Experiment 18A

Acid-Base Titration Curves

MATERIALS:

pH meter, buffer solution for calibration of pH meter, 0.10 M HCl solution, 0.10 M NaOH solution, 0.10 M acetic acid solution, 0.10 M NH_3 solution, bromthymol blue, methyl red, and phenolphthalein indicator solutions, 25 mL volumetric pipet, 250 mL beaker, two 100 mL beakers, magnetic stirrer and bar, 100 mL graduated cylinder, two 50 mL burets, two 50 mL beakers, grease pencils.

PURPOSE:

The purpose of this experiment is to produce two titration curves. From these curves, information about the behavior of strong and weak acids during a titration can be determined including:

1) The differences in titration of a strong acid versus a weak acid with a strong base;
2) How the end point of a titration can be determined both visually and graphically;
3) How to find the pKa of a weak acid from a titration curve

DISCUSSION:

A <u>titration</u> is a process wherein the capacity of a substance to combine with a reagent is quantitatively measured. Ordinarily this is accomplished by the controlled addition of a reagent of known concentration to a solution of the substance until reaction between the two is judged to be complete. The volume of reagent added is then measured.

The goal of every titration is the addition of a standard solution in such an amount as to be chemically equivalent to the substance with which it reacts. This condition is achieved at the <u>equivalence point</u>. For example, in the titration of sulfuric acid with sodium hydroxide, the equivalence point occurs when two moles of sodium hydroxide have been introduced for each mole of sulfuric acid.

$$H_2SO_4\,(aq) + 2\,NaOH\,(aq) \rightarrow 2\,H_2O\,(l) + Na_2SO_4\,(aq)$$

$$2\,H^+\,(aq) + 2\,OH^-\,(aq) \rightarrow 2\,H_2O\,(l) \qquad \text{net ionic equation}$$

The equivalence point in a titration is a theoretical concept. In actual fact we can only estimate its position by observing physical changes associated with it in the solution. The point in a titration where such changes manifest themselves is called the <u>end point</u>. It is to be hoped that the volume difference between the end point and the equivalence point will be small. Differences do arise, however, owing to inadequacies in the physical changes and in our ability to observe them. This results in an analytical error called the <u>titration error</u>.

One of the common methods of end-point detection involves the use of <u>indicators.</u> Acid-base indicators undergo a color change as a function of pH. Many acid-base indicators are known. For a specific titration, an indicator is chosen whose color changes over a pH range which includes the pH at the equivalence point of the titration of interest. (See Table 1)

In this experiment, rather than carrying out a titration, we will be preparing titration curves. These can be prepared by monitoring the pH of the solution during the course of a titration. Titration curves allow us to find out useful information about the materials being titrated. This information includes: the pH at the end point; the pK_a or pK_b of the weak acid or weak base being titrated; and the pH behavior of the solution in the buffer region. In addition, the titration curve can be used to determine the end point **graphically**. In this experiment, we will find the end point both visually (using an indicator) and graphically.

Table 1
Some Important Acid-Base Indicators

	Color Change		
Common Name	**pH Range**	**Color of Acidic Form**	**Color of Basic Form**
Methyl violet	0.5 -- 1.5	yellow	blue
Thymol blue	1.2 -- 2.8	red	yellow
	8.0 -- 9.6	yellow	blue
Methyl yellow	2.9 -- 4.0	red	yellow
Methyl orange	3.1 -- 4.4	red	yellow
Bromcresol green	3.8 -- 5.4	yellow	blue
Methyl red	4.2 -- 6.3	red	yellow
Chlorophenol red	4.8 -- 6.4	yellow	red
Bromthymol blue	6.0 — 7.6	yellow	blue
Phenol red	6.4 -- 8.0	yellow	red
Neutral red	6.8 -- 8.0	red	yellow-orange
Cresol purple	1.2 -- 2.8	red	yellow
	7.4 -- 9.0	yellow	purple
Phenolphthalein	8.0 -- 9.6	colorless	red
Thymolphthalein	9.3 — 10.5	colorless	blue
Alizarin Yellow	10.1 — 12.0	colorless	violet

Before beginning this procedure, complete calculations A1 - A3 and B1-B5 in the Data Treatment and Analysis section.

PROCEDURE: (Work in pairs.)

(Note to instructors: Since some calculations are to be carried out during the lab period, three titrations probably cannot be completed in two hours. If you wish to have some students carry out the titration of ammonia, it is strongly suggested that those groups do not carry out the titration of acetic acid. Groups doing the weak acid titration and groups doing the weak base titration could share data and analyze it outside of the laboratory.)

1. After your instructor has explained how to calibrate, use and care for the pH meter, calibrate the instrument with the buffer solutions provided.

2. Pipet 25 mL of the 0.1 M HCl solution into 100 mL of distilled water in a clean 250 mL beaker. The exact volume of distilled water is not critical but should be noted so that the theoretical equivalence point can be calculated.

3. Add 3 drops of bromthymol blue indicator solution.

4. Place the 250 mL beaker on the magnetic stirrer, add the stirring bar and position the pH electrode.

5. Carefully rinse, then fill, one of the burets with 0.10 M NaOH solution.

6. a. Carry out the titration taking suitable data to construct a pH vs mL of NaOH added curve. At the beginning and at the end of the titration, one mL additions of base between pH readings is satisfactory. In the vicinity of the equivalence point, however, drop-wise additions of base are required. While the calculations carried out in A3 will help you in determining when you are approaching the end point, you should also carefully observe the pH changes seen during the titration. When addition of a small amount of titrant causes the pH to change, you should slow your rate of addition. While few data points are needed at the beginning of the titration, many data points near the end point will give a better titration curve. Continue the titration and data-taking for at least 10 mL beyond the observed end-point.

   b. Record your data in the tables provided.

   c. Also on the data tables, note all color changes of the indicator as the titration progresses.

7. For titration B, repeat steps 1 through 6 using the 0.10 M acetic acid ($HC_2H_3O_2$) in place of the 0.10 M HCl. Use phenolphthalein as the indicator in place of bromthymol blue.

8. If your instructor so desires, you should titrate ammonia, NH_3, with 0.10 M HCl (Titration C). For this titration, repeat steps 1 through 6 using the 0.10 M NH_3 in place of the HCl in the beaker and 0.10 M HCl in place of the NaOH in the buret. Use the other buret for the acid (HCl) solution. Methyl red indicator should be used in place of the bromthymol blue.

	Buret	Beaker	Indicator
Titration #1	0.1 M NaOH	0.1 M HC1	bromthymol blue
Titration #2	0.1.M NaOH	0.1 M $HC_2H_3O_2$	phenolphthalein
Titration #3	0.1 M HC1	0.1 M NH_3	methyl red

Name _____ Section _____

Partner _____ Date _____

Data Section

Titration A: Solution being titrated: _____

Titrant being added: _____

Indicator: _____

Total vol. titrant	T * * pH	T * * Color	X 5 5 Total vol titrant	T * * pH	T * * Color

Titration B: Solution being titrated: _____

Titrant being added: _____

Indicator: _____

Total vol. titrant	T * * pH	T * * Color	X 5 5 Total vol titrant	T * * pH	T * * Color

Titration C: Solution being titrated: _____

Titrant being added: _____

Indicator: _____

Total vol. titrant	* pH *	T *Color *	T 5Total 5vol titrant	* pH *	* Color *

DATA TREATMENT AND ANALYSIS
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Unless otherwise indicated by your instructor, all data in this experiment will be analyzed using a spreadsheet program.

Titration A: *Strong Acid (Hydrochloric Acid) and Strong Base (Sodium Hydroxide)*

(A.1) Before starting your titration, write a chemical equation that represents the reaction of the hydrochloric acid with the sodium hydroxide.

(A.2) Before starting your titration, calculate the volume of titrant (buret) needed to reach the equivalence point.

(A.3) Before starting your titration, calculate the pH of the solution in the beaker at the equivalence point.

(A.4) Enter the pH and volume of titrant data into a spreadsheet program. Plot a graph of pH of solution versus total volume of titrant (V) added to the beaker, i.e., a titration curve. Annotate the graph to indicate the range of pH values where the indicator changed color. Label the position of the equivalence point found in (A.2) and (A.3).

(A.5) Beginning with the second set of data, calculate $\Delta pH/\Delta V$ and V'. The quantity V' is given by

$$V' = V_1 + \left(\frac{(V_2 - V_1)}{2} \right)$$

where V_1 and V_2 are successive volume readings.

(A.6) Plot a graph of $\Delta pH/\Delta V$ versus V'. The maximum in this plot is the end point of the titration. The pH at the endpoint is taken to be the value of the pH midway between the pH at the maximum and the pH at the point

directly before the maximum. The volume at the endpoint is given by the value of V ´.

(A.7) Annotate the titration curve and the plot of $\Delta pH/\Delta V$ versus V ´ to include the values of pH and volume at the graphically determined endpoint.

(A.8) Record the value of pH at the endpoint below.

(A.9) Calculate the percent error in pH of this graphically determined endpoint (A.6) compared to the equivalence point (A.3).

(A.10) Record the value of pH where the indicator first changed color below. This is the endpoint of the titration determined by the *indicator*.

(A.11) Calculate the percent error in the pH of the endpoint determined by the indicator (A.9) compared to equivalence point (A.3).

(A.12) Explain why the equivalence point (A.3), the endpoint determined graphically (A.6), and the endpoint determined using the indicator (A.9) all differ.

Titrations B and C: **B:** *Weak Acid (Acetic Acid) and Strong Base (Sodium Hydroxide)*
C: *Weak Base (Ammonia) and Strong Acid (Hydrochloric Acid)*

(B.1) Before starting your titration, write a chemical equation that represents the reaction of the acid with the base for titrations **B** and **C**.

B: **C:**

(B.2) In titrations **B** and **C**, what type of system is formed in the beaker after the addition of a small amount of titrant? (Hint, examine the equations in (B.1).)

(B.3) Before starting your titration, write a chemical equation that represents the chemical species that are present in the beaker at the equivalence point for titrations **B** and **C**.

B: **C:**

(B.4) Before starting your titration, calculate the volume of titrant needed to reach the equivalence point for titrations **B** and **C**.

B: **C:**

(B.5) Before starting your titration, calculate the pH of the solution in the beaker at the equivalence point for titrations **B** and **C**.

B: **C:**

(B.6) For titrations **B** and **C**, enter the pH and volume of titrant data into a spreadsheet program. Plot a graph of pH of solution versus total volume of titrant (V) added. Annotate the graph to indicate the range of pH values where the indicator changed color and the region of most effective buffering. Label the position of the equivalence points found in (B.4) and (B.5).

(B.7) For titrations **B** and **C**, calculate $\Delta pH/\Delta V$ and V´ and plot a graph of $\Delta pH/\Delta V$ versus V´. The extrema in these plots are the graphically determined end points of the titrations.

(B.8) For titrations **B** and **C**, annotate the titration curves and the plots of $\Delta pH/\Delta V$ versus V´ to include the values of pH and volume at the endpoints (B.7).

(B.9) For titrations **B** and **C**, record the value of pH at the endpoint below. Calculate the percent error in pH of the graphically determined endpoint (B.7) compared to the equivalence point (B.5).

B: **C:**

(B.10) For titrations **B** and **C**, record the value of pH where the indicator first changed color below. This is the endpoint of the titration determined by the *indicator*.

(B.11) For titrations **B** and **C**, calculate the percent error in the pH of the endpoints determined by the indicators (B.10) compared to equivalence points (B.5).

B: **C:**

(B.12) Explain why the equivalence point (B.5), the endpoint determined graphically (B.7), and the endpoint determined using the indicator (B.10) differ in both titrations.

(B.13) Write the appropriate ionization equations for the chemical reaction that occurs when acetic acid is added to water (Titration **B**) and when ammonia is added to water (Titration **C**).

B: **C:**

(B.14) Write the ionization constant expressions that result from the chemical reactions in part (B.13).

B: **C:**

(B.15) When one half of the titrant needed to reach the equivalence point has been added to the beaker, what is the relationship between the number of moles of titrated acid (A^-) and the number of moles of acid (HA) remaining?(This point is referred to as the half-equivalence point.)

(B.16) What is the significance of achieving this relationship between HA and A^-. Think of the ionization constant expression for the titration.

(B.17) Use the value of pH at the half-equivalence point to calculate the acid ionization constant (K_a) and the base ionization constant (K_b) for titrations **B** and **C**, respectively.

B: **C:**

(B.17) Record the accepted values for the base ionization constant (K_b) and the acid ionization constant (K_a).

B: **C:**

(B.18) Comment on the degree of agreement between the accepted values of ionization constants and the experimentally determined values (B.16).

QUESTIONS
Experiment 18 A

(Q.1)Can methyl red be used as an indicator for titration B, the titration of acetic acid with sodium hydroxide? Explain your answer.

(Q.2) Can phenolphthalein be used as an indicator for the titration of HCl with sodium hydroxide? Explain your answer.

(Q.3) If you did not titrate ammonia with hydrochloric acid, sketch the approximate titration curve you would expect for such a titration.

(Q.4) Which of the two acid titration does this sketch most closely resemble? Explain your answer.