

## D. LAB 4. ACID-BASE TITRATIONS, ALKALINITY, AND BUFFER CAPACITY

### Introduction

In this lab, you will titrate several solutions of known composition as well as the samples collected in the first weeks of the term. From the results of these titrations you will calculate the concentrations of the various inorganic carbon species. The titration curves will yield information on the buffering capacities of the waters, the ions responsible for that buffering, and, together with results from other analyses, the causes of any acidification or pH increases that exist.

### Objectives

The objective of these exercises is to review the definitions of and a method for measuring the different components of alkalinity (including caustic, carbonate and total alkalinity). In addition, you will review the definition of buffer capacity and the pH regions in which acids and bases are best able to buffer. Through titrating the natural water samples, we will learn the susceptibility of these waters to acidification, we will delineate the contribution of various species to alkalinity, and we will determine if any components other than carbonate species are important contributors to the alkalinity.

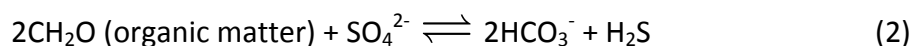
### Significance of alkalinity and buffer capacity

The alkalinity of a water represents its ability to neutralize inputs of acids. For natural water samples the alkalinity is most important in the context of inputs of acids caused by human activities; e.g., acid rain, acid mine drainage, excessive fertilization with ammonium. However, natural processes such as decomposition also can consume or generate alkalinity; the background alkalinity of the water will determine the magnitude of the pH change that results from these natural processes. Alkalinity also is an important consideration in waters to be used for drinking and industrial applications, as well as in water and wastewater treatment. Most microorganisms can function best in neutral pH; should the pH of wastewaters go outside of this neutral range (e.g., through denitrification, nitrification, anaerobic fermentation reactions) the entire waste treatment can be affected disastrously. The oxidation of  $\text{Fe}^{2+}$  that results when anaerobic groundwaters are exposed to air can cause a marked acidification in drinking waters that are poorly buffered with alkalinity; such acidity can enhance pipe corrosion. The most common and costly cause of pipe corrosion is removal of carbonate, the major contributor to alkalinity, through precipitation of calcium carbonate.

Within the context of acid rain, the susceptibility of a lake to acidification depends on the alkalinity of the lake water. Lakes with less than 200  $\mu\text{eq/L}$  of alkalinity are considered vulnerable to acidification. The alkalinity in turn is determined by the types of minerals present in the watershed and on the rates of microbial processes within the lake that generate alkalinity. Lakes in watersheds that have carbonate minerals have high alkalinity and are not susceptible to acidification. Carbonate minerals such as limestone and dolomite weather rapidly to produce bicarbonate ions:



However, regions such as the Adirondacks and Scandinavia that do not have carbonate minerals are much more vulnerable to acid inputs. The basalts in the Keweenaw Peninsula weather very slowly, and hence produce little alkalinity. However, the glaciers that scoured the basin of Lake Superior deposited some glacial till containing carbonates on the Peninsula. Thus, alkalinity of lakes on the Keweenaw Peninsula is determined both by the amount of carbonate in the watershed and by in-lake processes such as sulfate reduction. For example, bacteria in lake sediments utilize sulfate to oxidize organic matter, and in the process alkalinity is generated:



The amount of alkalinity generated through this process depends on the productivity of the lake (the more organic matter, the more alkalinity) and on the residence time of water in the lake. If the lake is flushed rapidly, only a small fraction of the sulfate will be reacted while it is in the lake.

The alkalinity of rain and snow depends on the balance between inputs of acids and bases. One acid that is present in all rain and snow is carbonic acid from the dissolution of atmospheric  $\text{CO}_2$  in the precipitation. Were this the only acid or base present, the precipitation would have a pH of approximately 5.7. Rain or snow with a lower pH must have other acids present; most commonly the other acids are sulfuric and nitric acid whose precursors were emitted to the atmosphere from burning of fossil fuels. Snow or rain with a pH higher than 5.7 must contain bases in excess of the carbonic acid and anthropogenic (human-derived) acids. Possible bases include ammonia ( $\text{NH}_3$ ) from agricultural activity and carbonates from soil dust. Precipitation collected under tree canopies (especially under conifers) often contains organic acids.

### Definitions of carbonate alkalinity

Alkalinity is the ability of a solution to accept acid inputs without becoming “too acidic”. The definition of “too acidic” typically refers to a cutoff in the pH range of 4.5 to 4.7 and is based on chemistry and ecology of natural systems. Because the alkalinity of most freshwaters is due to carbonate species, we may define alkalinity in terms of the concentrations of the species capable of reacting with protons.

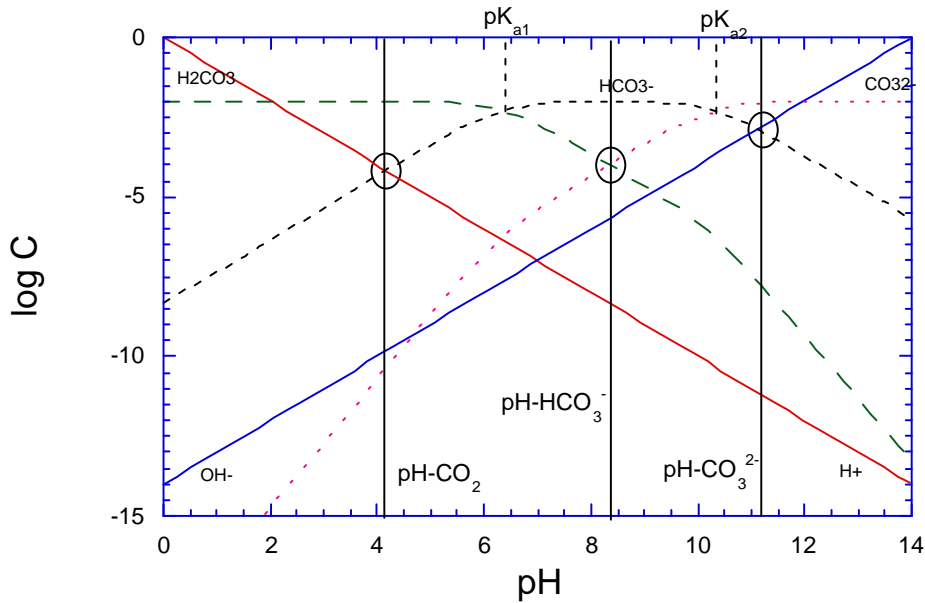
$$\text{Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (3)$$

Because each carbonate ion can react with two protons, its concentration is multiplied by two. The units for alkalinity are equivalents per liter, where an equivalent is defined as the ability to react with one mole of protons.

As you saw in the first labs, most natural waters have pH values between 6 and 9. In this pH range, the dominant carbonate species is bicarbonate (Figure 1). For these reasons, the alkalinity of many waters is nearly equal to the bicarbonate concentration.

In addition to the total alkalinity discussed above, several subcategories of alkalinity have been defined strictly in terms of the transformations among carbonate species. Further, because acidity is the opposite of alkalinity (i.e., the ability to neutralize strong base), one may define total acidity and two subcategories of acidity also in terms of the carbonate system. To

understand these definitions, one must understand the speciation of the carbonate system as a function of pH (Figure 1).



**Figure 1.** Distribution of carbonate species with pH in a closed system. Each line represents the concentration of a particular species in a  $10^{-3}$  M carbonate solution. Dotted lines denote concentrations of  $H^+$  and  $OH^-$ . Vertical lines denote the equivalence points for titration of caustic alkalinity ( $pH_{CO_3}$ ), carbonate alkalinity ( $pH_{HCO_3}$ ), and total alkalinity ( $pH_{CO_2}$ ). The points that satisfy the three proton conditions (one for each proton reference level) are circled.

If  $X$  moles of  $NaHCO_{3(s)}$  were added to one liter of water, some of the bicarbonate that was formed upon dissolution of the salt would react with protons to form  $H_2CO_3$ , and some would dissociate to form  $CO_3^{2-}$  according to Equations 4 and 5 below. The reactions are written according to the usual convention for acids, as dissociation reactions, but in the particular system under consideration here, Reaction (4) would proceed in reverse.



The equilibrium  $\{H^+\}$  for the solution would lie midway between the two equilibrium constants for Reactions 4 ( $pK_{a1} = 10^{-6.35}$ ) and 5 ( $pK_{a2} = 10^{-10.33}$ ), and the pH would be 8.3. This pH is identified in Figure 1 as  $pH_{HCO_3}$ . (Note that this pH also can be identified as the point satisfying the proton balance equation:  $[H_2CO_3] + [H^+] = [CO_3^{2-}] + [OH^-]$ , where  $H_2O$  and  $HCO_3^-$  make up the proton reference level.) If the same  $X$  moles of  $Na_2CO_3$  (instead of  $NaHCO_{3(s)}$ ) were added to one liter of water, what would be the resultant pH? Some of the carbonate ions would react with protons to form bicarbonate (Reaction 5 in reverse), and this consumption of protons would raise the pH. The resultant pH would lie at the point where Equations 6 and 7 are satisfied:

$$TOTCO_3 = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] \quad (6)$$

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (7)$$

This pH is identified in Figure 1 as  $pH_{CO_3}$  (approx. pH 10.5). This point satisfies the proton condition when  $H_2O$  and  $CO_3^{2-}$  make up the PRL:  $2[H_2CO_3] + [HCO_3^-] + [H^+] = [OH^-]$ . Similarly,  $pH_{CO_2}$  may be defined as the pH of a solution in which  $X$  moles of  $CO_2$  are dissolved; this pH is approximately 4.7. (Note that the exact pH values depend on the concentration,  $X$ , of carbonate in the water.)

The various categories of carbonate alkalinity are defined in terms of these three pH values ( $pH_{CO_3}$ ,  $pH_{HCO_3}$ ,  $pH_{CO_2}$ ). **Total alkalinity** is defined as the amount of acid required to lower the pH to  $pH_{CO_2}$ ; i.e., to convert essentially all of the bicarbonate and carbonate to  $H_2CO_3$ . **Carbonate alkalinity** is the amount of strong acid required to lower the pH of a sample to  $pH_{HCO_3}$ ; at this point the carbonate is converted to bicarbonate, and at lower pH values it would be converted to  $H_2CO_3$ . **Caustic alkalinity** is the amount of strong acid required to lower the pH of a sample to  $pH_{CO_3}$ ; such alkalinity must result from bases stronger than  $CO_3^{2-}$ . Similarly, the categories of acidity may be defined as: **Mineral acidity** is the amount of strong base required to raise the pH of a sample to  $pH_{CO_2}$  (stronger acids than  $H_2CO_3$  must be present); **carbon dioxide acidity** is the amount of strong base required to raise the pH of a sample to  $pH_{HCO_3}$ ; and **total acidity** is the amount of strong base required to raise the pH of a sample to  $pH_{CO_3}$ . Based on Figure 1, why do you think that the endpoint for each component of alkalinity also is called an equivalence point?

Each category of alkalinity and acidity also may be defined in terms of the species involved in reactions with protons or hydroxide ions as was done in Equation 3.

$$\text{total alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad (3)$$

$$\text{carbonate alkalinity} = [CO_3^{2-}] + [OH^-] - [H^+] - [H_2CO_3] \quad (8)$$

$$\text{caustic alkalinity} = [OH^-] - [H^+] - [HCO_3^-] - 2[H_2CO_3] \quad (9)$$

$$\text{total acidity} = 2[H_2CO_3] + [HCO_3^-] + [H^+] - [OH^-] \quad (10)$$

$$\text{carbon dioxide acidity} = [H_2CO_3] + [H^+] - [OH^-] - [CO_3^{2-}] \quad (11)$$

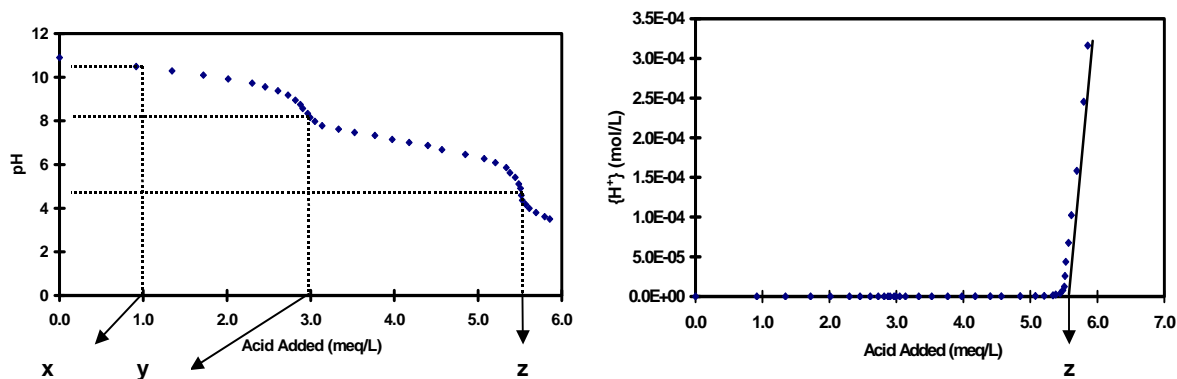
$$\text{mineral acidity} = [H^+] - [HCO_3^-] - 2[CO_3^{2-}] - [OH^-] \quad (12)$$

All of these terms may be calculated if one knows the original pH, the concentration of any one of the carbonate species (or the total concentration of all carbonate species combined), and the equilibrium constants for Reactions 4 and 5. (A detail not to be overlooked is that Equations 3 and 8-12 are defined in terms of concentrations, while the equilibrium constants for Reaction 4 and 5 are defined in terms of activities.)

### Titration curves, endpoint analysis

In this lab you will add acid to various samples and record the resultant pH values. The data that you obtain will look similar to that shown in Figure 2. There are regions where the pH changes rapidly with each acid addition, and regions where the response is much less. You must determine from these titration curves the endpoints ( $x$ ,  $y$ ,  $z$ ) for the various alkalinity species (see discussion above). From visual inspection of the titration curve, you can determine the approximate endpoints (Figure 2). However, there are two much more quantitatively exact methods for determining endpoints. The first method is to plot the derivative of the titration curve ( $-\Delta pH/\Delta \text{acid added}$ ). The second method is called Gran analysis, and it is depicted in the

right-hand graph of Figure 2. Once you pass the inflection point for total alkalinity, the concentration of  $H^+$  increases linearly with the amount of acid that you add. In this region of the titration curve, the amount of  $HCO_3^-$  left to convert to  $H_2CO_3$  is small; any additional acid added will result primarily in an increase in the concentration of free  $H^+$ . Extrapolation of the linear portion of the Gran curve to the x-axis will yield the endpoint (z) of the titration.



**Figure 2.** Titration (left) and Gran analysis (right) curves. Addition of acid to a carbonate solution will yield a titration curve similar to that shown on the left above. Approximate endpoints of the titration are shown in the left-hand plot (point z for total alkalinity, point y for carbonate alkalinity, point x for caustic alkalinity). Point z may be determined exactly through the Gran Analysis shown in the right-hand

plot. 
$$\text{Acid Added (meq/L)} = \frac{(\text{Vol. Acid})(\text{Conc. Acid in meq/L})}{(\text{Vol. Sample} + \text{Vol. Acid})}$$

### The contribution of other weak acids and bases

The discussion above focuses entirely on carbonates as the source of alkalinity. In most waters carbonate species are indeed the predominant source of alkalinity. However, the definition of alkalinity is the ability to neutralize acid inputs. Hence any ion or molecule that can accept a proton (i.e., any substance that acts as a base) will contribute to alkalinity.

What other ions present in natural waters can act as bases? In seawater, silicate and borate are present in high concentrations and contribute to the alkalinity:



Because the  $pK_a$  for the reaction that proceeds in the opposite direction as that shown in Equation 13 is 8.9, close to the pH of seawater, borate exhibits its maximal buffering capacity in the oceans. In fresh waters, the other ions of importance are those of Fe, Al, and humic and fulvic acids. Despite over twenty years of research, scientists still have not devised a totally consistent definition for and method for measuring the alkalinity from these species.

Among the water samples collected in Lab 1, some may have alkalinity contributed by DOM (dissolved organic matter). Dissolved organic matter is comprised of a heterogeneous mix of complex molecules for which we do not know the exact chemical structure. We do know

that many of the molecules contain carboxylic acid functional groups (-COOH). These functional groups typically have  $pK_a$  values between 3.5 and 5.5. In other words, above pH 3.5 to 5.5, the carboxylic groups are dissociated.



This means that at pH values above 5.5 they can accept a proton (i.e., Reaction 14 runs in reverse), and hence they contribute to alkalinity or acid neutralization. In general, there are 10-15  $\mu\text{eq}$  of carboxylic groups per mg DOC. Thus, a water with 20 mg/L DOC potentially could have an alkalinity of 200-300  $\mu\text{eq/L}$  due to the organic matter alone. In softwater lakes such as on the Keweenaw Peninsula, this would represent a major fraction of the total alkalinity. Natural waters with low concentrations of DOC (e.g., rain, snow) will not have any significant alkalinity from this source.

### Buffer Intensity

A buffer has the capacity to resist change. A pH buffer, therefore, is a solution with components that resist changes in pH by either taking up or liberating protons. Thus pH buffers are weak acids or bases. The neutralization capacity of a buffer is the amount of acid or base required to titrate the buffer to some pre-selected endpoint. Generally, we are more interested in the buffer intensity, or the ability of the buffer to resist small pH changes. The buffer intensity ( $\beta$ ) is merely the derivative of the titration curve:

$$\beta = \frac{dC_{\text{OH}^- \text{ added}}}{dpH} = -\frac{dC_{\text{H}^+ \text{ added}}}{dpH} \quad (15)$$

where  $C_{\text{OH}^- \text{ added}}$  is the concentration of strong base added, and  $C_{\text{H}^+ \text{ added}}$  is the concentration of strong acid added. The buffer intensity tells us how much strong acid or base must be added to change the pH.

For a diprotic acid (e.g.,  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{S}$ , etc.), the buffer intensity is equal to:

$$\beta = 2.303 \left( [\text{OH}^-] + [\text{H}^+] + \frac{[\text{H}_2\text{A}][\text{HA}^-]}{[\text{H}_2\text{A}] + [\text{HA}^-]} + \frac{[\text{HA}^-][\text{A}^{2-}]}{[\text{HA}^-] + [\text{A}^{2-}]} \right) \quad (16)$$

where  $\text{H}_2\text{A}$ ,  $\text{HA}^-$ , and  $\text{A}^{2-}$  refer to the various forms of the diprotic acid. Alternatively, the concentration of each species could be expressed in terms of the total concentration of acid ( $C_{\text{H}^+ \text{ added}}$ ) and the appropriate distribution coefficient,  $\alpha$ , as follows:

$$\beta = 2.303 \left( \frac{K_w}{[\text{H}^+]} + [\text{H}^+] + \frac{\alpha_0 \alpha_1 C_{\text{H}^+ \text{ added}}}{\alpha_0 + \alpha_1} + \frac{\alpha_1 \alpha_2 C_{\text{H}^+ \text{ added}}}{\alpha_1 + \alpha_2} \right) \quad (17)$$

where:

$$[\text{H}_2\text{A}] = \alpha_0 \text{ TOTA} \quad (18)$$

$$[\text{HA}^-] = \alpha_1 \text{ TOTA} \quad (19)$$

$$[A^{2-}] = \alpha_2 \text{ TOTA} \quad (20)$$

Analysis of Equation 16 will indicate that the buffer capacity is at a maximum at the  $pK_{a1}$  of the weak acid (e.g., the point where  $[H_2A]$  equals the concentration of  $[HA^-]$ ).

### Procedure

You will first titrate several solutions of known composition to gain practice in titration, and to demonstrate the characteristics of carbonate (and non-carbonate) alkalinity. In addition, you will titrate the water samples collected earlier in the term. For a few of the solutions, you will add small increments of acid and measure the pH after each addition; for others, you will use a faster technique of titrating to a fixed endpoint that will be indicated by a colorimetric indicator.

#### *I. Calibration of the pH Meter*

Calibrate your pH meter using the steps below (identical to Lab 1):

1. If your meter was used in a lab section earlier in the day, remove the calibration that was stored previously. Make sure the probe is in open position and the black end cap is removed. Rinse the electrode with Milli-Q water into the waste beaker. Place the electrode in the beaker with pH 7 buffer.
2. Press meas./monitor button until the "key" icon **does not** show. You are now in monitor mode (S for stable or U for unstable appears in the lower right hand corner).
3. Switch to **mV** scale by pushing the mV button;
4. Using the pH 7 buffer **record the mV reading**;
5. Set the Isopotential to the recorded value by pressing: setup, 2, key in the recorded mV from step 4, enter, clear (to return to the main menu);
6. Switch to the pH 10 (or 4) buffer and read and record the mV (remember to rinse the electrode before switching);
7. Calculate the slope:  $slope = \frac{\Delta mV}{3.0}$  (The 3.0 accounts for the three pH units between 7 and 10 and between pH 7 and 4);
8. Set default slope to the calculated slope by pressing: setup, 3, 2, key in calculated slope, enter, clear (to return to the main menu)
9. Switch to pH scale;
10. Standardize with pH 7 buffer:
  - a. Rinse electrode
  - b. Press **standardization**
  - c. Press **1** to add a standard (Now in the Prepare Buffer/Standard Screen)
  - d. After ~30-60 seconds, press **enter**;
11. Check calibration by reading the pH of the 10 (or 4) buffer.

#### *II. Titration of Known Solutions*

Solutions A-D contain varying mixtures of NaOH and  $NaHCO_3$ ; Solution E contains 100 mg/L of a humic acid mixture. Each group should titrate at least one of the samples A, B, C, D, or E. You will obtain the titration data for other solutions from other groups.

1. Using a graduated cylinder, measure 60 mLs of Solution A and pour it into the Erlenmeyer flask. Place the stirring magnet in the beaker.
2. Measure the initial pH. For Solution D (and E, if applicable) you will follow the same procedure as below, except that you will add small acid increments and record the pH and volume of acid added after each addition. You must allow the pH to stabilize after each incremental acid addition. You should get at least one reading per 0.2-pH unit change. Titrate the solution until a pH of 3.0 is reached.
3. Slowly add acid ( $\sim 0.01$  M  $\text{H}_2\text{SO}_4$ ) from the burette to the flask, stirring continuously, until the pH reads 10.5. Record the volume of acid.
4. Continue to titrate down to pH 9.0. Slow the flow of acid such that the pH meter reaches a stable reading after each drop of acid. Titrate to pH 8.3 and record the volume of acid required.
5. You can speed up the acid addition and titrate down to pH 5.0. Again slow the acid addition so as to accurately record the volume of acid required to reach pH 4.7. Record this volume of acid.
6. You have finished the titration of Solution A. The solution can be poured into the waste beaker. Rinse the Erlenmeyer flask and the magnet with de-ionized water.
7. If time permits, repeat steps 1-6 with Solutions B and C.

### *III. Titration of Natural Water Samples*

You are to obtain a detailed titration curve for (one of) your samples. Choose the one with the highest pH. For the other samples, you will perform fast, fixed endpoint titrations.

1. Measure 25 mL of your sample with a graduated cylinder and pour it into an Erlenmeyer flask.
2. Stir the sample with a magnetic stir bar.
3. Titrate the sample with the 0.01 M acid to pH 4.7.
4. Record the volume of acid required.
5. Discard this titrated sample into the waste beaker.
6. Measure 60 mL of the sample into the Erlenmeyer flask using the graduated cylinder.
7. You must choose an acid of an appropriate strength to titrate your sample; if the acid is too weak, it will take a very large volume to titrate your sample, but if it is too strong, you will not have adequate resolution in your titration curve. You will base this selection on the preliminary analyses performed in steps 1-4 above. If your sample required from 1 to 3 mL of the 0.01 M acid solution to reach the endpoint (the color change), replace the acid in the burette with the 0.002 M acid solution; if your sample required less than 1 mL of the  $\sim 0.01$  M acid then replace it with 0.5 mM acid. Be sure to rinse the burette with Milli-Q water after draining out the 0.01 M acid in this case.
8. Record the initial pH.
9. Slowly add increments of acid and record the volume of acid added and the pH after it stabilizes following each addition. You should get at least one reading per 0.2-pH unit change in pH.
10. Continue to titrate in small increments until a pH of 3.0 is reached.



#### IV. Fixed Endpoint Titrations

1. Measure 60 mL of your sample with a graduated cylinder and pour it into an Erlenmeyer flask.
2. Add 3 drops of Methyl Orange indicator solution and a magnetic stir bar to the sample.
3. While stirring slowly, titrate the sample with the appropriate acid until the color changes.
4. Record the volume of acid required and the pH at the point of the color change.

#### Data analysis for following week:

1. Prepare a table containing the initial values of species concentrations (Table 1) and your experimentally-determined concentrations for the various alkalinity components in solutions A, B, C, and D. Use the approximate method to compute the species concentrations from the total, carbonate, and caustic approximate alkalinities, as shown in Method 1 below. Think about why initial values differ from those you measured. (See example data for details on calculations.)

**Table 1.** Initial Solution Compositions

Solution	[OH <sup>-</sup> ]	[CO <sub>3</sub> <sup>2-</sup> ]	[HCO <sub>3</sub> <sup>-</sup> ]	Total Alk
A	3.0 mM	0	0	3.0 meq/L
B	2.0 μM	30 μM	2.9 mM	3.0 meq/L
C	2.2 mM	2.6 mM	0.20 mM	7.5 meq/L
D	0.33 mM	2.5 mM	1.3 mM	6.6 meq/L

2. Plot the titration curve(s) for Solution(s) D (and E) on one graph. Label the theoretical  $pK_a$  values for the carbonate species. Do the inflection points on your titration curve for Solution D correspond to the  $pK_a$  values and the expected endpoints?
3. Plot the titration curve of an imaginary water sample containing 1 meq/L of total alkalinity. How does *the shape* of this plot differ from that shown for (2)?
4. On the same graph as for (3), plot the titration curve for your natural water sample. Calculate and plot on the same graph a titration curve for pure water. How do the curves differ?
5. For Solutions D and (E as well as for) your natural water sample, calculate the buffer intensity (i.e.,  $-\Delta\text{acid added}/\Delta\text{pH}$ ) for each step in your titration. Subtract from this the buffer intensity of pure water (calculate from the computed titration curve for pure water; step 4 above). Plot the resultant buffer intensity as a function of pH. From these curves, can you say what species were responsible for the buffering of your sample? What is the relationship between the maxima and minima in the buffer intensity and the  $pK_a$  and equivalence points?
6. Calculate the total alkalinity of the natural water sample for which a detailed titration was performed. Use the Gran plot technique to calculate the exact total alkalinity.
7. Now that you have bicarbonate ion concentrations you can calculate ionic strength and the charge balance; make a table containing ionic strength and the ratio of total cations to total anions for the 3 samples that your group analyzed.

## Lab Report

1. In the Introduction, briefly explain why alkalinity is of interest to an environmental engineer.
2. In the Results section, present the tables and figures described under points 1, 2, 3, 4, and 5 under Data Analysis.
3. Devote the first part of the Discussion section to the known Solutions A-D (also E, if it was titrated). Explain the differences among them in light of the graphs and tables presented in the Results. (What is the region of buffering for sample E?) Why are your measured values for alkalinity components different from those in the table above? What effect does atmospheric CO<sub>2</sub> have on the alkalinity and the carbonate species distribution of these solutions?
4. Devote the second part of your Discussion to the samples. Present a table listing the alkalinity for all the samples that you measured and the bicarbonate for all the samples that you measured in Lab 2. Discuss and compare these results and discuss whether any of these samples would be susceptible to acidification from acid rain. Evaluate whether there is a relationship between alkalinity and pH. Is there evidence of non-carbonate alkalinity?

### Materials needed:

Per group:

- 1 100-mL graduated cylinder
- 125-mL Erlenmeyer flask
- Stirring plate and bar
- Stirbar retriever
- Burette
- Waste beaker
- pH meter, electrode
- Squirt bottle with Milli-Q water
- Kimwipes

Reagents:

- 0.01 M H<sub>2</sub>SO<sub>4</sub>
- 0.002 M H<sub>2</sub>SO<sub>4</sub>
- 0.5 mM H<sub>2</sub>SO<sub>4</sub>
- Methyl Orange indicator solution
- Solution A: Dilute 3 mL of 1 M NaOH made up to 1 liter with Milli-Q water
- Solution B: Dilute 3 mL of 1 M NaHCO<sub>3</sub> made up to 1 liter with Milli-Q water
- Solution C: Dilute 5 mL of 1 M NaOH plus 3 mL of 1M NaHCO<sub>3</sub> made up to 1 liter with Milli-Q water
- Solution D: Dilute 3 mL of 1 M NaOH and 4 mL of 1 M NaHCO<sub>3</sub> made up to 1 liter with Milli-Q water
- Solution E: Dissolve 100 mg Aldrich Humic Acid in 1 liter of Milli-Q water

### Example Data Analysis

Below is presented a step-by-step analysis of titration data similar to the analysis that you are asked to perform on solutions A-E and your natural sample. The titration data are summarized in the table below.

**Table 2.** Example titration data of a 50-mL natural water solution containing carbonate species. The titrant is 0.01 M H<sub>2</sub>SO<sub>4</sub>.

Acid added (mL)	pH		Acid added (mL)	pH		Acid added (mL)	pH
0	10.9		8.8	8.16		18.2	5.86
2.4	10.49		9.0	7.98		18.4	5.62
3.6	10.29		9.3	7.78		18.7	5.41
4.7	10.10		10.0	7.62		18.9	5.11
5.6	9.92		10.7	7.47		19.0	4.91
6.5	9.73		11.6	7.33		19.05	4.59
7.0	9.56		12.4	7.15		19.1	4.36
7.5	9.38		13.2	7.01		19.3	4.17
7.9	9.18		14.1	6.87		19.5	3.99
8.2	8.95		14.8	6.68		19.9	3.80
8.4	8.75		16.0	6.46		20.4	3.61
8.5	8.57		17.0	6.27		20.7	3.50
8.7	8.34		17.6	6.09			

**Step 1. Determine the concentrations of total alkalinity, carbonate alkalinity, and caustic alkalinity, and from these, calculate the initial concentrations of OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and HCO<sub>3</sub><sup>-</sup> in the solution.**

SOLUTION:

#### Method 1. Approximate Alkalinity

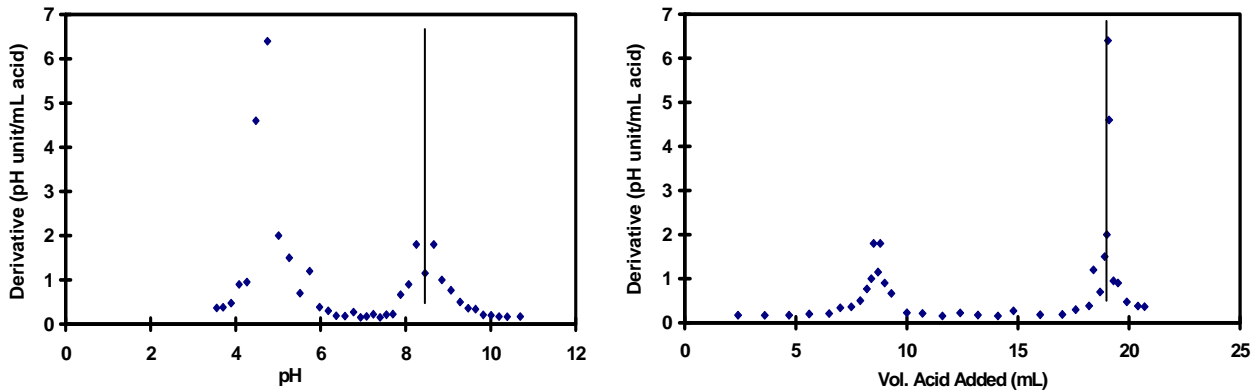
The endpoints for caustic, carbonate and total alkalinity are at approximately pH 10.5, 8.3 and 4.7. From the table above, we can get the acid volumes that correspond to these endpoints as 2.4 mL, 8.8 mL, and 19.0 mL. To calculate the total alkalinity,

$$\text{total alkalinity (eq/L)} = \frac{(\text{volume of acid added})(\text{conc'n. of acid added, eq/L})}{(\text{volume of sample} + \text{volume of acid})}$$
$$\text{total alkalinity} = \frac{(19.0 \text{ mL}) \left( 0.01 \frac{\text{mole H}_2\text{SO}_4}{\text{L}} \times \frac{2 \text{ eq}}{\text{mole H}_2\text{SO}_4} \right)}{(50 \text{ mL} + 19.0 \text{ mL})} = 0.00551 \frac{\text{eq}}{\text{L}} = 5.51 \text{ meq/L}$$

Similarly, the carbonate alkalinity may be calculated as 2.99 meq/L, and the caustic alkalinity as 0.92 meq/L.

*Method 2. Inflection Points from Plot of Buffer Intensity vs. pH*

The endpoints for the titration can be more accurately identified from either the first or second derivative of the titration curve. The first derivative is merely  $-\Delta\text{pH}/\Delta\text{acid added}$  (i.e.,  $-(\text{pH}_2 - \text{pH}_1)/(\text{Vol}_2 - \text{Vol}_1)$ ). As shown in the graph below, there are clear maxima at the two endpoints. The endpoint at pH 8.3 appears to have a dip in the peak due to a faulty pH measurement at this point. By plotting against volume of acid added we can identify the exact endpoints in terms of the amount of acid added (8.6 and 19.0 mL). Comparing these volumes with those estimated from the titration curves (8.8 and 19.0 mL) we see that the approximate alkalinity above was fairly accurate. The accurate values for carbonate and total alkalinity are 2.94 meq/L and 5.51 meq/L, respectively.



*Calculation of Carbonate Species from Alkalinity Values*

From the values of caustic, carbonate and total alkalinity one can calculate the concentrations of  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{HCO}_3^-$ . For these calculations we use Equations 3, 8 and 9.

$$\begin{aligned} \text{Total Alkalinity} &= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] & (3) \\ \text{Carbonate Alkalinity} &= [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] - [\text{H}_2\text{CO}_3] & (8) \\ \text{Caustic Alkalinity} &= [\text{OH}^-] - [\text{H}^+] - [\text{HCO}_3^-] - 2[\text{H}_2\text{CO}_3] & (9) \end{aligned}$$

The caustic alkalinity measures essentially the concentration of  $\text{OH}^-$ ; the other terms in Equation 9 are very small relative to  $[\text{OH}^-]$  at  $\text{pH} > 10$ . Thus, we equate  $[\text{OH}^-]$  to the caustic alkalinity (0.92 meq/L). We can compare this to what we would calculate from the initial pH (10.9). Ignoring activity corrections, pH 10.9 corresponds to a  $\text{OH}^-$  concentration of 0.79 mM, close to that estimated from the caustic alkalinity.

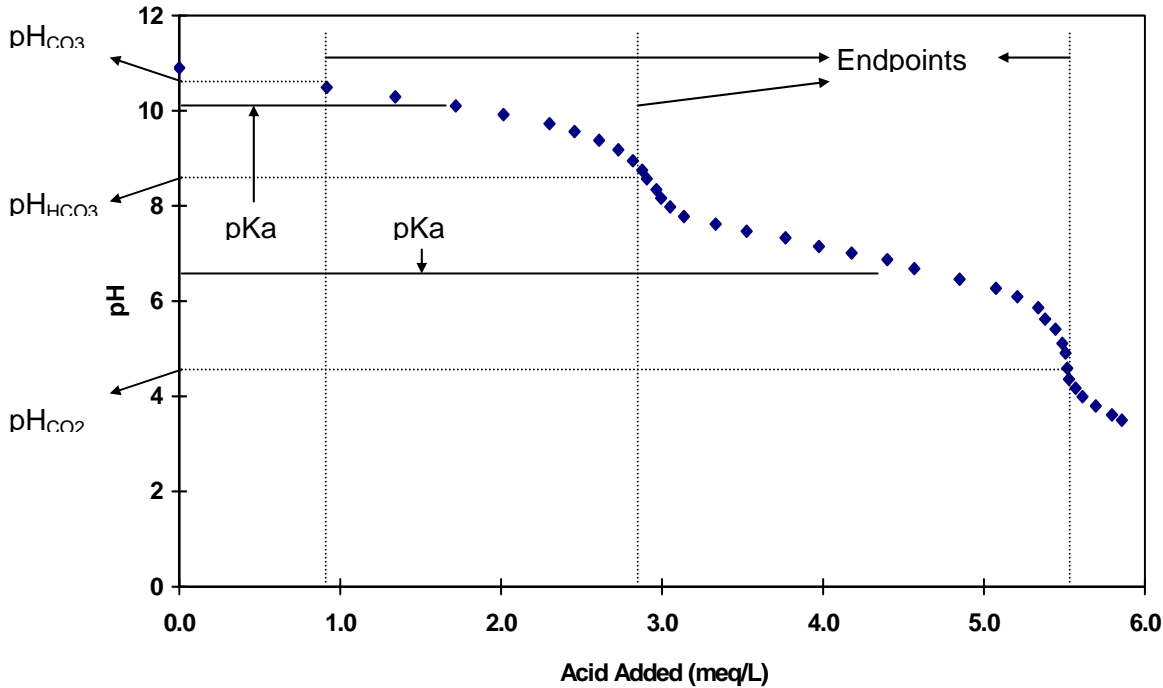
Having  $[\text{OH}^-]$ , one can calculate  $[\text{CO}_3^{2-}]$  from the carbonate alkalinity (Equation 8). Again, at  $\text{pH} > 8.3$ , concentrations of  $\text{H}^+$  and  $\text{H}_2\text{CO}_3$  are negligible relative to  $\text{CO}_3^{2-}$  and  $\text{OH}^-$ . Thus,  $[\text{CO}_3^{2-}]$  equals carbonate alkalinity minus caustic alkalinity or  $2.94 - 0.92 = 2.02$  mM. Note that the resultant concentration is in mmole/L; i.e., we have assumed that there is only one

equivalent per mole of carbonate. This assumption is made because in this phase of the titration, we are converting  $\text{CO}_3^{2-}$  to  $\text{HCO}_3^-$ , and only one proton is consumed per mole of  $\text{CO}_3^{2-}$ .

It remains to calculate the  $[\text{HCO}_3^-]$  from the total alkalinity. If one subtracts  $[\text{OH}^-]$  (caustic alkalinity) and two times the  $[\text{CO}_3^{2-}]$  calculated above from the carbonate and caustic alkalinity, one is left with  $[\text{HCO}_3^-] - [\text{H}^+]$  (see Equation 3). Again, we can make the assumption that  $[\text{H}^+]$  is small relative to  $[\text{HCO}_3^-]$  at  $\text{pH} > 4.7$ . Thus,  $[\text{HCO}_3^-] = \text{total alkalinity} - [\text{caustic alkalinity} + 2(\text{carbonate alkalinity} - \text{caustic alkalinity})] = \text{total alkalinity} - 2(\text{carbonate alkalinity}) + \text{caustic alkalinity}$ . From the data used here  $[\text{HCO}_3^-] = 5.51 - 2(2.94) + 0.92 = 0.55 \text{ mM}$ .

### 1. Plot of titration curve with $\text{pK}_a$ and endpoints indicated

The titration curve may be plotted simply as pH (y-axis) vs. acid added (x-axis). The inflection points on the curve should correspond to the  $\text{pK}_a$ s for the carbonate system (6.35, 10.33) and the equivalence points ( $\text{pH}_{\text{CO}_3}$ ,  $\text{pH}_{\text{HCO}_3}$ , and  $\text{pH}_{\text{CO}_2}$ ). This graph and the corresponding points are presented below.



### 2. Pure Water Titration

Pure water, of course, has no buffers. As one adds strong acid, the concentration of  $[\text{H}^+]$  will increase nearly linearly, and as one adds strong base the concentration of  $[\text{OH}^-]$  will increase nearly linearly. The inflection points due to the carbonate system will not be present, but there will be an inflection point due to the buffering of water itself. There are several ways of calculating the titration curve for pure water. Below is outlined the most exact method.

In this titration, we will have four variables:  $[H^+]$ ,  $[OH^-]$ ,  $[A^-]$  (the acid anion), and  $[B^+]$  (the base cation). For instance, if we added HCl to lower the pH, the acid anion would be  $Cl^-$ . If we added NaOH to raise the pH,  $Na^+$  would be the base cation. We will assume that we use strong acids and bases such that we do not need to consider the concentrations of HA and BOH. Four equations are needed to solve for the four unknowns. Two of the equations are simply the mass balances for  $A^-$  and  $B^+$ . At each step of the titration, we know how much acid or base was added, so the concentrations of  $A^-$  and  $B^+$  are known at each titration step. A third equation is the equilibrium constant for water:

$$K_w = [H^+][OH^-] \quad (a)$$

For simplicity, we will titrate only from pH 12 to pH 2; a range in which activity corrections are minor. The fourth equation is the charge balance:

$$[H^+] + [B^+] = [OH^-] + [A^-] \quad (b)$$

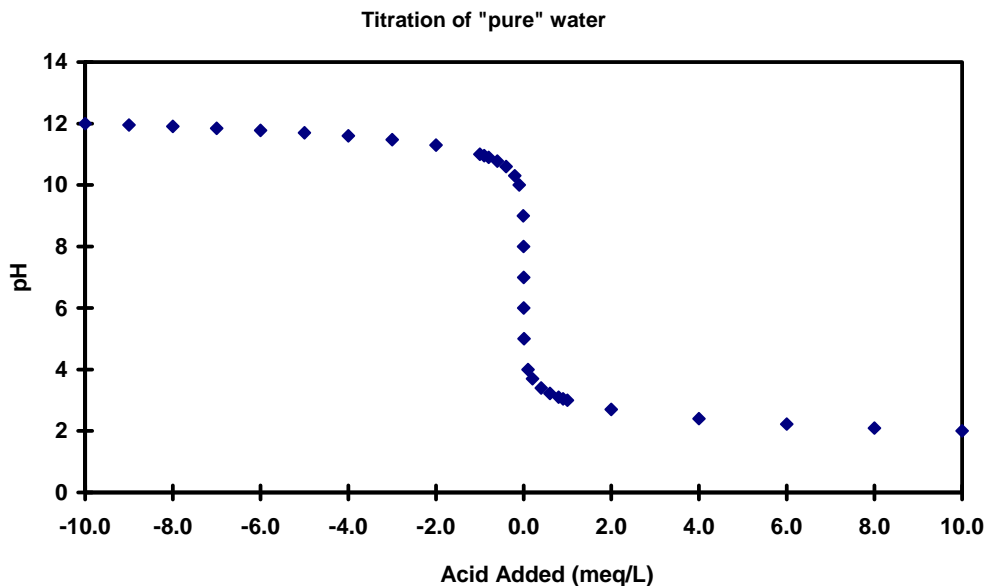
Solving equation *a* for  $[OH^-]$ , and substituting into equation *b*, we obtain a quadratic equation in  $[H^+]$ :

$$[H^+]^2 + [H^+][B^+] - [A^-] - K_w = 0$$

The solution is:

$$[H^+] = 0.5\left([A^-] - [B^+] + \left(\left([B^+] - [A^-]\right)^2 + 4K_w\right)^{0.5}\right)$$

It remains only to specify reasonable values of  $[A^-]$  and  $[B^+]$ , and to solve for the corresponding pH values. A sample titration curve is shown in the graph below. In the graph below, negative



concentrations of acid correspond to positive concentrations of a base.

## 5. Buffer intensity

The buffer intensity represents the ability of a solution to resist changes in pH with addition of acid (or base). The buffer intensity of a solution of unknown composition would be calculated with Equation 15. If the composition of the solution were known, Equations 16 or 17 could be used. For the sample data presented in Table 2 above, the calculated buffer intensity  $((\text{vol}_2 - \text{vol}_1)/(\text{pH}_2 - \text{pH}_1))$  is tabulated below. Transform the values of buffer intensity to units of meq acid added/L-pH using the equation  $\text{Acid Added (meq/L)} = \frac{(\text{Vol. Acid})(\text{Conc. Acid in meq/L})}{(\text{Vol. Sample} + \text{Vol. Acid})}$ , and

then correct these values for the buffering of pure water. Because one calculates the buffer intensity between two measured pH values, it is most accurate to graph it using the pH mid-way between the two original pH values. A graph of the buffer intensity vs. pH is shown for the sample data below. Note that the maxima in buffer intensity should occur at the  $\text{p}K_a$ s of the acid present (carbonate species in this case). The discrepancy in this case must result from not having allowed the pH to equilibrate completely at each step of the titration.

mid pH	$\beta$ (mL acid/ pH change)		mid pH	$\beta$ (mL acid/ pH change)		mid pH	$\beta$ (mL acid/ pH change)
10.7	5.85		8.3	0.56		6.2	3.33
10.4	6.00		8.1	1.11		6.0	2.61
10.2	5.79		7.9	1.50		5.7	0.83
10.0	5.00		7.7	4.37		5.5	1.43
9.8	4.74		7.5	4.67		5.3	0.67
9.6	2.94		7.4	6.43		5.0	0.50
9.5	2.78		7.2	4.44		4.8	0.16
9.3	2.00		7.1	5.71		4.5	0.22
9.1	1.30		6.9	6.43		4.3	1.05
8.9	1.00		6.8	3.68		4.1	1.11
8.7	0.56		6.6	5.45		3.9	2.11
8.5	0.87		6.4	5.26		3.7	2.63

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## 6. Gran plot

The gran plot is constructed by calculating the value of  $[\text{H}^+]$  at each pH value and plotting  $[\text{H}^+]$  as a function of the volume of acid added. Above the total alkalinity endpoint (approximately  $\text{pH} > 4.7$ ), the plot should follow a straight line. Using the points from the

straight portion of this line, one can perform a linear regression. The value of x-axis intercept corresponds to the exact volume of acid required to reach the endpoint  $f = 0$ .

### 7. Calculation of carbonate species from alkalinity (corrected for the amount of titrant consumed by water) and pH

Given the alkalinity and the pH of a natural water sample, one can calculate the concentrations of all of the carbonate species. The simplifying assumption that usually is made is that the alkalinity is equal to the concentration of bicarbonate. Given the bicarbonate concentration and pH, one can calculate concentrations of carbonic acid and carbonate ion from the appropriate  $K_a$  definitions as shown below.

$$[H_2CO_3] = \frac{\{H^+\}\{HCO_3^-\}}{K_{a1}}$$

$$[CO_3^{2-}] = \frac{K_{a2}\{HCO_3^-\}}{\{H^+\}\gamma_{CO_3}}$$

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