

UNDERSTANDING CARBONATE EQUILIBRIA BY MEASURING ALKALINITY IN EXPERIMENTAL AND NATURAL SYSTEMS

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ABSTRACT

Carbonate equilibria is a fundamental concept within the geosciences. An understanding of carbonate equilibria is necessary for geologic studies of weathering, surface and ground water chemistry, and global climate. Equilibria and acid-base relationships are difficult to understand without hands-on examples. Alkalinity titrations, in combination with theoretical calculations, offer a simple and inexpensive method to experiment with carbonate equilibria using both known standards and surface water samples. The acquired data provide a link between theory and application in geochemistry.

Keywords: Laboratory, Geochemistry

INTRODUCTION

Carbonate equilibria is often a difficult concept for undergraduate students, and even graduate students, to fully understand. In part, this difficulty arises because the student is immersed in calculations, but doesn't actually perform experiments and analyses that demonstrate the concept of carbonate equilibria. At best, the student is asked to perform calculations and generate titration curves or Bjerrum plots. At worst, the student is asked to understand carbonate equilibria from a purely theoretical viewpoint, with the only demonstration being that of a diagram in a book. In part, this is a result of the historical nature of geology being devoted to rocks. Unlike chemistry departments, many geology departments lack chemical laboratories that can accommodate multiple students.

Carbonate equilibria, however, is critically important to understanding low temperature geochemical and biogeochemical reactions at the Earth's surface. Carbonic acid (H_2CO_3^0) is the dominant natural acid in the weathering process, although human caused acid rain may increase the weathering rates of rocks (Miller et al., 1993; Likens et al., 1996; Wright, 1988; April et al., 1986; Johnson et al., 1981). Additionally, weathering by organic acids (e.g., oxalic acid) has bicarbonate as an end product indistinguishable from inorganic weathering (Berner and Berner, 1996). Carbon dioxide is a major greenhouse gas that influences climate, and therefore carbonate equilibria can help determine whether surface waters are a net source or sink of carbon dioxide.

Furthermore, the measurement of alkalinity, or acid neutralizing capacity, is important for two reasons. First, the measurement of alkalinity is used to estimate the concentration of bicarbonate in water, which allows the

calculation of charge balance error (Freeze and Cherry, 1979), a measure of analytical precision. Second, the acid neutralizing capacity, which is related to mineral composition of bedrock and regolith, is an important environmental indicator of the ability of the environment to buffer against acid rain (Newton et al., 1987; Bricker and Rice, 1989).

The purpose of this paper is three-fold. First, carbonate equilibria will be briefly reviewed, along with the methods of constructing a Bjerrum plot and a theoretical titration curve. Second, a detailed explanation of the method for measuring alkalinity using the Gran titration method will be given, and results compared to the theoretical calculations. This gives the students an opportunity to demonstrate in a laboratory experiment the theoretical calculations, and compare open and closed systems. Additionally, the Gran titration method and the low alkalinity titration method (Eaton et al., 1995) will be compared. Third, the application of the titration method to natural stream samples will be used as a way for the students to develop hypotheses and test them in the laboratory. This set of exercises can be completed in two sequential laboratory sessions, doesn't require much space, and doesn't require extensive amounts of expensive equipment. Various parts of this set of experiments can be used from high school through graduate school, depending on the level of explanation. Theory is presented before practice as a matter of pedagogical necessity; instructor knowledge of the system is critical to clear instruction. Combined with simple experiments demonstrating the relationship of P_{CO_2} and pH (Spear, 1996), the exercises will increase the students understanding of carbonate equilibria and improve algebraic manipulation and graph construction skills.

CARBONATE EQUILIBRIA THEORY

The theoretical aspects of carbonate equilibria are covered in great detail elsewhere (e.g., Drever, 1997; Langmuir, 1997; Stumm and Morgan, 1981), so this will be just a brief overview of the carbonate equilibria equations necessary for the construction of the titration and Bjerrum graphs (Table 1). Full derivation of the equations used in this paper can be found in the cited references. All equations will assume that in dilute surface waters the activity coefficient is 1.0 for all ionic species and therefore activity equals concentration. Graduate and upper level undergraduate classes may want to include the effect of ionic strength and temperature on carbonate equilibria. The inclusion of ionic strength allows the calculation of activity

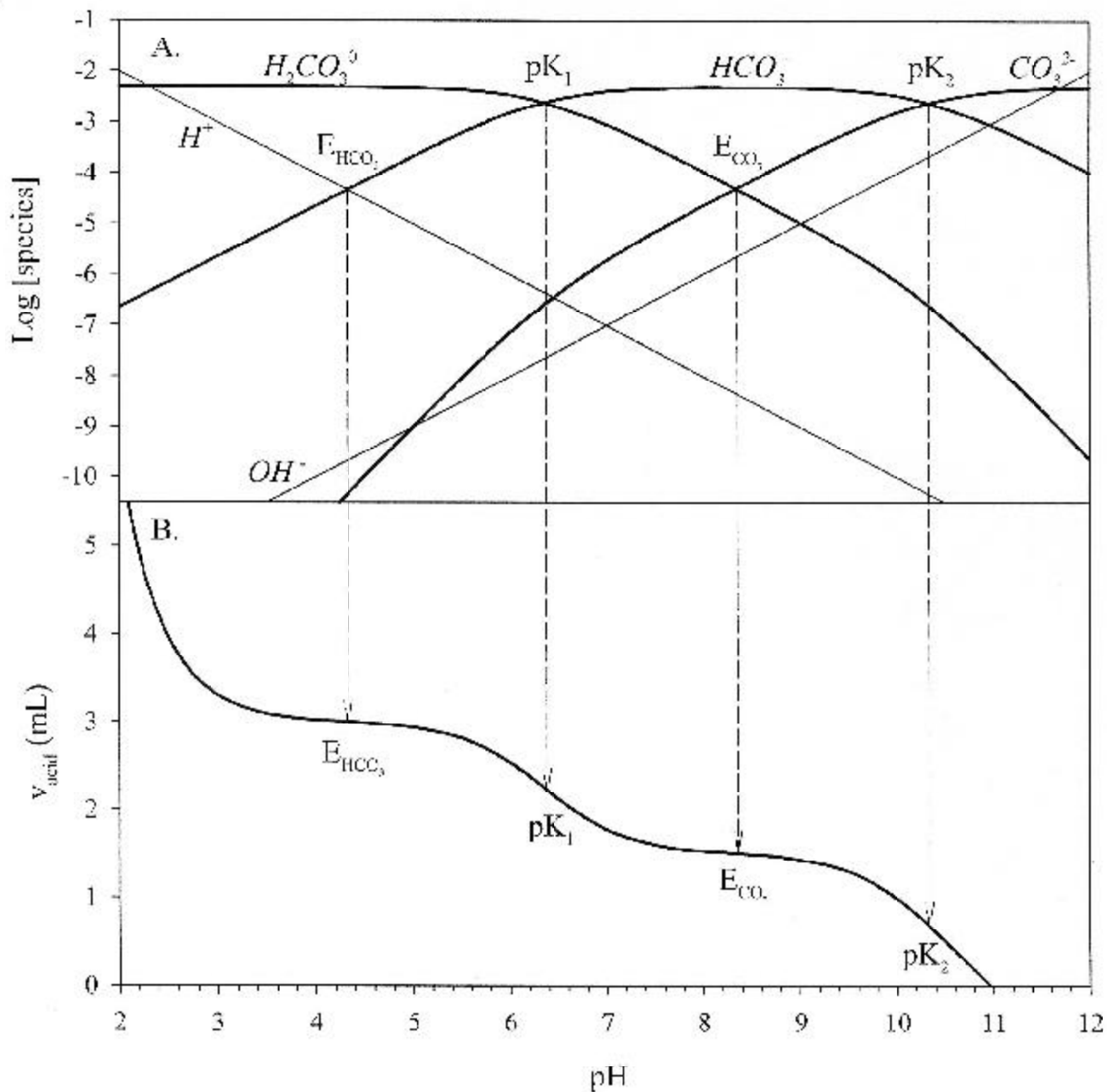
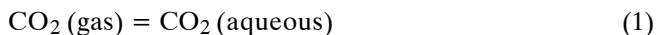


Figure 1. Bjerrum plot and theoretical titration curve for the carbonate system at 25°C, 1 atm, and $C_T = 5 \times 10^{-3}$ M. A) Bjerrum plot for the aqueous species of the carbonate. Calculations assume a dilute solution so activity coefficients equal 1.0 and activity equals concentration. Equilibrium constants are shown as pK_a and titration endpoints are shown as E_{species} . B) The titration curve for a theoretical NaCO_3 solution. Equilibrium constants and titration endpoints are extrapolated from Figure 1a for reference.

coefficients other than 1.0. This may be necessary for seawater and some groundwater. For any analyses of natural waters, the assumption of activity equaling concentration can be checked using a speciation program such as PHREEQ.

The starting point is the dissolution of carbon dioxide in water to form carbonic acid.



$$K_H = \frac{[\text{CO}_2(\text{aqueous})]}{P_{\text{CO}_2}} \quad (2)$$

In equation 2, K_H is Henry's constant and P_{CO_2} is the partial pressure of carbon dioxide in the atmosphere

EES 52: Carbonate Equilibria Speciation Diagram								
A Berjrum Plot for carbonic acid speciation								
See Langmuir (1997) pages 153-155 for equations								
Also, see notes for derivations of equations								
Let								
C(tota)=		0.001						
Variation of equilibrium constants with T								
Let	C		K					
T=	25.00		298.15					
K1=	4.43E-07		pK1=	6.35				
K2=	4.68E-11		pK2=	10.33				
The calculation of the equilibrium constants is based on table 1.7, p. 23								
in Mackenzie and Morse (1990). The original data are from Plummer								
and Busenberg (1982).								
				Log [Species]				
pH	[H]	[H2CO3]	[HCO3]	[CO3]	[H]	[OH]	alpha H+	
1	1E-01	-3.00	-8.35	-17.68	-1.00	-13.00	4.82E+14	
2	1E-02	-3.00	-7.35	-15.68	-2.00	-12.00	4.82E+12	
3	1E-03	-3.00	-6.35	-13.68	-3.00	-11.00	4.83E+10	
4	1E-04	-3.00	-5.36	-11.68	-4.00	-10.00	4.85E+08	
5	1E-05	-3.02	-4.37	-9.70	-5.00	-9.00	5.04E+06	
6	1E-06	-3.16	-3.51	-7.84	-6.00	-8.00	6.36E+04	
7	1E-07	-3.73	-3.09	-6.42	-7.00	-7.00	2.82E+03	
8	1E-08	-4.68	-3.01	-5.34	-8.00	-6.00	2.19E+02	
9	0.000000001	-5.67	-3.02	-4.35	-9.00	-5.00	2.24E+01	
10	1E-10	-6.81	-3.17	-3.50	-10.00	-4.00	3.14E+00	
11	1E-11	-8.40	-3.75	-3.08	-11.00	-3.00	1.21E+00	
12	1E-12	-10.33	-4.88	-3.01	-12.00	-2.00	1.02E+00	
13	1E-13	-12.32	-5.67	-3.00	-13.00	-1.00	1.00E+00	
14	1E-14	-14.32	-6.67	-3.00	-14.00	0.00	1.00E+00	
Log carbonate species concentration at given pH:								
6.55	2.82E-07	3.41	-3.21	-6.99	-6.55	-7.45	9.35E+03	
Percent carbonate species at given pH:								
		38.90	61.09	0.01				

Figure 2. Spreadsheet data table format used to graph Bjerrum plots. The example is given for carbonate species, but the same format is used for all polyprotic acids. The main difference from the other polyprotic acids here is that the equilibrium constants are calculated using the temperature dependent equations given in Table 1. The graph is generated by plotting pH against the log of the concentrations of the various species. The species concentrations are calculated using the equations in Table 1.

($10^{-3.5}$ atmospheres). At 25°C , $K_H = 3.38 \times 10^{-2}$ mol/L/atm, which makes carbon dioxide one of the more soluble gases in the atmosphere. The dissolved carbon dioxide then speciates into carbonic acid, bicarbonate, and carbonate ions, so the total concentration of carbon (C_T) is the sum of all the species (Table 1). However, carbonic acid is not what it seems. In fact, most of the dissolved carbon dioxide remains as carbon dioxide in the aqueous form (CO_2 aqueous); only about 0.3% actually forms carbonic acid (Langmuir, 1997). For the purposes of equilibrium calculations the total dissolved carbon dioxide is substituted ($\text{H}_2\text{CO}_3^* = \text{H}_2\text{CO}_3^0 + \text{CO}_2(\text{aq})$) for

dissolved carbon dioxide in the Henry's law expression (Eq. 3).

$$K_H = \frac{[\text{H}_2\text{CO}_3^*]}{P_{\text{CO}_2}} = K_{\text{CO}_2} \quad (3)$$

A table of equilibrium constants for the carbonate system at different temperatures, including the Henry's law constant, can be found in Drever (1997). The various studies that have developed equations for the equilibrium constants and temperature are summarized in Morse and Mackenzie (1990). The equations of Plummer and Busenberg (1982), which allow you to

calculate equilibrium constants at any temperature, are given in Table 1.

Substitution of equilibrium relationships into the above equation allows for the calculation of apparent P_{CO_2} in surface waters using measured alkalinity (for full explanation see Stallard and Edmond, 1987 or Langmuir, 1997). Assuming that bicarbonate is the main generator of alkalinity in the water, then $[HCO_3^-] > [H^+]$ and the equation can be simplified considerably (Eq. 4). In essence, this amounts to combining the equations for K_{CO_2} (Eq. 3) and K_1 (Table 1), and rearranging the equation to solve for P_{CO_2} . Taking the log of the equation converts $[H^+]$ to pH. The assumption that bicarbonate is the dominant carbonate species will be demonstrated to be true for the majority of surface waters later in the paper.

$$\log P_{CO_2} = -pH + \log \frac{[HCO_3^-]}{K_{CO_2}K_1} \quad (4)$$

Interestingly, as alkalinity is essentially constant in most surface waters, and the equilibrium constants are only a function of temperature, variations in the apparent partial pressure of carbon dioxide are a major control over pH. This relationship can be demonstrated experimentally in the classroom by exhaling through a tube into a beaker of deionized water and observing a decrease in pH (Spear, 1996). Some of the chemical reactions and processes that control the CO_2 concentration of natural surface waters include weathering of minerals, photosynthesis and respiration, anaerobic bacterial consumption of organic matter (e.g., sulfate reduction, respiration), and carbon dioxide dissolution and exsolution (Table 5.3 in Langmuir, 1997).

In general, river water P_{CO_2} tends to be supersaturated with respect to atmospheric P_{CO_2} (e.g., Huh et al., 1998a, 1998b; Huh and Edmond, 1999; Gislason et al., 1996). Swift flowing rivers, such as those found in the Andes, can be undersaturated with respect to atmospheric P_{CO_2} . For lakes and streams, apparent P_{CO_2} varies diurnally, with low apparent P_{CO_2} during the day and high P_{CO_2} at night (Cole et al., 1994; Neal et al., 1998). Apparent P_{CO_2} also varies seasonally, with lowest pressures in the spring and highest during the summer and winter (Neal et al., 1998; Neal et al., 2000). Thus, the apparent P_{CO_2} is an indicator of the balance between photosynthesis and respiration and the dynamic physical state of surface waters (Stallard and Edmond, 1987; Jarvie et al., 1997). Importantly, P_{CO_2} can be calculated from alkalinity concentrations measured in an open system (Stallard and Edmond, 1987). For samples collected in headwater streams with high dissolved organic content, however, special closed system techniques may be necessary to obtain research grade data (Hope et al., 1995).

Alkalinity - Alkalinity is the ability of water to buffer against the addition of hydrogen ions. In this respect,

alkalinity is often called acid neutralization capacity (ANC). Several anions in water can act as buffers, so whenever alkalinity is measured in the laboratory, what actually is being measured is total alkalinity. Total alkalinity is measured in units of equivalent charge, most often in milliequivalents per liter (meq/L). Milliequivalents per liter is related to concentration using equation 5. In this equation, gfw is gram formula weight and z is the charge of the ion. Equivalent charge units are used because hydrogen ions are neutralized by charge rather than mass. So, a carbonate ion (CO_3^{2-}) can neutralize two hydrogen ions and therefore $[H^+] = 2[CO_3^{2-}]$, with concentration in molarity.

$$meq/L = \frac{mg/L}{gfw} (z) \quad (5)$$

$$\begin{aligned} Alkalinity_{total} (meq/L) = & [HCO_3^-] + 2[CO_3^{2-}] \\ & + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [H_3SiO_4^-] + [H_2BO_2^-] \\ & + [CH_3COO^-] + [OH^-] - [H^+] \end{aligned} \quad (6)$$

Several polyprotic weak bases and organic anions can generate alkalinity in water (Eq. 6). Acetate from acetic acid is used as the organic anion, but any organic anion can be substituted. For most surface waters, however, the pH ranges from circumneutral to slightly acidic. Bjerrum graphs constructed by the students (see below discussion) can be used to show that the pK_a values of dissociation for nitric, sulfuric, boric, silicic, and phosphoric acids are such that the acids would only contribute to alkalinity in unusual conditions such as alkaline lakes (Langmuir, 1997). As a result, total alkalinity (Eq. 6) can be assumed to be equivalent to total carbonate alkalinity (Eq. 7).

$$Alkalinity_{Carbonate} (meq/L) = [HCO_3^-] + 2[CO_3^{2-}] \quad (7)$$

For waters of pH=6.3 - 8.3, hydrogen, carbonate, and hydroxide concentrations are negligible (Figure 1a), and therefore alkalinity can be assumed to be equivalent to the concentration of bicarbonate ions unless there is significant dissolved organic carbon.

Thus, for many surface waters, the measurement of alkalinity is equivalent to the measurement of bicarbonate. Surface waters that contain high concentrations of dissolved organic carbon, such as the Congo or black water rivers of the southeastern U.S., typically have pH values less than 4.5. Although these rivers would have abundant organic anions, these rivers would have little or no alkalinity and the hydrogen ion becomes an important cation (Beck et al., 1974; Negrel et al., 1993; Lewis et al., 1987). For surface waters that are alkaline and contain other alkalinity-generating ions the direct measurement of carbonate-generated alkalinity is

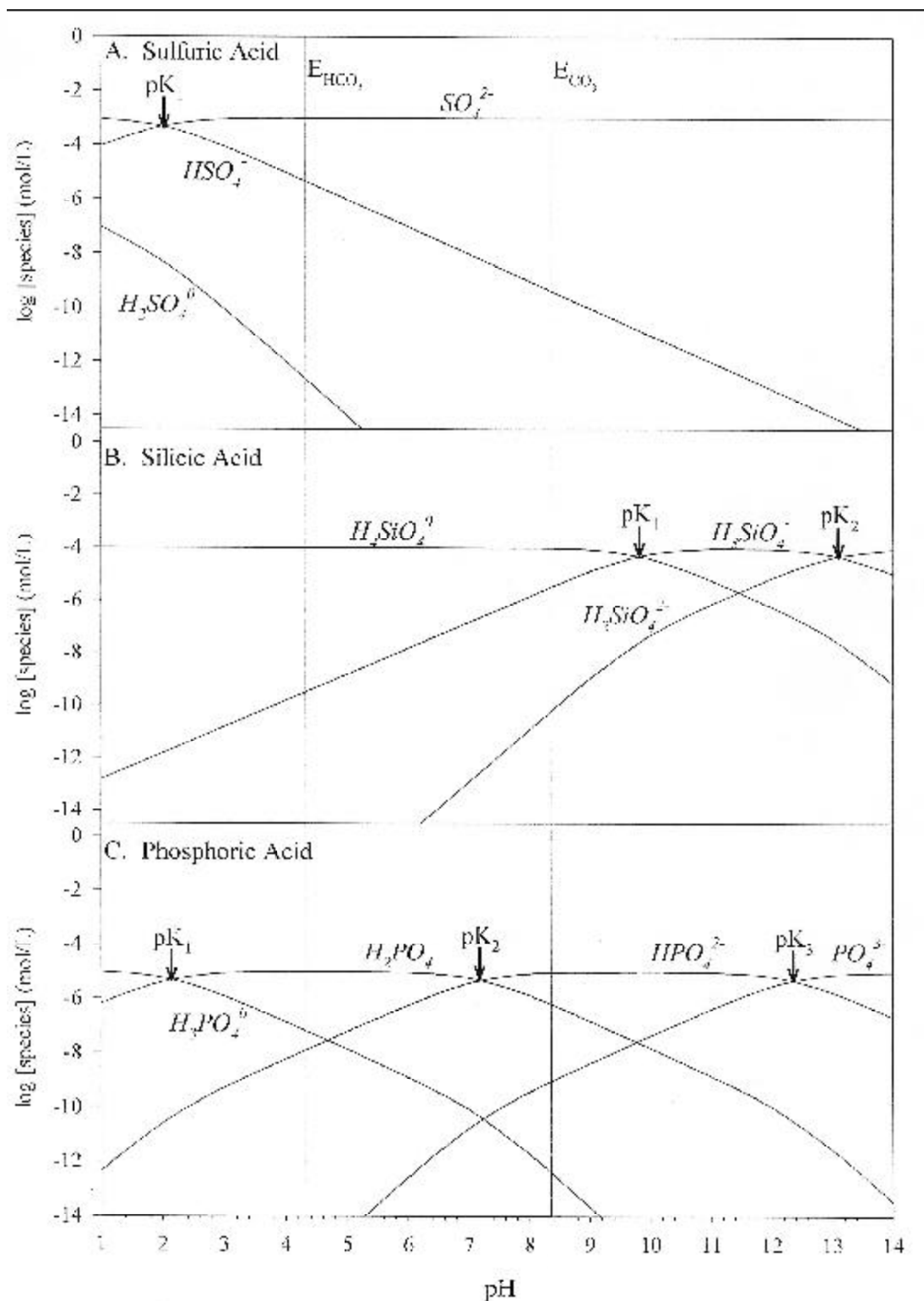


Figure 3. Few polyprotic acids other than carbonic acid contribute to alkalinity in natural freshwater systems. **A)** For strong acids, such as sulfuric or nitric acid, regions of buffering occur at pH values below the titration endpoint for bicarbonate. As a result, acid streams typically have little or no alkalinity. **B)** For weak acids such as silicic and boric acid, regions of buffering are above the titration endpoint for carbonate. As a result, the only natural systems where these acids contribute to alkalinity are alkaline lakes and seawater. **C)** In contrast, phosphoric acid does contain a region of buffering at a pH in the range of natural freshwater systems. Phosphate concentrations, however, typically are very low because it is a limiting nutrient and $[P] < [C]$.

not possible. For these waters, and seawater or groundwater collected at depth, bicarbonate and carbonate alkalinity must be calculated from the measurement of ΣCO_2 by potentiometric titration in a closed system (Edmond, 1970).

EXERCISE SET #1: EXPLORATION OF THEORETICAL CARBONATE EQUILIBRIA

The construction of the theoretical graphs is useful for three reasons. First, graph construction allows students to practice basic algebraic manipulation of equations. Second, spreadsheet programs on computer give students practice with entering formulas, make calculations quick, and allow practice in preparing high quality graphs. Third, and most fundamental, since less time is spent actually calculating numerical solutions, more time can be spent interpreting the results of the graphs and testing the effect of temperature variation on speciation and titration results.

After this set of exercises, the student should be able to put a pH electrode into any surface water and predict what anionic, alkalinity generating species will be dominant in the solution based on the pH of the water. A second way to emphasize theoretical considerations is to perform a numerical titration. This allows the student to develop the ability to predict how an actual titration will work, and compare open and closed systems.

The following two exercises, construction of a Bjerrum plot and calculation of a theoretical alkalinity titration curve, can either be done as a laboratory exercise or as a homework assignment. I find that the choice depends on the familiarity of the students with spreadsheet programs.

The Bjerrum Plot - The Bjerrum plot is a graph that shows the distribution of the species of a polyprotic acid as a function of pH, total concentration, and temperature. For the carbonate system, the species are H_2CO_3^0 , HCO_3^- , and CO_3^{2-} . By knowing the total carbon in the system, C_T , and using the temperature dependent equations for the various equilibrium constants, a set of equations can be derived for the construction of a Bjerrum plot (Table 1). Alternatively, the equilibrium constants could be entered manually by selecting the appropriate value from the table in Drever (1997).

The plot is constructed by entering the equations into a spreadsheet (Figure 2). This allows the calculation of the log of the species concentration for any pH. The graph is constructed by plotting pH versus the log of each of the species concentrations (H^+ , OH^- , H_2CO_3^0 , HCO_3^- , and CO_3^{2-}). The Bjerrum plots for other polyprotic acids (e.g., silicic, boric, sulfuric, and phosphoric acids) are constructed using the exact same method. The equilibrium constants (25°C) for these polyprotic acids are found in Langmuir (1997).

The Bjerrum plot for carbonate (Figure 1a) shows the pH regions where the three carbonate species are dominant and shows that equivalence points ($\text{pH}=\text{pK}$) occur where concentration curves intersect. Additionally, the shape of the curve is independent of the total carbonate concentration (C_T) and the concentrations of H^+ and OH^- are independent of C_T . The pH of equivalence points, however, will vary with temperature. This diagram indicates that CO_3^{2-} is the dominant species for a pH greater than 10.3, HCO_3^- is the dominant species for a pH range from 6.3 to 10.3, and H_2CO_3^0 is the dominant species for a pH less than 6.3. The carbonate titration endpoint (E_{CO_3}), where $\text{H}_2\text{CO}_3^0=\text{CO}_3^{2-}$, occurs at a pH of 8.3. The total alkalinity titration endpoint (E_{HCO_3}), where $\text{H}^+=\text{HCO}_3^-$, occurs at a pH of 4.5. Therefore, at 25°C and below a pH=8.3, bicarbonate is the primary alkalinity generator in the carbonate system.

One way to emphasize the dominance of the bicarbonate ion in natural waters is to have the students prepare a series of Bjerrum plots for polyprotic acids (carbonic, sulfuric, phosphoric, boric, silicic) and determine the pK_a values. This information will clearly show that for most natural waters below a pH of 8.3, the primary source of alkalinity will be bicarbonate. Other pK_a values are too low (e.g., sulfuric acid) or too high (e.g., silicic acid) to generate any alkalinity (Langmuir, 1997) (Figure 3). The only exception to this is phosphoric acid, which has an equivalence point at pH of ~7.2. Phosphorous, however, normally has a very low concentration in surface water, because of low concentrations in the crust, ecosystem retention, and biological extraction as a limiting nutrient. The concentration of bicarbonate, therefore, tends to be much greater than the concentration of phosphorous ions (Berner and Berner, 1996). As a result, the contribution of phosphorous to alkalinity can normally be ignored.

A number of questions can be asked of the student, and answered very quickly simply by either examining the graphs or substituting values for temperature and C_T . Example questions include:

- In what pH ranges are the carbonate (or other polyprotic acid) species dominant?
- How does the distribution of species change with a change in C_T ?
- How does the distribution of carbonate species change with a change in temperature?
- How do the equivalence point pH's change with changes in temperature?
- In what type of environment would bicarbonate not be the dominant source of alkalinity?

In addition, advanced classes should derive the equations in table 1.

Sample	ER-11 6-28-00		v (endpoint) = 1.35	
V (sample)	100 mL		[Alkalinity]= 13.50	
v (initial)	0.43 mL		[HCO ₃]= 16.47	
			V (sample) +	(V+v)10 ^{-pH}
pH	v (meas)	v (acid)	v (acid)	x10 ⁻⁴
7.00	0.43	0.00	100.00	0.1
6.53	0.88	0.45	100.45	0.3
6.04	1.30	0.87	100.87	0.9
5.52	1.59	1.16	101.16	3.1
5.05	1.75	1.32	101.32	9.0
4.95	1.77	1.34	101.34	11.4
4.82	1.81	1.38	101.38	15.3
4.69	1.84	1.41	101.41	20.7
4.61	1.87	1.44	101.44	24.9
4.50	1.92	1.49	101.49	32.1
4.40	1.96	1.53	101.53	40.4
4.30	2.02	1.59	101.59	50.9
4.18	2.10	1.67	101.67	67.2
3.99	2.30	1.87	101.87	104.2
3.76	2.65	2.22	102.22	177.6
3.68	2.85	2.42	102.42	214.0
3.53	3.30	2.87	102.87	303.6

Figure 4. An example spreadsheet table used to calculate the Gran function. The measured volume in the microburet is set to 0.0 mL for the initial volume (v_{acid}). The last column is the Gran function [(V_{sample} + v_{acid})*10^{-pH}]. The Gran plot is constructed by constructing a graph of v_{acid} versus (V_{sample} + v_{acid})*10^{-pH}. The numbers in the column are all scaled by 10⁻⁴ in order to make them legible. The titration endpoint (v_{endpoint}) is determined as in Figures 5 and 7 and the total alkalinity and bicarbonate concentrations are calculated using

Theoretical Alkalinity Titration in a Closed System -

The next step is for the student to progress from graphing the species distribution to calculating a theoretical titration curve and relating it to the Bjerrum plot. Drever (1997) shows an example of how to construct a theoretical alkalinity titration for a dilute, closed carbonate system. In this paper, I have modified slightly the initial conditions set by Drever (1997) to 300 mL of 5x10⁻³ M Na₂CO₃ solution (C_T=SCO₂=5x10⁻³ M/L) in a closed container with no gas phase present. The solution is titrated with a theoretical 1.00 M HCl solution. The purpose of this slight modification is to allow the students to perform this exact same titration experiment in an open system (below). Manipulation of the charge balance equation and equilibrium expressions results in an equation that will solve for the volume of acid added for a given pH (Eq. 8).

$$10^{-3}v = 10^{-2} \cdot \frac{5 \times 10^{-3} K_1(1 + 2K_2 / m_H)}{m_H + K_1 + K_1 K_2 / m_H} - \frac{10^{-14}}{m_H} + m_H \quad (8)$$

In this equation, v is the volume in mL of acid titrated into the sample, 10⁻² is the molar concentration of sodium in the sample, and 5x10⁻³ is C_T. The volume of acid, v, is multiplied by 10⁻³ in order to give the concentration of acid per milliliter rather than per liter (1 M/L / 1000 mL/L = 10⁻³ M/mL). For a full explanation and derivation of the equation, see Drever (1997; note the error in the final equation in the 1997 edition). A more advanced discussion of this equation is given in Langmuir (1997).

To construct the graph, the equation is solved for v and the equation is entered into a spreadsheet program. Equilibrium constants are either selected from the table in Drever (1997) or calculated as for the Bjerrum plot. Hydrogen ion concentrations (10^{-pH}) are entered, and a graph is constructed of pH versus volume of acid in milliliters (Figure 1b).

The students then compare the graph of the titration curve with the Bjerrum plot (Figure 1a). The comparison shows that regions dominated by a species are weakly buffered, whereas the equivalence or crossover points (pK values) are regions of strong buffering. Titration endpoints correspond to the crossover points where [H₂CO₃] becomes greater than [CO₃²⁻] and where [H⁺] becomes greater than [HCO₃⁻].

The construction of this graph, using a spreadsheet for calculations and graphing, leaves time for interpretation of the graph guided by directed questions. Example questions include:

- At what pH is the logical endpoint for the titration of CO₃²⁻? HCO₃⁻?
- In what pH ranges will the pH change quickly? Slowly?
- If the concentration of Na₂CO₃ solution is lowered, how will the volume of acid used in the titration change?
- At what concentration Na₂CO₃ solution should a lower concentration of acid be used in the titration (i.e., 0.02 N instead of 1.00 N)?
- Why is this a closed system?

Substitution of different concentrations for the Na₂CO₃ solution and titrant into the spreadsheet allows rapid, graphical answers to the last two questions. The goal of the questions is for the student to predict what will happen during a real titration before actually performing a titration. Lower level classes may just use the equation to plot the graph; upper level classes may want to derive the equation itself. Upper level classes may want to examine the effect of temperature on the titration curve.

Alkalinity Titrations - One of the excellent teaching aspects of alkalinity titrations using the potentiometric method is that a minimum of equipment and expendable supplies are needed, and even basic equipment can produce good results. The minimum equipment needed includes a pH meter with glass electrode, a graduated

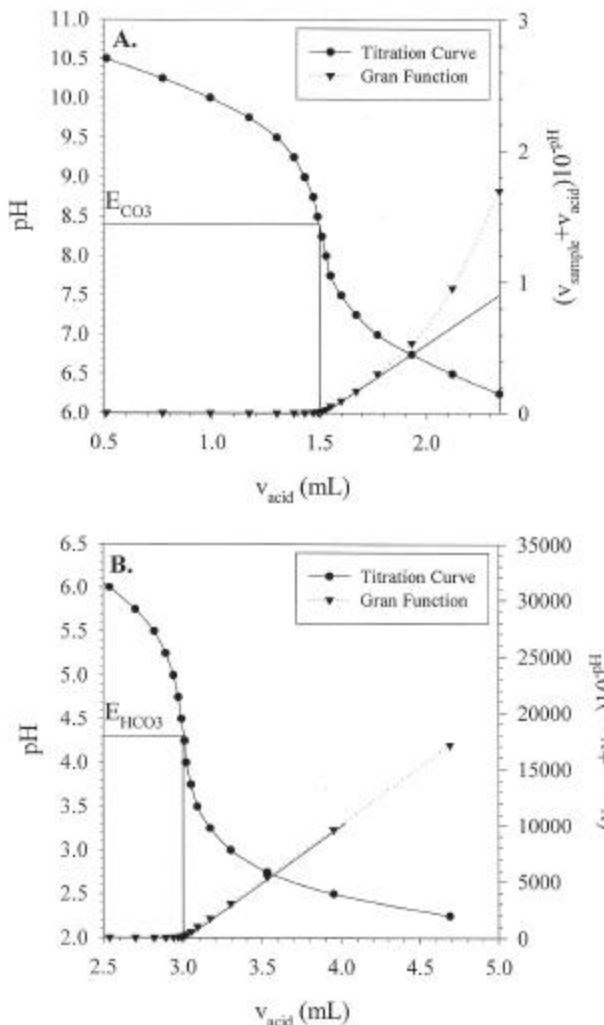


Figure 5. The theoretical titration curves and Gran functions for titration of the A) carbonate endpoint and B) bicarbonate endpoint for the 5×10^{-3} Na_2CO_3 solution at 25°C and 1 atm. The determination of the carbonate endpoint is difficult because of the curved nature of the Gran function in the pH range of 6.0 to 7.0.

cylinder, a magnetic stirrer, a 5 or 10 mL microburet with support, standard buffer solutions, and 0.02N and 1.00 N acid (normally sulfuric or hydrochloric). For teaching laboratories, very basic benchtop pH meters, or even portable pH meters can be used along with class B glassware. For undergraduate research projects, research grade benchtop pH meters and class A glassware are recommended. Standard pH = 4.01 and pH = 7.01 buffer solutions and standard 0.02 N and 1.00 N acid solutions are inexpensive and readily available. The 0.02 N acid is preferred for titration of dilute surface waters. For strongly buffered, high conductivity waters (e.g., those

in equilibrium with limestone), the 1.00 N standard acid solution is preferable. Reagent grade Na_2CO_3 is used to make the solution for the experimental titration.

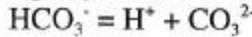
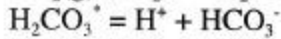
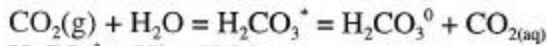
The Method of Potentiometric Titration - The potentiometric titration measures the change in electric potential using a standard glass electrode. The change in electric potential is converted to hydrogen ion concentration using the Nernst equation (Rossotti and Rossotti, 1965). Modern pH meters do this for the scientist, although research grade benchtop pH meters also indicate the electrical potential of the sample in millivolts during the titration. The potentiometric titration is preferred over indicator solutions because it allows the measurement of the actual endpoint. Two problems are inherent with the use of indicator solutions. First, the change in color of the indicator (such as methyl orange for the bicarbonate endpoint) occurs over a range of pH (Harris, 1982), so picking the actual endpoint is difficult. Second, the bicarbonate endpoint shifts with bicarbonate concentration, varying from pH = 5.2 for $C_T = 10^{-4}$ M to pH = 3.9 at $C_T = 10^{-1.5}$ M (Langmuir, 1997). Thus, for accurate alkalinity measurements, the potentiometric method is preferred.

The problem faced in the use of the potentiometric method is that titrating the exact endpoint is very difficult, and picking the inflection point in lieu of the end point is also very difficult. The Gran titration and the low alkalinity titration methods have been developed to deal with the problem of determining an endpoint.

Gran (1952) surmounted the problem of endpoint determination by developing the Gran function, which allows a graphical method of finding the titration endpoint. The most important facet of this method is that whether or not the actual end point is titrated is insignificant. Additionally, for polyprotic acids, multiple end points can be determined with accuracy. The titration is simple as only the pH and the volume of acid used need be recorded. In this method, the sample is titrated to a pH of approximately 3.5, with about 10 or so data points (v , pH) recorded between pH 5.0 and 3.5 (Table 3). The data are entered in to a spreadsheet and the Gran function, $(v_{\text{sample}} + v_{\text{acid}})10^{\text{pH}}$, is calculated (Figure 4). The graph of v_{acid} versus $(v_{\text{sample}} + v_{\text{acid}})10^{\text{pH}}$ is the Gran plot (Figure 5). For the carbonate system, the slope of the straight-line portion of the Gran function is the dissociation constants K_1 and K_2 , assuming that the activity coefficients are 1.0 in a dilute solution. Extrapolation of the straight-line portion of the graph to the v_{acid} axis locates v_{endpoint} with great precision. The Gran titration method is the preferred method for measuring alkalinity in the research setting (e.g., Huh

Table 1. Carbonate Equilibria Equations.

Chemical reactions



Equilibrium Constants

$$K_{\text{CO}_2} = [\text{H}_2\text{CO}_3]/P_{\text{CO}_2}[\text{H}_2\text{O}]$$

$$K_1 = [\text{HCO}_3^-][\text{H}^+]/[\text{H}_2\text{CO}_3^*]$$

$$K_2 = [\text{CO}_3^{2-}][\text{H}^+]/[\text{HCO}_3^-]$$

$$K_w = [\text{H}^+][\text{OH}^-]$$

Bjerrum Plot Equations

$$C_T = [\text{H}_2\text{CO}_3^0] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = \Sigma\text{CO}_2$$

$$[\text{CO}_3^{2-}] = C_T/\alpha_H$$

$$[\text{HCO}_3^-] = C_T[\text{H}^+]/K_2\alpha_H$$

$$[\text{H}_2\text{CO}_3^0] = C_T[\text{H}^+]^2/K_1K_2\alpha_H$$

$$\alpha_H = ([\text{H}^+]^2/K_1K_2) + ([\text{H}^+]/K_2) + 1$$

Equilibrium Constant Functions¹

$$\ln K_{\text{CO}_2} = 249.5708 - 15932.9T^{-1} - 40.45154 \ln T + 0.04570836T + 1541279T^{-2}$$

$$\ln K_1 = -820.4380 + 50275.82T^{-1} + 126.8339 \ln T - 0.1402736T - 3879685T^{-2}$$

$$\ln K_2 = -248.4208 + 11862.51T^{-1} + 38.92561 \ln T - 0.0749001T - 1298007T^{-2}$$

¹Equations from data in Plummer and Busenburg (1982). Valid for T=0-250°C

and Edmond, 1999; Lewis et al., 1987; Anderson et al., 2000).

The low alkalinity titration method (Eaton et al., 1995) is the method used in the Standard Methods for the Examination of Water and Wastewater, and thus is an EPA approved method. The method states that the sample should be titrated to a pH of between 4.3 and 4.7, the volume recorded, and then titrated down 0.3 pH units exactly, and the volume recorded again. I have modified the method slightly to titrate to pH of 4.5 and then 4.2, so that the method is consistent for all students. The low alkalinity method is typically used if the total alkalinity is less than 20 mg/L CaCO₃. Alternatively, the potentiometric titration to a preselected end point method can be used for higher total alkalinity.

The alkalinity of a sample is calculated using the volume of acid used to titrate to the end point, the normality of the acid, and the volume of the sample (Eq. 9). The equation is slightly modified for the low alkalinity titration method (Eq. 10).

$$\text{Alkalinity (mg/L)} = \frac{v_{\text{acid}} * N_{\text{acid}} * \text{gfw}}{v_{\text{sample}} * |z|} \quad (9)$$

$$\text{Alkalinity (mg/L)} = \frac{(2B - C)_{\text{acid}} * N_{\text{acid}} * \text{gfw}}{v_{\text{sample}} * |z|} \quad (10)$$

In equations 9 and 10, N_{acid} is the normality of the acid (equivalent to molarity at dilute concentrations), gfw is the gram formula weight in mg/mole, and z is the absolute value of the charge associated with the carbonate species. In equation 10, B is the volume of acid used to titrate to the first recorded pH (between 4.3 and 4.7), and C is the total volume of acid used to reach 0.3 pH lower. The calculation 2B-C gives the estimated end point of the titration for the low alkalinity method. Alkalinity can be calculated directly as mg/L CaCO₃, mg/L HCO₃⁻, or mg/L CO₃²⁻ by substituting the appropriate gram formula weight in milligrams and absolute value of the charge. Total alkalinity is measured as mg/L CaCO₃, and z is 2 because the carbonate ion neutralizes the hydrogen ion. Generally, total alkalinity

Table 2. Comparison of Gran and Low Alkalinity potentiometric titration methods for samples collected near the Furman campus.

Sample	Method		%Difference ²
	Gran	Low Alkalinity	
PMWA #1 4/1/00	5.49	5.84	+6.4
PMWA #2 4/1/00	6.75	6.83	+1.2
PMWA #3 4/1/00	5.64	5.31	-5.9
PMWA #4 4/1/00	5.98	6.53	+9.2
Grace #1 3/29/00	16.65	16.15	-3.0
Grace #3 3/29/00	14.81	14.99	+1.2
Grace #4 3/29/00	20.58	19.59	-4.8
ER08 3/27/00	10.79	10.71	-0.7
ER08 3/21/00	6.72	6.72	0.0
ER17 3/27/00	20.65	20.90	+1.2
ER17 3/21/00	9.09	9.09	0.0

¹Alkalinity in units of mg/L HCO₃⁻

²% Difference = [(Low Alkalinity/Gran) - 1]*100

(mg/L CaCO₃) is reported and then used to calculate bicarbonate concentrations based on the assumption that no other anion contributes significantly to acid neutralization capacity. If this assumption cannot be met, then the only way to measure carbonate species concentrations is by measurement of ΣCO₂ in a closed system (Edmond, 1970). Comparison of the titration results from open and closed systems for samples from the Amazon River showed no difference between the two methods (Stallard and Edmond, 1987).

Comparison of the Gran method and low alkalinity method using samples I collected in South Carolina suggest that the difference between results for the two methods is less than 5% except for very dilute samples with very low alkalinity (Table 2). The Gran method probably is superior for alkalinity concentrations less than 10 mg/L. For any type of research, the Gran method is preferred because it allows the exact determination of the titration endpoint and accurate calculation of apparent P_{CO2}. This method, however, requires an additional time investment as it involves the construction of a graph to determine the end point volume. The advantage of the low alkalinity method is that it is faster than the Gran method, and apparently it does account for the variation in the bicarbonate endpoint. The problem with this method is that if the endpoint of titration is missed, the sample must be reanalyzed. The following exercises all use the Gran method because it is the most commonly used method in the literature.

EXERCISE SET #2 – ALKALINITY TITRATIONS USING THE GRAN METHOD

The objectives of the following exercises are twofold. First, the student is introduced to the Gran function and learns how to calculate alkalinity using the Gran method. Second, the student performs two alkalinity titrations

using the Gran method, one on a known solution and one on an unknown sample collected from a nearby surface water. The overall goal is to apply carbonate equilibria theory to a real world problem.

Application of the Gran method to the theoretical titration - For the first exercise, students use the theoretical titration curve calculated in exercise set #1. The students are required to calculate a Gran function for the curve, create a Gran plot, and then determine the titration endpoints for both carbonate alkalinity and bicarbonate alkalinity (Figure 5). The volumes of acid used to reach the titration endpoints are used in the alkalinity equation (Eq. 8) to calculate total alkalinity, carbonate alkalinity, and bicarbonate alkalinity.

One very important feature of the theoretical titration curve is shown when applying the Gran function to the determination of the carbonate endpoint. Textbooks, such as Drever (1997) or Harris (1982), show the Gran function for the bicarbonate endpoint and suggest that the determination of the carbonate endpoint is just as simple. Examination of the theoretical titration curve, however, shows that the curve is linear only in the range of pH=6.0 to pH=6.5 (Figure 5). This is also a range in which the rate of pH change is rapid. Thus, in order to get enough data points to extrapolate a straight line to v_{endpoint} , the increments of acid added during a real titration must be small in this range. Careful application of the Gran function to the theoretical titration curve results in titration endpoints that match the Bjerrum plot equivalence points and predicts the amount of acid needed to reach the endpoint.

The purpose of this exercise is to get the student to think about how a real sample would respond to a titration. Example questions include:

- At what pH do you need to begin considering the contribution of carbonate ions to alkalinity?
- In what pH ranges will you need to titrate slowly in order to get enough data points for a Gran plot, particularly for the carbonate endpoint?
- Why is the choice of acid strength important to the alkalinity titration (e.g., why not use 0.02 N acid for this exercise)?
- What effect will temperature have on the titration?

Titration of an experimental open system - The titration of a real 5×10^{-3} M Na₂CO₃ solution is used for comparison with the theoretically calculated titration curve. Students should know how to make this solution, although for a more expedient lab I generally make the solution ahead of time. The initial pH of this solution is near 11, so that the student will titrate through both the carbonate and bicarbonate endpoints. Although this solution is geochemically dilute (ionic strength is less than 10⁻¹), the total alkalinity is very high. As a result, the titration is performed using a standard 1.0 N HCl acid

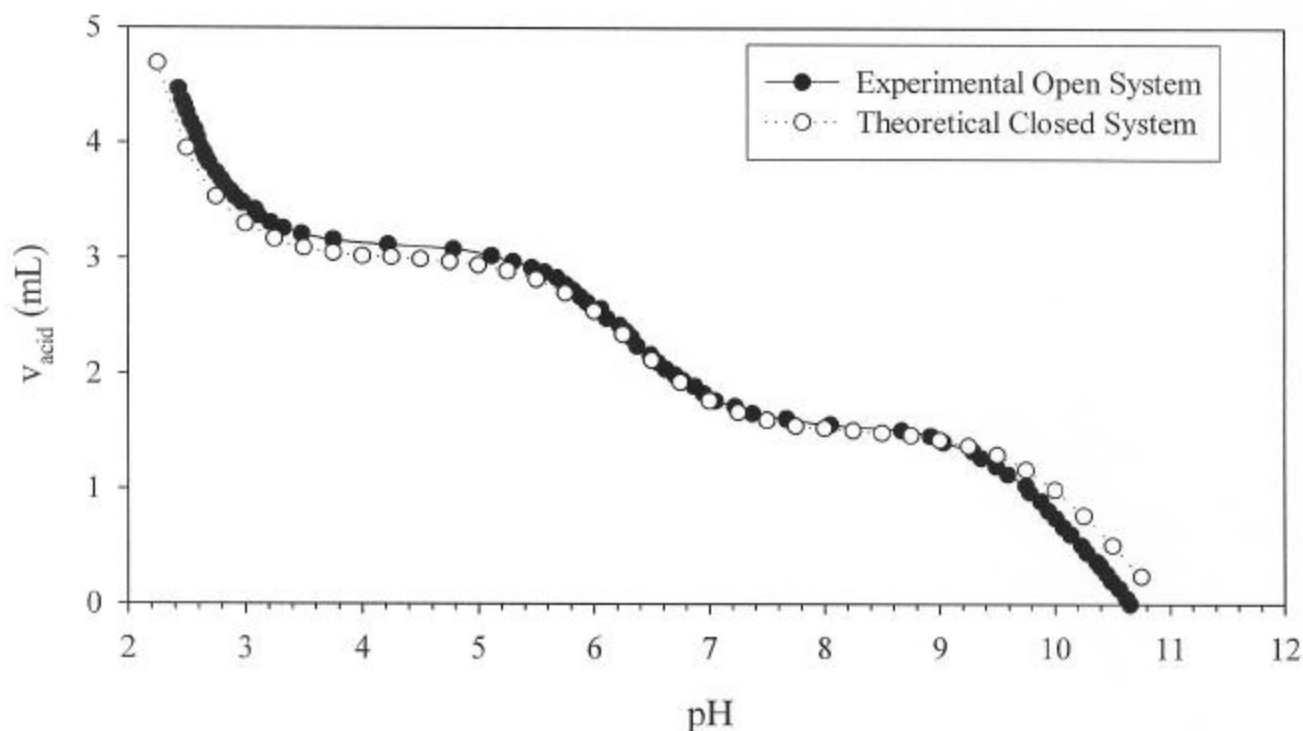


Figure 6. A comparison of the calculated titration curve for a closed system with the actual titration curve for an open system. Both closed and open systems are 5×10^{-3} M Na_2CO_3 solutions. The closed system is for 25°C and 1 atm. The difference between the two curves is a function of CO_2 solubility and temperature difference.

solution and a sample volume of 100 mL or less. The primary difference between the theoretical calculation and the real titration is that the theoretical calculation is for a closed system, whereas the experimental method is a titration of an open system in equilibrium with atmospheric CO_2 (Langmuir, 1997).

A comparison of the calculated titration of a 5×10^{-3} M Na_2CO_3 solution in a closed system with an actual titration of a 5×10^{-3} M Na_2CO_3 solution in an open system demonstrates the difference between open and closed systems (Figure 6). In the high pH range, the open system pH is lower than that of the closed system, whereas at low pH, the open system pH is higher than that of the closed system. Additionally, a greater volume of acid is required to reach the carbonate and bicarbonate endpoints, especially for the bicarbonate endpoint. A carefully done titration, therefore, shows the effect of dissolved CO_2 and difference in temperature on the open system. At the beginning of the titration, the sample never reaches the theoretical initial pH because dissolved carbon dioxide lowers the pH of the system. At the end of the titration, HCO_3^- is being converted to

H_2CO_3^* ($\text{H}_2\text{CO}_3^* = \text{H}_2\text{CO}_3^0 + \text{CO}_{2(\text{aq})}$). Because H_2CO_3^* is 97% dissolved carbon dioxide gas, CO_2 is lost from the system, and more acid must be added in order to lower the pH. Whether the temperature is warmer or cooler than 25°C can also affect the solubility of carbon dioxide. When the Gran function is applied to the open system the concentration of carbonate alkalinity is 5.17 meq/L and the concentration of bicarbonate alkalinity is 10.17 meq/L (Figure 7). The total alkalinity for the titration I did is 5.16×10^{-3} M, which is slightly higher than that of the theoretical calculation. The ultimate goal would be to have the student predict that this would occur and then correctly interpret the results.

The purpose of this exercise is to have the student perform a Gran titration that includes both the carbonate and bicarbonate endpoints. The results are then compared to the results of the calculated titration. Some example questions might include:

- What is the quality of your titration (i.e., how smooth is the curve) compared to the calculated titration? What types of error may cause deviation from the smooth curve?

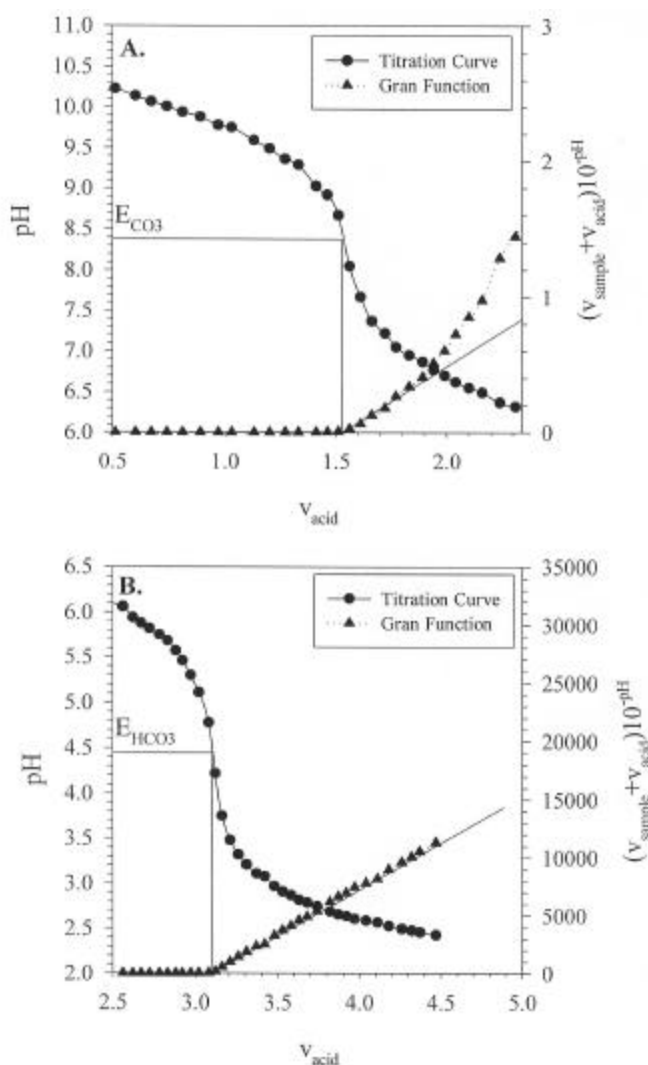


Figure 7. The titration curve and Gran functions for titration of the A) carbonate endpoint and B) bicarbonate endpoint for the 5×10^{-3} M Na_2CO_3 open system solution at 25°C and 1 atm. The determination of the carbonate endpoint by the Gran function is made possible only by additions of acid in very small increments. The results from the open system match those predicted from the closed system reasonably well (see text for discussion).

- Do the theoretical and experimental titrations match up when graphed together? -Can you explain any differences between the curves as a function of the experimental system being open rather than closed?
- How well do your carbonate, bicarbonate, and total alkalinities match those of the theoretical curve? What would account for any observed difference?

These questions are important because it forces the student to focus on the quality of the titration they have performed. A well performed titration gives reasonable, interpretable results. A poorly performed titration will give results that are difficult to interpret.

Titration of a Natural Open System - After students have performed the titration of the dilute Na_2CO_3 solution, they are requested to collect a water sample from a nearby stream. The sample is completely analyzed, cations by ICP-AES, anions by ion chromatography, and alkalinity by Gran titration. Analytical accuracy is determined by charge balance error calculations. The students are asked, prior to sampling, to predict 1) the pH of the stream based on rock type and atmospheric deposition pH, and 2) the main carbonate species that will be present in the sample. They can also predict the relative amount of CO_2 oversaturation based on the turbulence and size of the river.

A full review of field protocol is given in Andersen (2001); what follows are minimal guidelines for samples collected for alkalinity titrations. In the field, water samples should be collected in a pre-cleaned HDPE bottle with zero head-space and transported on ice to the laboratory where they should be kept refrigerated until analysis. Because alkalinity is generally considered conservative, samples do not necessarily need to be filtered before analysis. If filtered, samples should be filtered into a 250 mL pre-cleaned HDPE bottle using a 0.45 mm membrane filter with positive pressure using an inert gas such as N_2 . Positive pressure filtration with an inert gas (e.g., N_2) is necessary to keep CO_2 in the sample from degassing, and minimal head-space, ice, and refrigeration are needed to reduce the potential of bacterial activity changing the alkalinity. 250 mL bottle is the minimum amount of sample that should be collected as 80-150 mL are typically used in student alkalinity analyses. The additional 100 mL then can be used if the first analysis goes wrong. Eaton et al. (1995) suggest that field samples should be analyzed within 24 hours, but our results indicate that if the sample is kept refrigerated and tightly capped, samples can be stored for at least one week without any change in the alkalinity. This suggests that alkalinity can be treated as a conservative ion, at least for streams draining non-carbonate rocks. In situations where stream water is in equilibrium with calcite, an increase in temperature after sample collection could cause the precipitation of colloidal calcite, which can be lost during the filtering step. In such cases, the titration is generally performed on the unfiltered sample.

Students perform the Gran titration in the laboratory (Table 3). The results are transferred from notebook to spreadsheet, a graph is constructed, the titration endpoint is determined using the Gran plot, and alkalinities are calculated using the endpoint volume.

Table 3. Performing a Gran Titration.

Equipment and supplies

250 mL graduated cylinder, 5 mL or 10 mL microburet with support stand, pH meter (preferably a benchtop model), magnetic stirrer and stir bar, 0.02 N and 1.00 N standard acid solutions, standard pH buffer solutions.

Sample preparation

1. Pour 80 to 150 mL of sample into a graduated cylinder and record the sample volume and sample name in a notebook. In general, a smaller volume of sample should be used for higher alkalinity samples and a greater volume of sample should be used for lower alkalinity samples.
2. Pour the sample from the graduated cylinder into a 400 mL beaker.
3. Place the beaker on a magnetic stirrer with a stir bar added to the beaker.

Titration procedure

1. Calibrate pH meter using pH = 4.01 and pH = 7.01 standard buffers.
2. Fill microburet with standard acid solution and record initial volume. The choice of acid strength depends on the sample. For high alkalinity samples (e.g., solutions in contact with limestone or the Na_2CO_3 solution) use a standard 1.00 N acid. For low alkalinity samples (e.g., surface waters not in contact with limestones) use a standard 0.02 N acid.
3. Place beaker with sample on the magnetic stirrer. With magnetic stirrer on its lowest setting, place pH electrode in the sample. After the pH has stabilized, record initial pH next to initial volume in notebook. If initial pH drifts, pick a pH and start titrating! The accuracy of the initial pH doesn't matter for a Gran titration.
4. Add about 0.10 mL of acid to the solution, wait for pH to stabilize, and record pH and new volume.
5. Repeat step 2 until a pH of about 5.0.
6. Add about 0.05 mL of acid, wait for pH to stabilize, and record pH and new volume.
7. Continue titration until a pH of about 3.5, recording pH and volume for each incremental addition of acid. About 10 data points are needed to draw a reasonably straight line.
8. If the acid runs out, record the final volume and add more acid to the buret. Then start at step 4 and proceed until completion.

Calculation of alkalinity

1. Transfer data from notebook to spreadsheet, if necessary.
 1. Calculate the Gran function in the spreadsheet and create a Gran plot.
 2. Draw a line on the Gran plot in the spreadsheet. The intercept of this line with the x-axis is the volume of acid required for the titration end-point.
 3. Enter this volume in the spreadsheet to calculate the alkalinity and the bicarbonate concentrations (Eq. 8).
-

Students are then asked a series of questions based on the results of their analysis. Example questions include:

- How is alkalinity generated in a natural system?
- How well did your predicted and measured stream pH match?
- Calculate the distribution of carbonate species using your speciation spreadsheet and the pH and temperature of your stream. Does the dominant carbonate species match your prediction? (This question makes use of the spreadsheet used to calculate carbonate species; see Figure 2)
- Using equation 4, calculate the P_{CO_2} of your stream. Is it oversaturated or undersaturated with respect to the atmosphere?
- How might P_{CO_2} vary on a seasonal basis? What would cause this variation? What effect might this have on pH?
- How would the alkalinity increase or decrease if the stream drained a different rock type?
- How are the solubility's of the minerals in your rock type related to alkalinity?

Obviously, this would work best if several samples could be collected from streams draining rock types with minerals of different solubilities, such as carbonate and non-carbonate rocks. Such samples would allow direct comparison of rock types. I don't have that luxury, however, so I know that a single rock type will work okay with some guidance from the instructor.

DISCUSSION AND SUMMARY

In chemistry courses, students often find acid-base and buffering relationships difficult to understand. For the geoscience major, this is in part because of the type of example used to explain acid-base relationships. One often-used example is the titration of a weak acid with a base, which bears little relationship to the natural environment. As a result, connecting the concept learned in a chemistry class with carbonate equilibria in the geologic setting is a difficult task.

Carbonate equilibria relationships, however, are extraordinarily important in Earth systems and are applied to numerous problems in the geosciences ranging from weathering studies to global climate change. Such a significant aspect of geochemistry should demand a accessible, hands-on approach to developing an understanding of a difficult, yet critical, subject (e.g., Spear, 1996).

The measurement of alkalinity allows a simple and relatively inexpensive approach to teaching carbonate equilibria. The two basic parts of this laboratory experience are divided into theoretical considerations and application of theory to experimental and natural systems. Theoretical considerations include the calculation of theoretical speciation diagrams for polyprotic acids and a theoretical titration curve for a 0.5

M Na_2CO_3 solution in a closed system. This is followed by application of the theory to the titration of a 0.5 m Na_2CO_3 solution in an open system and the titration of a sample from a natural open system, such as a stream. For upper level classes, it is critical to include two or more journal articles that make use of alkalinity data. This gives at least two examples of the context within which alkalinity is used in research or applied problems.

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