solution absorbs weakly.

5. Measure the absorbance of each of the five buffered solutions made in step 2 at λ_1 and λ_2.