

Alkalinity and Acidity

13.1 INTRODUCTION



Key idea: It is possible to probe a system and determine its ability to buffer against changes in pH.

Chapter 12 provided an overview of how to quantitatively analyze mixtures of acids and bases. In Chapter 12, you learned that titrations can be used to probe the chemistry of a system. In addition, you discovered that titration curves give important information about the buffering capacity of a water. (Remember that a water is well buffered if its pH does not change very much upon addition of an acid or base.) If we combine these two ideas, it should be possible to probe a system and determine its ability to buffer against changes in pH.

An important water quality parameter that comes from the probing of a water through titration and allows for the determination of the extent of buffering is *alkalinity*. In this chapter, the concept of alkalinity is developed. The properties and units of alkalinity will be presented. In addition, you will learn about a companion parameter called *acidity*. The practical applications of alkalinity and acidity to solve aquatic chemistry problems will be discussed.

13.2 ALKALINITY AND THE ACID NEUTRALIZING CAPACITY

13.2.1 Partially titrated systems

You know that the titration of a weak acid with a strong base generates a characteristic titration curve. The shape of the curve depends on the total acid concentration, the number of exchangeable protons on the acid, and the pK_a value(s). The weak acid partially neutralizes the basic titrant. In other words, the strong base from the titrant does not affect the solution pH as much as it would if the strong base was added to pure water. Similarly, the titration of a weak base with a strong acid generates a characteristic titration curve, the shape of which depends on the total base concentration, the number of exchangeable protons on the base, and the pK_b value(s). The weak base partially neutralizes the acidic titrant.

In this chapter, you shall explore *partially* titrated acids and bases. Imagine that a weak acid *already* has been combined with a strong base. In other words, the weak acid already has been titrated to some arbitrary point. You are at some unknown value of f that is greater than zero.



Key idea: Adding strong acid to a partially titrated weak acid will retrace the titration curve of the weak acid.

Thoughtful Pause

What happens if you now start to add strong acid to the system?

To answer this question, recall from Section 12.3.4 that the titration of an acid with a strong base and the titration of the conjugate base of the acid with a strong acid trace out the same titration curve. Thus, adding strong acid to a partially titrated weak acid will retrace the titration curve of the weak acid with a strong base.

An example may make this important point clearer. Say that your lab partner secretly makes up a 10^{-2} M acetic acid solution and adds 3×10^{-3} N NaOH to it. She hands it to you, and you probe the system by titrating with a strong acid (say HCl). You would generate a titration curve that looks like Figure 13.1. It is clear that the original solution (at the beginning of the titration) is capable of partially neutralizing the acid added in the titration. To illustrate this point, the titration curve for the titration of pure water with strong acid is shown in Figure 13.1. Note that the pH of the unknown solution generally is larger. This indicates that the unknown solution is buffered to a greater extent than pure water.

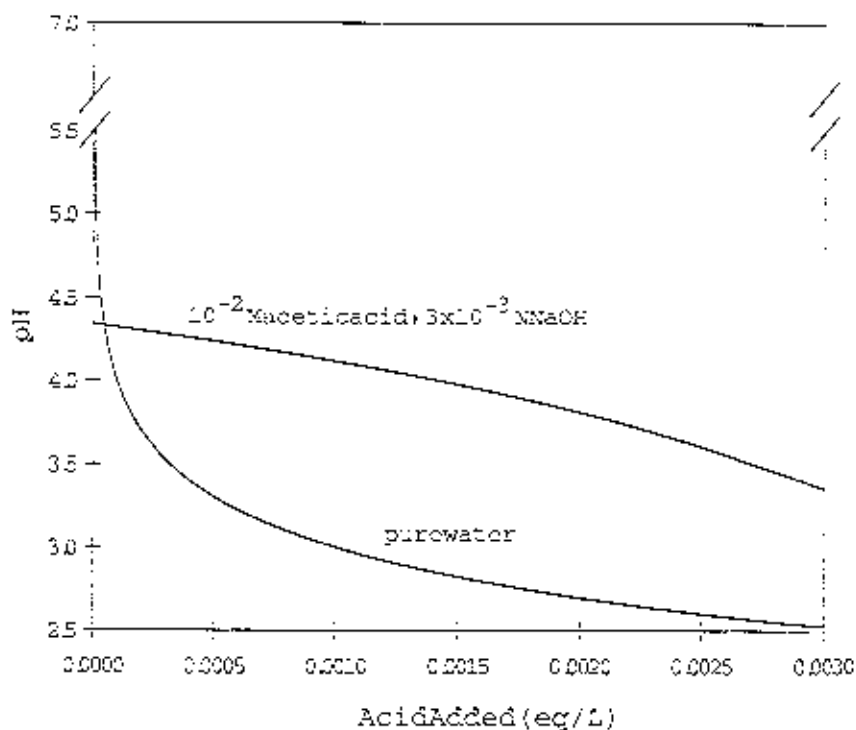


Figure 13.1: Titration Curves for a 10^{-2} M Acetic Acid + 3×10^{-3} N NaOH Solution and Pure Water

You could reorder the x -axis to obtain Figure 13.2. The titration curve for the titration of the acetic acid + base solution with strong acid (bottom x -axis in Figure 13.2; titration proceeds right to left) is the same as the titration curve for the titration of acetic acid with strong base (top x -axis in Figure 13.2; titration proceeds left to right). This makes sense: the starting solution (right side of Figure 13.2) is obtained by titrating acetic acid (left side of Figure 13.2) up to $f = 0.3$ (i.e., up to the addition of 3×10^{-3} N NaOH).

13.2.2 Base and acid neutralizing capacity

How much of the acidic titrant has been neutralized by the original solution? You can use any measure of the neutralizing ability that you want. By convention, the *acid neutralizing capacity* (ANC) of a water is defined as the equivalents per liter[†] of strong acid required to reach the zeroth equivalence point. Why pick the zeroth equivalence point? Recall from Chapter 12 that the buffer capacity is low at the zeroth equivalence point. The buffering at pH values less than the pH at $f = 0$ is not due to the original composition of the solution (see Section 12.3.5). Thus, it makes sense to stop at $f = 0$.

In a similar fashion, the *base neutralizing capacity* (BNC) of a water is defined to be the equivalents per liter of strong base required to reach the first equivalence point ($f = 1$ and $g = 0$). The ANC and BNC are very useful concepts, especially for systems partially titrated to between $f = 0$ and $f = 1$ (or, if starting with the conjugate base, partially titrated between $g = 0$ and $g = 1$). Recall from Chapter 12 that solutions are fairly well buffered between $f = 0$ and $f = 1$, with maximum buffering at $f = 1/2$. Thus, ANC and BNC tell you how much added acid or base could be added without significantly changing the pH of the system.

The ANC is the amount of strong acid required to bring a solution to $f = 0$. For a monoprotic acid, ANC is the amount of acid required to make the solution equivalent to an HA solution. Thus, at the end of the titration, the solution is equivalent to an HA solution and its proton condition is:

$$[H^+] = [A^-] - [OH^-] \text{ or:} \\ \alpha_1 A_T + [OH^-] - [H^+] = 0$$

At the end of the titration, you are at $f = 0$. Obviously, it takes *no* acid to get from the end of the titration to $f = 0$. Thus, $ANC = 0$ at the end of the titration. At any other point in the titration, $\alpha_1 A_T + [OH^-] - [H^+] \neq 0$. Thus, you can think of ANC as the amount of strong acid needed to change $\alpha_1 A_T + [OH^-] - [H^+]$ from its current value to zero. Therefore, for a monoprotic acid:

[†] Formally, ANC has units of equivalents, not equivalents per liter. We will find it convenient to use the units of equivalents per liter in this text.

acid neutralizing capacity

(ANC): equivalents per liter of strong acid required to reach the zeroth equivalence point of a solution ($f = 0$)

base neutralizing capacity

(BNC): equivalents per liter of strong base required to reach the first equivalence point of a solution ($g = 0$)



Key idea: ANC and BNC tell you how much added

acid or base can be added without significantly changing the pH of the system



Key idea: For a monoprotic acid, ANC is the amount

of strong acid needed to change $\alpha_1 A_T + [OH^-] - [H^+]$ from its current value to zero, so $ANC = \alpha_1 A_T + [OH^-] - [H^+]$

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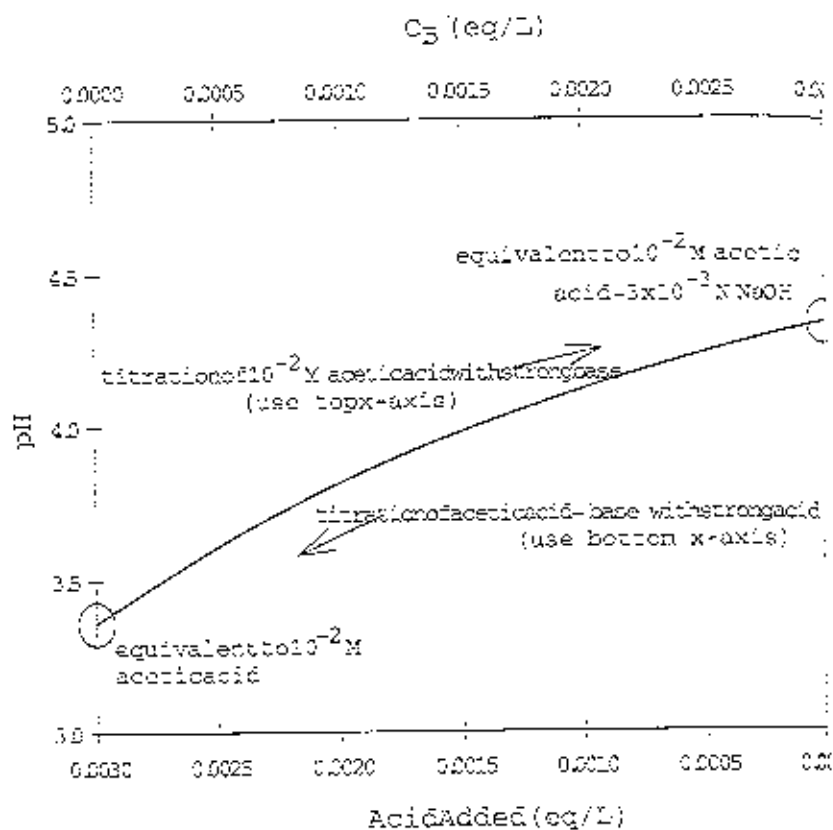


Figure 13.2: Redrawn Titration Curves for a 10^{-2} M Acetic Acid 3×10^{-3} N NaOH Solution

$$\text{ANC} = \alpha_1 A_T + [\text{OH}^-] - [\text{H}^+] \quad \text{eq. 1}$$

Similarly, BNC is the amount of strong base required to bring a solution $g = 0$. For a monoprotic base, BNC is defined by the proton condition the base (say, NaA):

$$\text{BNC} = [\text{HA}] + [\text{H}^+] - [\text{OH}^-] = \alpha_0 A_T + [\text{H}^+] - [\text{OH}^-] \quad \text{eq. 1}$$



Key idea: For a monoprotic base, BNC is the amount of strong base needed to change $\alpha_0 A_T + [\text{H}^+] - [\text{OH}^-]$ from its current value to zero, so $\text{BNC} = \alpha_0 A_T + [\text{H}^+] - [\text{OH}^-]$

In this way, BNC for a monoprotic base is the amount of strong base needed to change $\alpha_0 A_T + [\text{H}^+] - [\text{OH}^-]$ from its current value to zero.

13.2.3 Alkalinity and acidity

In most natural waters, the main weak acids are HCO_3^- and H_2CO_3^* and main weak bases are HCO_3^- and CO_3^{2-} . By analogy with eq. 13.1 substituting the proton condition for the H_2CO_3 system:

$$\begin{aligned} \text{ANC} &= [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \\ &= (\alpha_1 - 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+] \end{aligned}$$

where $C_T = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$. The coefficient of 2 in front of α_2 stems from the fact that carbonate has two fewer protons than carbonic acid. Similarly, from the proton condition for Na_2CO_3 , the BNC is given by:

$$\begin{aligned} \text{BNC} &= 2[\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{H}^+] - [\text{OH}^-] \\ &= (2\alpha_0 + \alpha_1)C_T + [\text{H}^+] - [\text{OH}^-] \end{aligned}$$

alkalinity (Alk): ANC in a water where the carbonic acid family is the dominant weak acid system and is used to define the ending point in the titration (i.e., titration to $f=0$ for carbonic acid)

The carbonic acid system is the dominant weak acid system in most natural waters. Therefore, it makes sense to use $f=0$ for the carbonic acid system as the ending point of the titration. For waters in which the carbonic acid system is used to define the ending point in the titration (i.e., for most natural waters), a special name is given to the ANC. The ANC is called **alkalinity** (often abbreviated Alk). Thus:

$$\text{Alk} = (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+] \quad \text{eq. 13.3}$$

acidity (Acy): BNC in a water where the bicarbonate and carbonate are the dominant weak bases and are used to define the ending point in the titration (titration to $g=0$ for carbonate)

In carbonate-dominated waters, another special name is given to the BNC. It is called the **acidity** (often abbreviated Acy):

$$\text{Acy} = (2\alpha_0 + \alpha_1)C_T + [\text{H}^+] - [\text{OH}^-] \quad \text{eq. 13.4}$$

You shall explore the characteristics of alkalinity and acidity further in Section 13.4. However, first the concept of alkalinity will be rederived in a different way to highlight another feature of the parameter.

13.3 ALKALINITY AND THE CHARGE BALANCE

So far in this text, you have performed charge balances on many aqueous systems where you *know* the starting materials. Can you develop a charge balance for a typical natural water where you *do not know* the starting materials? In short, no, you cannot write a complete charge balance without knowledge of the chemical species in the system. However, you can *guess* at the major ions in solution and write a fairly accurate charge balance.

Thoughtful Pause

What are the major cations and anions in natural waters?

From Section 12.1, you know that the major ions in the early oceans came from the weathering of rock caused by very, very acidic rainfall. Thus, you might guess the major ions from Figure 12.1.



Key idea: The major ions in most fresh waters are Na^+ , K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , Cl^- , and HCO_3^- .

The major ions in several water bodies from around the world are listed in Table 13.1. Although the cations and anions at the highest concentrations differ[†], the ions that dominate the charge balance usually are sodium, potassium, calcium, magnesium, sulfate, chloride, and bicarbonate ion. To this list, several ions usually are added that are important in aquatic chemistry, although typically much smaller in eq/L than the major ions. The minor ions are H^+ , OH^- , and CO_3^{2-} (carbonate ion). Thus, a good guess at a charge balance would be:

$$[\text{H}^+] + [\text{Na}^+] + [\text{K}^+] + 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + \text{other cations} =$$

$$[\text{OH}^-] + 2[\text{SO}_4^{2-}] + [\text{Cl}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + \text{other anions}$$

eq. 13.5

Table 13.1: Major Ions in Selected Water Bodies¹
(ion concentrations in meq/L)

	Great Lakes ²	Lake Tahoe	Ganges River	Colorado River	Mississippi River	Dead Sea
$[\text{Na}^+]$	0.28	0.27	0.28	4.13	0.93	1519
$[\text{K}^+]$	0.03	0.04	0.06	0.13	0.08	193
$[\text{Ca}^{2+}]$	1.50	0.47	1.10	4.14	2.03	788
$[\text{Mg}^{2+}]$	0.59	0.21	0.40	1.98	0.93	3453
Sum of cations	2.39	0.98	1.84	10.37	3.97	5954
$[\text{SO}_4^{2-}]$	0.38	0.05	0.06	1.71	0.52	11
$[\text{Cl}^-]$	0.37	0.05	0.16	7.61	1.52	5859
$[\text{HCO}_3^-]$	1.65	0.66	1.70	2.21	2.03	4
Sum of anions	2.40	0.76	1.93	11.53	4.08	5874
TDS (mg/L)	176	64	149	694	280	309,040

Notes: 1. Source: United Nations Environment Programme's Global Environment Monitoring System Freshwater Quality Programme (UNEP GEMS/WATER)

2. Average values for the Laurentian Great Lakes (Superior, Michigan, Huron, Erie, and Ontario)

[†] For most temperate zone lakes, the order of predominance ions is $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$. Examples in Table 13.1 include the Great Lakes, Lake Tahoe, the Ganges River, and the Mississippi River. For igneous and soft waters (e.g., Colorado River): $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^-$. For saline lakes (e.g., the Dead Sea), Na^+ and Cl^- usually dominate, although the dominant anion can vary (Wetzel, 1983).

In eq. 13.5, the ion concentrations are in mol/L, and the coefficients in front of each concentration term (here, 1 or 2) have units of eq/mol = number of charges/ion. You can assign each ion in eq. 13.5 into one of three categories: (1) ions coming from the dissociation of strong acids or bases (e.g., SO_4^{2-} and Cl^- from strong acids and K^+ , Ca^{2+} , and Mg^{2+} from strong bases), (2) ions coming from weak acids or bases (e.g., HCO_3^- and CO_3^{2-} from the weak acid H_2CO_3), and (3) H^+ and OH^- . As in Chapter 12, use the symbol C_A to represent the sum of the eq/L of strong acid anions and the symbol C_B to represent the sum of the eq/L of strong base cations. Equation 13.5 becomes:

$$[\text{H}^+] + C_B = [\text{OH}^-] + C_A + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad \text{eq. 13.6}$$

Or:

$$C_B - C_A = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad \text{eq. 13.7}$$

Equations 13.6 and 13.7 include all "other" ions from strong bases and acids in C_B and C_A , respectively, and ignore "other" ions from weak acids and bases (but see Section 13.6). One more simplification: express the ions bicarbonate and carbonate in terms of their alpha values. Thus, the charge balance becomes:

$$C_B - C_A = (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+] \quad \text{eq. 13.8}$$

In eq. 13.8, C_T again is the total dissolved carbonate concentration: $C_T = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$.

How does all this relate to alkalinity? Comparing eqs. 13.3 and 13.8:

$$\text{Alk} = C_B - C_A = (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+] \quad \text{eq. 13.9}$$

alkalinity equation: $\text{Alk} = C_B - C_A = (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+]$

Equation 13.9 is called the *alkalinity equation*. It is one of the few equations in this text that you should memorize (although you can derive it quickly from the charge balance).

13.4 CHARACTERISTICS OF ALKALINITY AND ACIDITY

13.4.1 What does alkalinity mean?

Remember that alkalinity is the acid neutralizing capacity for waters in which the acid-base chemistry is dominated by the carbonate family. Alkalinity tells you how much acid the water can accept to make it equivalent to a H_2CO_3 solution ($f = 0$). Sometimes, alkalinity is thought of as a measure of buffering: high alkalinity waters are thought to be well buffered. Although natural waters with high alkalinities usually are well buffered, you must be careful not to confuse alkalinity with buffer intensity.

Alkalinity is a *capacity*: it measures the total amount of acid a water can accept (to a specified equivalence point). Buffer intensity measures the *response* of a system to acid (or base) input.

As an example, consider a 1×10^{-3} N NaOH and 1×10^{-3} M NaHCO₃ solution. You can show (see Section 13.5.3) that both solutions have the same alkalinity. In other words, it takes the same amount of acid to make each solution equivalent to a H₂CO₃ solution containing the same C_T as the starting solution[†]. However, the pH values for the two solutions along the path from the starting solutions to $f = 0$ are *very* different (see Figure 13.3). The bicarbonate solution clearly provides better pH buffering near neutral pH.



Key idea: Alkalinity commonly is used as an indicator of buffering, even though it is not a measure of buffer intensity

Although we have emphasized that alkalinity is not a measure of the buffer intensity, *alkalinity still commonly is used as an indicator of buffering*. Why? Alkalinity is a great measure of buffering if the lower pH of interest is near $f = 0$ for the C_T in your system. As you shall see in Section 13.4.2, this is a pH of about 4.3–4.7 for most natural waters. No coincidentally, this lower pH of 4.3 to 4.7 corresponds to the pH at which aquatic biota begin to be adversely affected in natural water bodies.

If you are more interested in a different pH range, however, alkalinity may be misleading. Say, for example, that you have a water with pH 7.4, $C_T = 1.08 \times 10^{-3}$ M, and Alk = 1×10^{-3} eq/L (you should verify that these values are consistent with eq. 13.3), and you are concerned about the pH dropping below 6.8 as a result of an acidic input. Although the alkalinity is 1×10^{-3} eq/L, it takes only about 1.8×10^{-4} eq/L of strong acid (about 18% of the alkalinity) to reduce the pH to 6.8. In this case, alkalinity is not so valuable. *Use caution when accepting alkalinity as an indicator of buffering if the lower pH range of interest is different than 4.3–4.7*. Alternative types of alkalinity for different pH ranges of interest will be developed in Section 13.4.3. Another example of the relationship between alkalinity and the desired pH range is shown in Example 13.1.



Key idea: Use caution when accepting alkalinity as an indicator of buffering if the lower pH range of interest is different than 4.3–4.7.

13.4.2 Measuring alkalinity and acidity by titration

Alkalinity is the amount of strong acid required to make a water equivalent to an H₂CO₃ solution ($f = 0$ for H₂CO₃), and acidity is the amount of strong base required to make water equivalent to an Na₂CO₃ solution ($g = 0$ for Na₂CO₃). This means that alkalinity and acidity are intimately tied to the H₂CO₃ titration curve. It also means that titration with strong acid is an excellent way to measure alkalinity. Similarly, titration with strong base is used to measure acidity.

Alkalinity is measured by titrating the water sample to the zeroth equivalence point for H₂CO₃ for that sample.

Example 13.1: Alkalinity and the pH Range of Interest

A river water has $C_T = 7.8 \times 10^{-4}$ M and pH 7.9. If the trout population in the river is to be maintained, the river pH cannot drop below 7.5. If the trout are relocated, the river pH can drop to as low as 5.8. Explain the value of alkalinity in determining the vulnerability of the river pH.

[†] Note that the C_T values of the starting solutions are different: 1×10^{-3} N NaOH has $C_T = 0$, and 1×10^{-3} M NaHCO₃ has $C_T = 1 \times 10^{-3}$ M.

Solution:

First, calculate the alkalinity.

At pH 7.9, $\alpha_1 = 0.971$ and $\alpha_2 = 0.00487$. From eq. 13.3, $\text{ALK} = 7.66 \times 10^{-4}$ eq/L. After an acidic input, the charge balance is:

$$[\text{H}^+] = (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] + C_A$$

To get to pH 7.5 requires $C_A = 3 \times 10^{-5}$ eq/L, or 4% of the alkalinity. To get to pH 5.8 requires $C_A = 5.8 \times 10^{-4}$ eq/L, or 76% of the alkalinity.

Thus, alkalinity is a reasonable estimate of the acidic input required to reach pH 5.8 but greatly overestimates the acidic input required to get to pH 7.5.

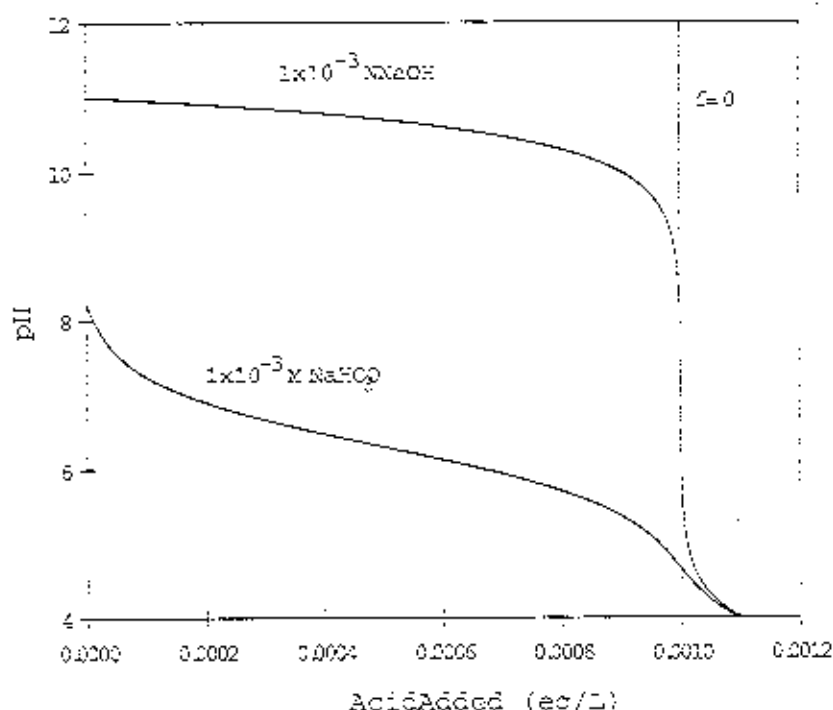


Figure 13.3: Comparison of the pH During Titration for 1×10^{-3} N NaOH and 1×10^{-3} M NaHCO_3 Solutions

Thoughtful Pause

How do you know what the zeroth equivalence point for H_2CO_3 is for a given water sample?



Key idea: The pH values at the equivalence points for

alkalinity and acidity depend on the total carbonate concentration (C_T) of the sample

The pH of the H_2CO_3 equivalence point depends on C_T ; waters with higher C_T have a lower pH at $f=0$ (more weak acid present at $f=0$). Similarly, waters with higher C_T have a higher pH at $g=0$ (more weak base present at $g=0$). This is shown graphically in Figures 13.4 and 13.5. In Figure 13.4, note that for natural waters ($C_T \approx 1$ mM), the pH at $f=0$ is about 4.7 and the pH at $g=0$ is about 10.5.

As shown in Figures 13.4 and 13.5, the exact pH at the $f=0$ and $g=0$ equivalence points varies with C_T . To be precise, you would have to measure C_T with every water sample, calculate the pH at the equivalence points, and titrate to those pH values. However, because the range of C_T values in most natural waters is small, we use one set of equivalence point

endpoint: a key point in a titration, usually selected to be an estimate of a true equivalence point in a titration

pH values for most waters. For routine analysis, alkalinity is determined by titration to pH 4.5. Since this pH value does not necessarily correspond to exactly $f = 0$, we refer to it as an **endpoint**, rather than an equivalence point. In general, the endpoint pH depends on the alkalinity (see Problem 13.4).

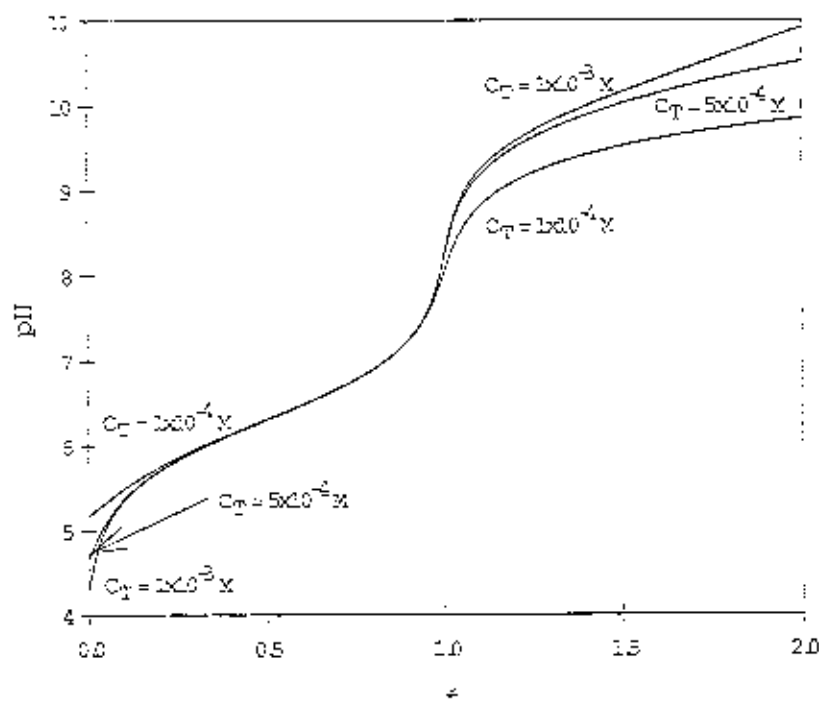
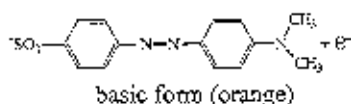
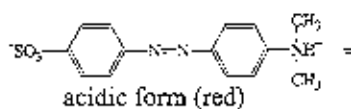


Figure 13.4: Carbonic Acid Titration Curve for Different C_T Value

methyl orange endpoint: a pH endpoint of about pH 4.5 to 3.2, formally used to estimate the alkalinity equivalence point ($f = 0$ for carbonic acid)



Endpoints generally are set in three ways: fixed pH (e.g., pH 4.5 as an indicator of $f = 0$), inflection points (where the entire titration curve generated in the laboratory, and the strong acid or base required to reach an inflection point is recorded), and pH indicators. A pH indicator is an acid-base pair where the acid (or conjugate base) is one color in solution and the conjugate base (or acid) is another color or colorless in solution. Only a small amount of the indicator is added to the sample to avoid changing the sample pH. If the pK_a of the acid is near the pH of the endpoint, then a color change is observed at pH values near the endpoint. In the older literature, the endpoint approximating the $f = 0$ equivalence point is called the **methyl orange endpoint** because the pH indicator methyl orange (see the structure in the left margin) was used to visualize the endpoint. The acidic form of methyl orange has a pK_a of 3.8, with a transition in color

(coming from higher pH) between pH 4.5 to 3.2 (Butler, 1998). The preferred pH indicator currently is bromocresol green (or the bromocresol green-methyl red mixed indicator).

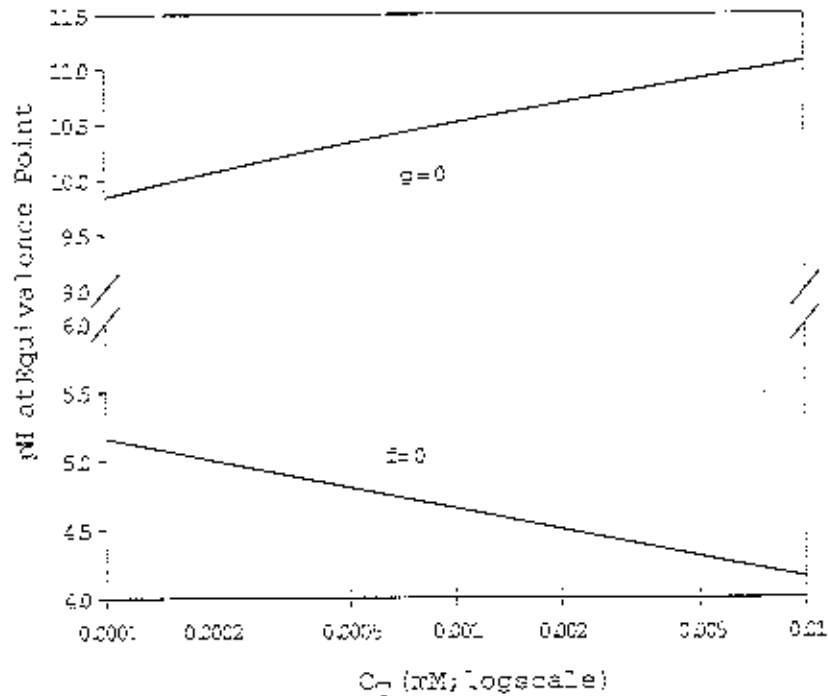


Figure 13.5: pH Values at the $f=0$ and $g=0$ Equivalence Points as a Function of C_T

13.4.3 Types of alkalinity

As discussed in Section 13.4.1, alkalinity is not always the best measure of buffering, especially if you are more interested in the ability to neutralize acids in the neutral pH range and are not interested in letting the pH drop to about 4.5. As a result, you can define several types of alkalinity, depending on the sample and pH range of interest (see also Sawyer and McCarty, 1978). Each type of alkalinity is related to the titration to a specific equivalence point (or, in practice, a specific endpoint). Each type will be discussed below and illustrated with example titration curves for three hypothetical samples. The samples all have $C_T = 1$ mM, where the equivalence points at $f=0$, 1, and 2 are about pH 4.7, 8.2, and 10.5, respectively. The samples have different pH and alkalinity values: sample A has a pH value of 7.0 (between the zeroth and first equivalence points), sample B has a pH value of 9.5 (between the first and second equivalence points), and sample C has a pH value of 10.8 (greater than the second equivalence point).



Key idea: Different types of alkalinity are defined for different endpoints

Alkalinity (also total alkalinity, or Alk). Alkalinity is defined as the amount of strong acid required to bring the sample to the $f = 0$ (H_2CO_3^*) equivalence point, an endpoint of about pH 4.5. The hypothetical titration curve for a sample at pH 7.0 is shown in Figure 13.6, along with the alkalinity. Alkalinity describes the total acid neutralizing capacity of water, within the pH range of biological interest. It can be calculated from the proton condition for H_2CO_3^* : $\text{Alk} = (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+]$. Near neutral pH, the main contributor to alkalinity is HCO_3^- .

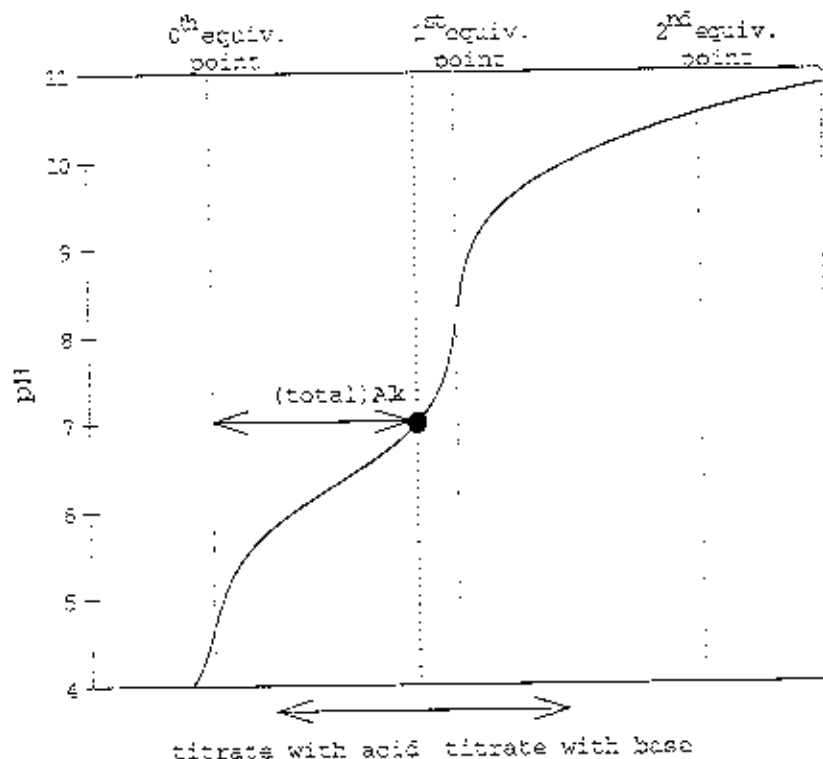


Figure 13.6: Example Alkalinity Titration for a Sample Initially at pH 7.0

phenolphthalein alkalinity: the amount of strong acid required to bring the sample to the $f = 1$ (NaHCO_3) equivalence point (an endpoint of about pH 8.2-8.3)

Phenolphthalein alkalinity (also p -alkalinity, or p -Alk). **Phenolphthalein alkalinity** is defined as the amount of strong acid required to bring the sample to the $f = 1$ (NaHCO_3) equivalence point, an endpoint of about pH 8.3. (Note from Figure 13.4 that the $f = 1$ equivalence point is fairly independent of C_T .) If the pH of the sample is less than 8.3, then the phenolphthalein alkalinity is less than zero, but usually reported as zero (i.e., no acid is needed to reach pH 8.3). The hypothetical titration curve for a sample at pH 9.5 is shown in Figure 13.7, along with the phenolphthalein alkalinity. Phenolphthalein alkalinity describes the acid

neutralizing capacity of a water near neutral pH. Phenolphthalein[†] alkalinity can be calculated from the proton condition for NaHCO_3 : $p\text{-Alk} = (\alpha_2 - \alpha_0)C_T + [\text{OH}^-] - [\text{H}^+]$. Except at very high pH, the main contributor to $p\text{-Alk}$ is CO_3^{2-} .

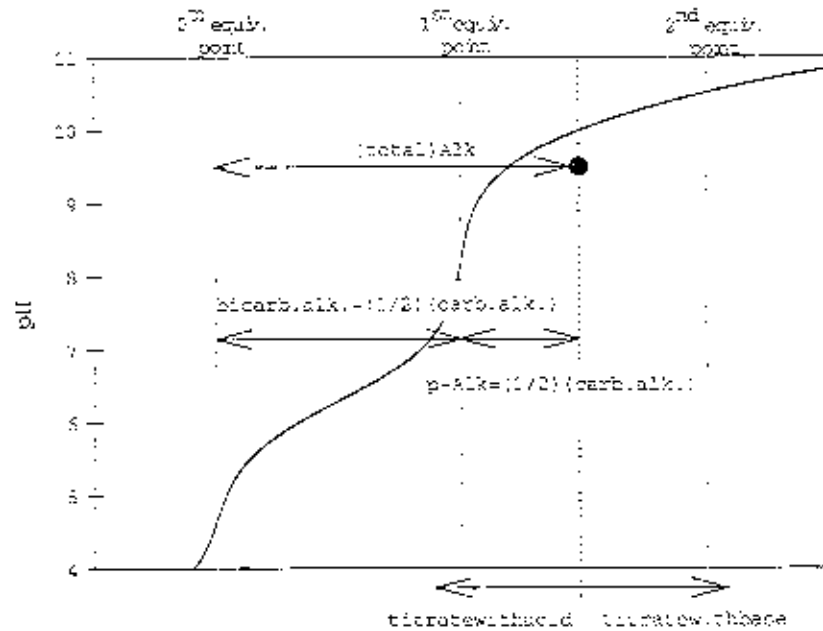


Figure 13.7: Example Alkalinity Titration for a Sample Initially at pH 9.5

Caustic alkalinity (also OH-Alk. or hydroxide alkalinity). *Caustic* (from the Greek *kaiein* to burn) *alkalinity* is defined as the amount of strong acid required to bring the sample to the $f = 2$ (Na_2CO_3) equivalence point, an endpoint of about pH 9.5-11. If the pH of the sample is less than

caustic alkalinity: the amount of strong acid required to bring a sample to the $f = 2$ (Na_2CO_3) equivalence point

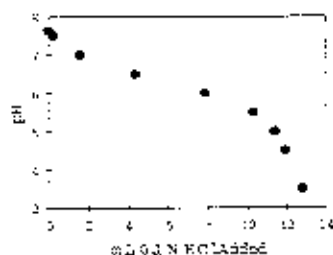
[†] The name stems from the pH indicator phenolphthalein, which is commonly used to indicate the endpoint. However, the name "phenolphthalein alkalinity" is used regardless of the manner in which the endpoint is determined. For example, the endpoint could be determined by pH, inflection point, or another pH indicator (e.g., metacresol purple). The word *phenolphthalein* comes from *phenol* (i.e., hydroxybenzene) + *phthal* (from naphtha) + *ein* (from *-ene*, meaning a double bond). The word *naphtha* comes from the Persian *nafā*, perhaps related to the Greek *nepheōs*, meaning a cloud or mist.

carbonate alkalinity: the portion of the total alkalinity contributed by CO_3^{2-}

bicarbonate alkalinity: the difference between the total alkalinity and the carbonate alkalinity

Example 13.2: Alkalinity Types from Titration Curves

A 250 mL lake water sample was titrated with 0.1 N HCl, and the titration curve shown below was obtained. Find the alkalinity, $p\text{-Alk}$, OH-Alk, carbonate alkalinity, and bicarbonate alkalinity.



the endpoint pH, then the caustic alkalinity is less than zero (but usually reported as zero). The hypothetical titration curve for a sample at pH 10, is shown in Figure 13.8, along with the caustic alkalinity. Caustic alkalinity can be calculated from the proton condition for Na_2CO_3 : $\text{OH-Alk} = [\text{OH}^-] - (\alpha_1 + 2\alpha_2)C_T - [\text{H}^+]$. The main contributor to caustic alkalinity is OH^- .

Carbonate alkalinity. As long as the pH of the sample is less than about 10.5, the total alkalinity is primarily from HCO_3^- and CO_3^{2-} . The total alkalinity can be divided into two parts: **carbonate alkalinity** (the portion of the total alkalinity contributed by CO_3^{2-}) and bicarbonate alkalinity (the portion of the total alkalinity contributed by HCO_3^-). After a sample has been titrated to the phenolphthalein endpoint, almost all of the carbonate has been converted to bicarbonate (since $\text{pH } 8.3 < \text{p}K_{a2} = 10.3$), but almost none of the bicarbonate has been converted to carbonic acid (since $\text{pH } 8.3 > \text{p}K_{a1} = 6.3$). Thus, only one-half of the alkalinity from carbonate has been titrated at the pH 8.3 endpoint. This means that the carbonate alkalinity is about twice the $p\text{-Alk}$. The relationship between the titration curve and the carbonate alkalinity is shown in Figures 13.7 and 13.8.

Bicarbonate alkalinity. The **bicarbonate alkalinity** is the difference between the total alkalinity and the carbonate alkalinity. The amount of strong acid required to move from the phenolphthalein endpoint to the pH 4.0 endpoint is the bicarbonate alkalinity plus the remaining one-half of the carbonate alkalinity. Thus:

$$\begin{aligned} \text{bicarbonate alkalinity} &= \text{total alkalinity} - \text{carbonate alkalinity} \\ &= \text{total alkalinity} - 2(p\text{-Alk}) + \text{OH-Alk} \\ &= \text{total alkalinity} - 2(p\text{-Alk}) \end{aligned}$$

The relationship between the titration curve and the carbonate alkalinity is shown in Figures 13.7 and 13.8. Other illustrations of the different types of alkalinity are presented in Example 13.2.

13.4.4 Types of acidity

Different types of acidity also can be defined, depending on the endpoint. The three types of acidity are total acidity, CO_2 acidity, and mineral acidity.

Acidity (also total acidity, or Acy). Acidity is analogous to alkalinity. Acidity is defined as the amount of strong base required to bring the sample to the $g = 0$ (Na_2CO_3) equivalence point. Acidity describes the total base neutralizing capacity of a water, within the pH range of biological interest. It can be calculated from the proton condition for Na_2CO_3 : $\text{Alk} = [\text{H}^+] - (2\alpha_2 + \alpha_1)C_T - [\text{OH}^-]$.

Formally, you must correct for OH-Alk when calculating the carbonate and bicarbonate alkalinity. Thus: carbonate alkalinity = $2(p\text{-Alk} - \text{OH-Alk})$, and bicarbonate alkalinity = total alkalinity - $2(p\text{-Alk}) + \text{OH-Alk}$.

Solution:

The initial pH of the sample is well below the caustic alkalinity endpoint (pH > 9.5), so OH-Alk = 0. The initial pH also is below the *p*-Alk endpoint (about pH 8.3 - note that the inflection point around the NaHCO₃ equivalence point is not fully developed). Thus, *p*-Alk = 0. Since the carbonate alkalinity is 2(*p*-Alk), then the carbonate alkalinity = 0.

The total alkalinity is the acid added to reach about pH 4.5 or about 12 mL. The Alk is (12 mL)(1 N HCl)/(250 mL) = 4.8×10^{-3} eq/L or 240 mg/L as CaCO₃ (see Section 13.4.5 for alkalinity units). The bicarbonate alkalinity is equal to the total Alk since OH-Alk and carbonate alkalinity are zero.

To summarize:

Alk = 4.8×10^{-3} eq/L
(240 mg/L as CaCO₃)
p-Alk = 0
OH-Alk = 0
carbonate alkalinity = 0
bicarbonate alkalinity =
 4.8×10^{-3} eq/L (240 mg/L
as CaCO₃)

CO₂-Acy: the amount of strong acid required to bring the sample to the *g* = 1 (NaHCO₃) equivalence point

mineral acidity (H-Acy): the amount of strong base required to bring the sample to the *g* = 2 (H₂CO₃) equivalence point

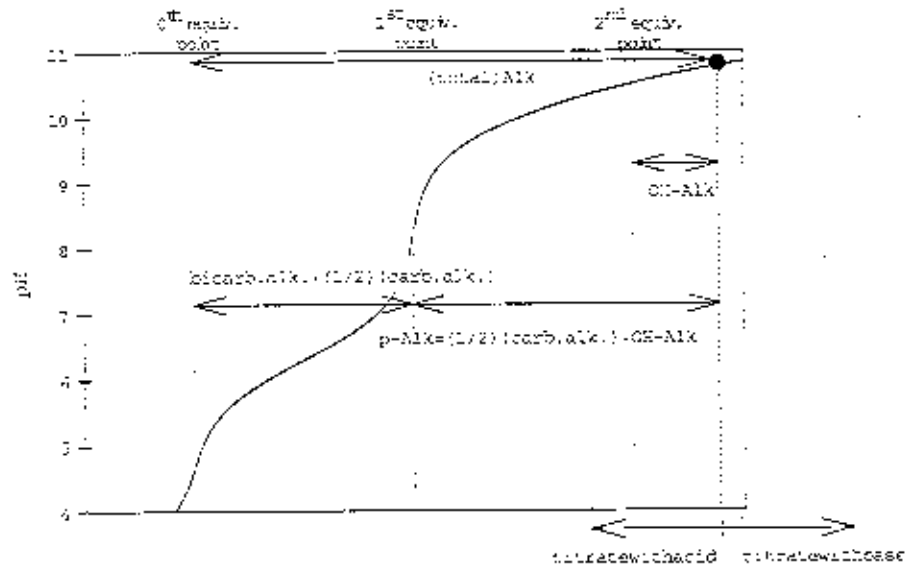


Figure 13.8: Example Alkalinity Titration for a Sample Initially at pH 10.8

CO₂ acidity (also CO₂-Acy). *CO₂-Acy* is analogous to *p*-Alk. It is defined as the amount of strong base required to bring the sample to the *g* = 1 (NaHCO₃) equivalence point, an endpoint of about pH 8.3. *CO₂ acidity* describes the base neutralizing capacity of a water near neutral pH. It can be calculated from the proton condition for NaHCO₃: $CO_2\text{-Acy} = [H^+] + (\alpha_0 - \alpha_2)C_T - [OH^-]$.

Mineral acidity (also H-acidity, or H-Acy). *Mineral acidity* is analogous to caustic alkalinity. *Mineral acidity* is defined as the amount of strong base required to bring the sample to the *g* = 2 (i.e., H₂CO₃) equivalence point, an endpoint of about pH 4.5. For all but the most acidic waters, the mineral acidity is less than zero. The main contributor to H-Acy is H⁺ (i.e., strong acids). Mineral acidity can be calculated from the proton condition for H₂CO₃: $H\text{-Acy} = [H^+] - (\alpha_1 + 2\alpha_2)C_T - [OH^-]$.

13.4.5 Units of alkalinity

One common set of units for alkalinity, from eqs. 13.3 and 13.9, is equivalents per liter (or meq/L). Clearly, from the alkalinity equation (eq. 3.9), alkalinity will be calculated in units of eq/L if C_B and C_A are in units of eq/L.

Thoughtful Pause

What are the units of alkalinity if calculated from $\text{Alk} = (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+]$?

Recall that eq. 13.9 was derived from a charge balance. Therefore, each term has units of eq/L = moles of charges/L. You could rewrite eqs. 13.3 and 13.9 as:

$$\text{Alk} = [(1 \text{ eq/mol})\alpha_1 + (2 \text{ eq/mol})\alpha_2]C_T + (1 \text{ eq/mol})[\text{OH}^-] - (1 \text{ eq/mol})[\text{H}^+]$$

**Key idea:**

Alkalinity will be calculated in units of eq/L if C_b and C_a are in units of eq/L.

The units of eq/mol on the coefficients usually are not written out but cannot be ignored. Thus, using either eq. 13.3 or 13.9, you can calculate the alkalinity in units of eq/L.

There is another common set of units for alkalinity based on the mass as nomenclature (see Section 2.4.2). *Alkalinity commonly is expressed in units of mg/L as CaCO₃.* Recall that this means we use the molecular weight of CaCO₃ for the molecular weight of alkalinity. Why use these units? As you shall see in Chapter 19, calcium carbonate (in the form of the mineral calcite) is a common source of alkalinity in natural waters. Also, calcium carbonate is a convenient choice for alkalinity units because the molecular weight of CaCO₃ is about 100 g/mol.

How do you convert units of eq/L to units of mg/L as CaCO₃? As calcium carbonate dissolves, it produces Ca²⁺, which has 2 eq of charge/ion. Thus: 1 eq/L Alk = (1 eq/L)(100 g CaCO₃/mol CaCO₃)/(2 eq/mol CaCO₃) = 50 g/L Alk as CaCO₃. To summarize:

$$\begin{aligned} 1 \text{ eq/L Alk} &= 50 \text{ g/L Alk as CaCO}_3 = 50,000 \text{ mg/L Alk as CaCO}_3 \\ 1 \text{ meq/L Alk} &= 50 \text{ mg/L Alk as CaCO}_3 \end{aligned}$$



Key idea: 1 eq/L Alk is equivalent to 50,000 mg/L Alk as

CaCO₃

As examples of units conversion, 2.1×10^{-3} eq/L Alk is equivalent to:

$$\begin{aligned} 2.1 \times 10^{-3} \text{ eq/L} &= (2.1 \times 10^{-3} \text{ eq/L})(50,000 \text{ mg/L as CaCO}_3 \text{ per eq/L}) \\ &= 105 \text{ mg/L as CaCO}_3 \end{aligned}$$

³ It may not be immediately apparent that alkalinity will be in units of eq/L if calculated from eq. 13.3. Recall that eq. 13.3 was derived from a proton condition. Thus, the units of the coefficients in eq. 13.3 are "excess or deficient protons over the zero proton level". Since the zero proton level is set here for uncharged species (H₂CO₃ and H₂O), x excess protons and x deficient protons correspond to x eq of charge per mole. Thus, alkalinity will be in units of eq/L if calculated from eq. 13.3.

An alkalinity of 175 mg/L as CaCO₃ corresponds to:

$$\begin{aligned} 175 \text{ mg/L as CaCO}_3 &= (175 \text{ mg/L as CaCO}_3) / (50 \text{ mg/L as CaCO}_3 \\ &\quad \text{per meq/L}) \\ &= 3.5 \text{ meq/L} \end{aligned}$$

You should practice converting the units of alkalinity between eq/L (or meq/L) and mg/L as CaCO₃ until the conversion becomes second nature to you.

13.5 USING THE DEFINITIONS OF ALKALINITY TO SOLVE PROBLEMS



Key idea: The alkalinity equation is really three

equations in one:

$$\begin{aligned} \text{Alk} &= (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+] \\ C_B - C_A &= (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+] \\ \text{Alk} &= C_B - C_A \end{aligned}$$



Key idea: If you know two of Alk, pH, and C_T, then you

can calculate the other parameter easily

13.5.1 Alkalinity definitions

It is very important to see that eq. 13.9 is really three equations in one. First, eq. 13.9 tells you that:

$$\text{Alk} = (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+]$$

This is identical to eq. 13.3. Second, eq. 13.9 tells you that:

$$C_B - C_A = (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+]$$

as in eq. 13.8. Finally, eq. 13.9 tells you that:

$$\text{Alk} = C_B - C_A$$

This is a new expression and a very powerful way to calculate alkalinity. *The secret to solving alkalinity problems is to select the most appropriate definition from among the three equations in eq. 13.9.* A few examples will illustrate that much effort can be saved by selecting the proper definition.

Example 13.3: Alkalinity Calculations: $\text{Alk} = (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+]$

Complete the water quality calculations for the following three water samples:

Sample #1: Alk = ?, C_T = 2.1 mM, pH 6.8

Sample #2: Alk = 157 mg/L as CaCO₃, C_T = ?, pH 7.2

Sample #3: Alk = 1.5 meq/L, C_T = 20 mg/L as C, pH ?

13.5.2 Alkalinity as $(\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+]$

According to this definition, alkalinity is related to two other parameters: pH and C_T. If you know two out of the three parameters (i.e., two of Alk, pH, and C_T), then you can calculate the other one easily. As an example, consider a water with C_T = 2 × 10⁻³ M and pH 7.5. For K_{a1} = 10^{-6.3} and K_{a2} = 10^{-10.3}, you can calculate that the alkalinity is 1.9 × 10⁻³ eq/L or 94 mg/L as CaCO₃. What is C_T if the alkalinity of a water is 140 mg/L as CaCO₃ (2.8 meq/L) and the pH is 7.8? You can show that:

$$C_T = (\text{Alk} - [\text{OH}^-] + [\text{H}^+]) / (\alpha_1 + 2\alpha_2)$$

or C_T = 2.9 × 10⁻³ M. The more challenging calculation is to find pH by knowing C_T and alkalinity. You can set up a spreadsheet and determine the pH by iteration or use a nonlinear solver. For example, for a water with C_T

Solution:

Sample #1:

At pH 6.8, $\alpha_1 = 0.760$ and
 $\alpha_2 = 3.02 \times 10^{-4}$, so:

$$\begin{aligned} \text{Alk} &= (0.760 - \\ &\quad 2 \times 3.02 \times 10^{-4}) \\ &\quad \times (2.1 \times 10^{-3}) + \\ &\quad 10^{-7.2} - 10^{-6.8} \\ &= 1.60 \times 10^{-3} \text{ eq/L or} \\ &\quad 80 \text{ mg/L as} \\ &\quad \text{CaCO}_3 \end{aligned}$$

Sample #2:

$$\begin{aligned} \text{Alk} &= (157 \text{ mg/L as} \\ &\quad \text{CaCO}_3) / (50 \text{ mg as} \\ &\quad \text{CaCO}_3 \text{ per meq}) \\ &= 3.14 \times 10^{-3} \text{ eq/L} \end{aligned}$$

Rearranging:

$$\begin{aligned} C_T &= (\text{Alk} - [\text{OH}^-] + \\ &\quad [\text{H}^+]) / (\alpha_1 + 2\alpha_2) \\ &= (3.14 \times 10^{-3} - 10^{-6.8} + \\ &\quad 10^{-7.2}) / (0.887 + \\ &\quad 2 \times 3.87 \times 10^{-4}) \\ &= 3.53 \times 10^{-3} \text{ M} \end{aligned}$$

Sample #3:

$$\begin{aligned} \text{Alk} &= 1.5 \text{ meq/L and:} \\ C_T &= (20 \text{ mg/L as C}) / (12 \\ &\quad \text{mg per mmol}) \\ &= 1.67 \times 10^{-3} \text{ M} \end{aligned}$$

Iterating: pH 7.24.

$= 1.5 \times 10^{-3} \text{ M}$ and $\text{Alk} = 1.2 \times 10^{-3} \text{ eq/L}$, you should be able to confirm that the pH is about 6.9. Other examples are worked out in Example 13.3.

The expression for Alk in the title of this section emphasizes that Alk is a function of pH and C_T . You could create a three-dimensional plot showing the relationship among Alk, pH, and C_T , but such plots are hard to read. A common approach is to plot lines of equal pH for pairs of Alk and C_T . This was introduced by Kenneth Deffeyes (Deffeyes, 1965), so these plots sometimes are called *Deffeyes diagrams*. An example is shown in Figure 13.9.

Deffeyes diagrams are easy to generate since a plot of Alk versus C_T clearly has a slope of $\alpha_1 + 2\alpha_2$ and an intercept of $[\text{OH}^-] - [\text{H}^+]$. Note that this intercept is nearly zero, except at extreme pH values (see also Figure 13.9). Another approach is to plot lines of equal Alk for pairs of C_T and pH. This plot is shown in Figure 13.10. You may wish to verify the Alk, pH, and C_T examples in the previous paragraph, using both Figures 13.9 and 13.10.

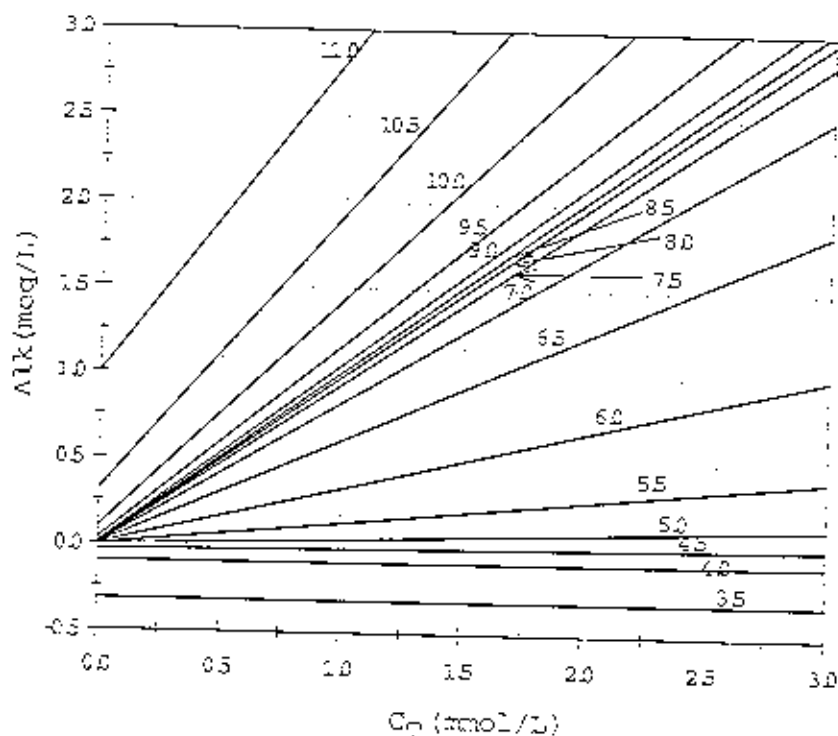


Figure 13.9: Deffeyes Diagram for Alkalinity
 (lines are constant pH)

A final lesson from $\text{Alk} = (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+]$ concerns the alkalinity near neutral pH. For reasonable values of C_T and pH conditions near neutral pH, $[\text{HCO}_3^-]$ is much greater than $[\text{CO}_3^{2-}]$, $[\text{OH}^-]$, and $[\text{H}^+]$.

In other words: $\alpha_1 C_T \gg \alpha_2 C_T$, $[\text{OH}^-]$, and $[\text{H}^+]$. Thus, for reasonable values of C_T and near neutral pH:

$$\text{Alk} = [\text{HCO}_3^-] = \alpha_1 C_T$$

(for reasonable values of C_T and near neutral pH)



Key idea: Near neutral pH (and for reasonable values of C_T), $\text{Alk} = [\text{HCO}_3^-] = \alpha_1 C_T$

This approximation is extremely useful. It allows you to estimate the alkalinity of many natural waters with ease. For example, from Table 13.1, you may estimate that the average alkalinity in the Great Lakes is about $[\text{HCO}_3^-] = 1.65 \text{ meq/L} = 83 \text{ mg/L as CaCO}_3$. The approximation also allows you to estimate C_T . For example, the C_T of a water with pH 7.7 and alkalinity = 125 mg/L as CaCO_3 (= 2.5 meq/L) is about $\text{Alk}/\alpha = (2.5 \times 10^{-3} \text{ eq/L}) / (0.959 \text{ eq/mol}) = 2.6 \times 10^{-3} \text{ M}$. The exact solution for C_T is $2.59 \times 10^{-3} \text{ M}$. C_T values of about $2.6 \times 10^{-3} \text{ M}$ also can be estimated from both Figures 13.9 and 13.10.

Example 13.4: Alkalinity Consumption

One way to remove ammonium from water is through the process of breakpoint chlorination. The overall reaction is: $2\text{NH}_4^+ + 3\text{Cl}_2 \rightarrow \text{N}_2(\text{g}) + 8\text{H}^+ + 6\text{Cl}^-$. How much alkalinity must be added per mg of $\text{NH}_4^+\text{-N}$ removed to maintain the pH during breakpoint chlorination?

Solution:

Breakpoint chlorination generates 4 eq of acidity (H^+) per mole of ammonium consumed or (4 meq Acy/mmol NH_4^+) / (14 mg N per mmol NH_4^+) = 0.286 meq Acy/mg N.

Thus, you need 0.286 meq of Alk per mg of $\text{NH}_4^+\text{-N}$ removed (about 11 mg Alk as CaCO_3 per mg of $\text{NH}_4^+\text{-N}$ removed) to maintain the pH.

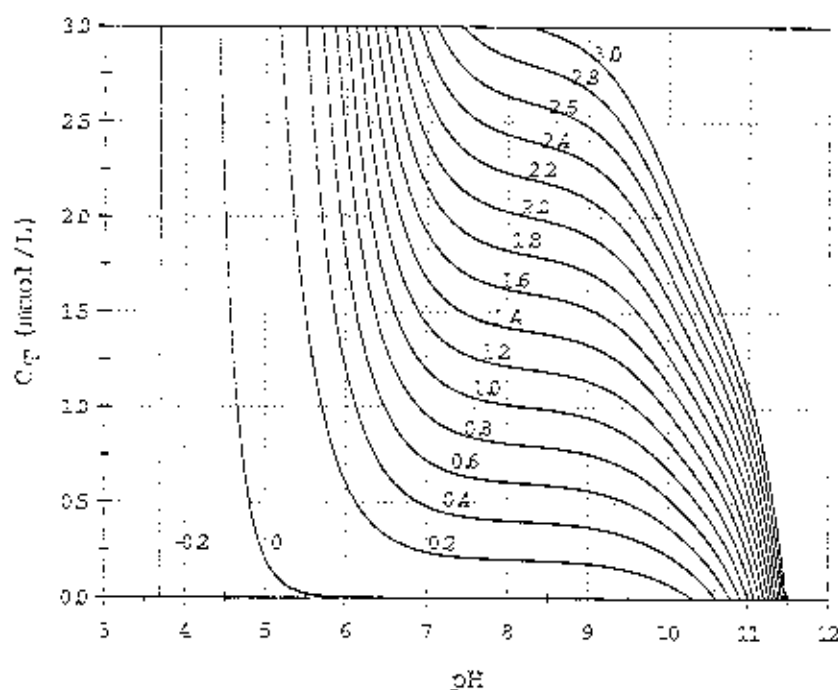


Figure 13.10: Another Approach to Showing the Relationship Among Alkalinity, pH, and C_T (lines are constant Alk in meq/L)

13.5.3 Alkalinity as $C_B - C_A$

This form of the alkalinity definition is very valuable when individual ion concentrations are known. As an example with a pure solution, what is the

alkalinity of a 1×10^{-3} N NaOH solution? You could calculate the alkalinity the *hard* way:

1. Find the pH

The charge balance, $[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-]$, and K_w expression allow you to calculate pH 11

2. Find C_T

$C_T = 0$ from starting materials

3. Use eq. 13.3 to calculate the alkalinity

Alk = 1×10^{-3} eq/L (from eq. 13.3 or Figures 13.9 or 13.10)

You can calculate the alkalinity much more easily in this case:

$$\text{Alk} = C_B - C_A = [\text{Na}^+] = 1 \times 10^{-3} \text{ eq/L}$$

Again, selecting the most appropriate definition of alkalinity saves a lot of computational time and effort. As another example, find the alkalinity of a 1×10^{-3} M NaHCO_3 solution. Hard way: find the pH (equilibrium calculation yields pH 8.3), find C_T ($C_T = 1 \times 10^{-3}$ M from starting materials), and use eq. 13.3 (or Figure 13.9 or Figure 13.10) to calculate the alkalinity (Alk = 1×10^{-3} eq/L). Easy way: Alk = $C_B - C_A = [\text{Na}^+] = 1 \times 10^{-3}$ eq/L.

The definition of alkalinity as $C_B - C_A$ also is useful with natural waters. From Table 13.1, you could estimate the average alkalinity in the Great Lakes as $C_B - C_A \approx [\text{Na}^+] + [\text{K}^+] + [\text{Mg}^{2+}] + [\text{Ca}^{2+}] - [\text{SO}_4^{2-}] - [\text{Cl}^-] = 1.64$ meq/L, close to the 1.65 meq/L value estimated in Section 13.4.2.

Another use of the $C_B - C_A$ definition of alkalinity is in calculating the *consumption* of alkalinity from natural and engineered processes. When H^+ is released from a process (i.e., when acidity is released), we say that alkalinity is consumed. Why is alkalinity consumed? The addition of strong acid moves you closer to the H_2CO_3 equivalence point. After the acid is added, the alkalinity is smaller than before the acid is added. In a true sense, alkalinity is consumed.

For example, a commonly used rule of thumb in environmental engineering is that adding alum to raw drinking water for turbidity removal consumes about 0.5 mg of alkalinity as CaCO_3 for every mg of alum added.



Key idea: When H^+ is released from a process, alkalinity is consumed

[†] This equation is written for the data in Table 13.1, where the ion concentrations are in meq/L. If the ion concentrations were in mol/L, the correct equation would be $C_B - C_A = [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] - 2[\text{SO}_4^{2-}] - [\text{Cl}^-]$.

Where does this rule of thumb come from? Alum dissolves initially in water to produce Al^{3+} and sulfate: $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} \rightarrow 2\text{Al}^{3+} + 3\text{SO}_4^{2-} + 18\text{H}_2\text{O}$. The aquo aluminum ion, Al^{3+} , hydrolyzes to produce aluminum hydroxide solid (see Chapter 19): $\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3(\text{s}) + 3\text{H}^+$. Overall, 1 mole of alum (666 g) produces six equivalents of acidity and thus consumes six equivalents of alkalinity, or $(6 \text{ eq})(50 \text{ g Alk as CaCO}_3 \text{ per eq}) = 300 \text{ g Alk as CaCO}_3$. This means $(300 \text{ g Alk as CaCO}_3)/(666 \text{ g alum}) = 0.45 \approx 0.5 \text{ mg of alkalinity as CaCO}_3 \text{ are consumed per mg alum}$. Another illustration of alkalinity consumption is given in Example 13.4.

13.5.4 Alkalinity and acidity as conservative properties

As discussed in this chapter, alkalinity can be expressed as $C_B - C_A$. Since strong base cations and strong acid anions are relatively unreactive in water, the alkalinities are additive when two water samples of equal volume are combined. There is an important exception to this rule: we are assuming that no solids precipitate. If solids precipitate, the situation becomes a bit more complex (see Chapter 19). If two streams with flows Q_1 and Q_2 and alkalinities Alk_1 and Alk_2 combine, the resulting stream has a flow of $Q_1 + Q_2$ (assuming the waters have the same density) and alkalinity = $\text{Alk}_1 + \text{Alk}_2$ (assuming no solids precipitate).

The conservation of alkalinity (and acidity) aids in the solution of water chemistry problems. For example, you can find the alkalinity C_T and pH of the river formed when two tributaries with the following characteristics combine:

Tributary A: flow = 1500 cfs
Alk = 200 mg/L as CaCO_3 , and:
pH 8.1

Tributary B: flow = 700 cfs
Alk = 100 mg/L as CaCO_3 , and:
 $C_T = 2.07 \times 10^{-3} \text{ M}$

First, you must calculate Alk, C_T , and pH for both tributaries. Using the approach in Section 13.5.2, you can find that C_T for Tributary A is $4.01 \times 10^{-3} \text{ M}$ and the pH of Tributary B is 7.7. Alkalinity is conserved, so:

$$Q_A \text{Alk}_A + Q_B \text{Alk}_B = (Q_A + Q_B) \text{Alk}$$

(if the densities of the waters are similar)

Thus: Alk = 168 mg/L as CaCO_3 (3.36 meq/L). If no inorganic carbon is lost to the atmosphere or precipitates, then carbon is conserved and:

$$Q_A C_{T,A} + Q_B C_{T,B} = (Q_A + Q_B) C_T \text{ or } C_T = 3.39 \times 10^{-3} \text{ M}$$

Using the alkalinity equation or Figure 13.9 or Figure 13.10, you can show



Key idea:
Alkalinity and
acidity are conserved

E

4'

6

2

that the pH of the combined rivers is 8.1. Conservation of alkalinity is shown again in Example 13.5.

13.6 EFFECTS OF OTHER WEAK ACIDS AND BASES ON ALKALINITY

Example 13.5: Conservation of Alkalinity

Acid rain falls on a lake with low Alk. How many inches of rain would have to fall to reduce the pH of the lake to 6.7? The lake characteristics are pH 7.0, Alk = 30 mg/L as CaCO₃, mean depth = 10 ft. The acid rain characteristics are pH 4 and [Cl⁻] = 1 × 10⁻⁴ M.

Solution:

Assume that C_T is unchanged after the acid rain addition, no minerals dissolve, and only rain falling on the lake surface is important (i.e., the alkalinity of the soil neutralizes acid rain falling in the drainage basin). Also, assume no inputs to or outputs from the lake.

The lake alkalinity is (30 mg/L as CaCO₃)/(50,000 mg/L as CaCO₃ per eq/L) = 6 × 10⁻⁴ eq/L. The lake C_T is (Alk - [OH⁻] + [H⁺])/(α₁ + 2α₂) = 7.19 × 10⁻⁴ M at pH 7.0.

After the acid rain addition, the pH is 6.7 and C_T (assumed constant) = 7.19 × 10⁻⁴ M. Thus, the lake Alk after acid rain addition is (α₁ + 2α₂)C_T + [OH⁻] - [H⁺] = 5.14 × 10⁻⁴ eq/L.

Alk is a conservative property. Thus:

$$(\text{Alk}_{LR})(V_{LR}) = (\text{Alk}_L)(V_L) + (\text{Alk}_R)(V_R)$$

where V = volume and the subscripts L, R, and LR are lake,

13.6.1 Introduction

For most natural waters, the members of the carbonate family are the dominate weak acids and weak bases. However, on some occasions, other weak acids or bases may be important. Other weak acids or bases can influence the alkalinity by increasing (for weak bases) or decreasing (for weak acids) the acid neutralizing capacity of the water. In such cases, the weak acids and bases must be included in the alkalinity calculation.

How should weak acids and bases be included in the alkalinity equation? The easiest way to include the other species is to return to the derivation of alkalinity as a proton condition. We already have established the endpoint of the alkalinity titration as about pH 4.5. Now, define the zero level of protons as the dominate species in the acid-base family at pH 4.5. The proton condition becomes:

$$\begin{aligned} &\Sigma(\text{species with excess protons over the zero level})(\text{no. of excess protons}) = \\ &\Sigma(\text{species with deficient protons over the zero level})(\text{no. of deficient protons}) \end{aligned}$$

Note that this definition works even for carbonate species, OH⁻, and H⁺. For the carbonate family, H₂CO₃ is the dominate species at pH 4.5 (since pK_{a,1} = 6.3) and for the "water family", H₂O is the dominate species at pH 4.5. Other examples are shown in Table 13.2.

Table 13.2: Zero Proton Levels for Common Species at pH 4.5

Family	pK _a Value(s)	Zero Level
H ₃ PO ₄ /H ₂ PO ₄ ⁻ /HPO ₄ ²⁻ /PO ₄ ³⁻	2.1, 7.2, 12	H ₂ PO ₄ ⁻
H ₃ BO ₃ /B(OH) ₄ ⁻	9.3	H ₃ BO ₃
NH ₄ ⁺ /NH ₃	9.3	NH ₄ ⁺
Monoprotic acid with pK _a > 4.5	>4.5	HA

13.6.2 Example

As an example of the effects of other weak acids and bases on alkalinity, consider the impact of naturally occurring organic acids on the alkalinity of natural waters. These acids are divided into several fractions, primarily fulvic and humic acids. A highly colored water body may have 10 mg/L

rain, and lake after rain addition, respectively. Note that $\text{Alk}_s = C_b - C_A = -1 \times 10^{-4} \text{ eq/L}$.

Now:

$$f_L = (\text{mean depth})(\text{surf. area})$$

$$f_R = (\text{rainfall rate})(\text{surf. area})$$

Thus:

$$\text{Alk}_{LR}(\text{mean depth} + \text{rainfall rate}) = (\text{Alk}_s)(\text{mean depth}) + (\text{Alk}_R)(\text{rainfall rate})$$

Or:

$$\begin{aligned} \text{rainfall rate} &= (\text{Alk}_L - \text{Alk}_{LR}) \times (\text{mean depth}) / (\text{Alk}_{LR} - \text{Alk}_s) \\ &= (6 \times 10^{-2} \text{ eq/L} - 5.14 \times 10^{-4} \text{ eq/L}) (120 \text{ inches}) \times (5.14 \times 10^{-4} \text{ eq/L} + 1 \times 10^{-4} \text{ eq/L}) \\ &= 16.7 \text{ inches or } 42.2 \text{ cm of rain} \end{aligned}$$

of dissolved organic carbon (DOC). Humic and fulvic acids have many acidic functional groups. At neutral pH, the acidic groups contributing to alkalinity are carboxylic acid groups with concentrations of up to 10 meq per gram of carbon and a typical pK_a between 1.5 and 6. This yields a total acid concentration, A_T , of $(10 \text{ meq/g C})(10 \text{ mg C/L})(10^{-3} \text{ g/mg}) = 0.1 \text{ meq/L}$. In this example, a typical pK_a of 5 will be used. Since the pK_a of the carboxylic acids is greater than the endpoint pH, use HA as the zero proton level for the carboxylate species. Thus, the proton condition is:

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

The alkalinity equation becomes:

$$\text{Alk} = (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] + [\text{A}^-] - [\text{H}^+]$$

The concentration of A^- at the endpoint pH is:

$$\alpha_{1,HA}A_T = (10^{-5})(1 \times 10^{-4} \text{ M}) / (10^{-4.5} + 10^{-5}) = 2.4 \times 10^{-5} \text{ M}$$

or 0.024 meq/L of ANC. This is a contribution of only about 1 mg/L of Alk as CaCO_3 . Since most natural waters have much higher alkalinity from carbonate species, fulvic and humic acids usually do not contribute very much to the alkalinity.

13.7 SUMMARY

In this chapter, water quality parameters were developed to measure the amount of acid or base a water requires to reach specified endpoints. Natural and process waters rarely are pure acid or base solutions. They usually are acid or base solutions that have been partially titrated to some unknown point in their titration curves. For general acids and bases, the acid neutralizing capacity (ANC) is defined to be the amount of strong acid required to reach the zeroth equivalence point. Similarly, base neutralizing capacity (BNC) is the amount strong base required to reach the first equivalence point (for monoprotic acids). If the carbonate system provides the dominate weak acids and bases, then the ANC is called *alkalinity* (titration to $f = 0$ for H_2CO_3) and the BNC is called *acidity* (titration with base to $g = 0$ for Na_2CO_3).

Expressions for alkalinity and acidity can be developed from proton conditions or charge balances. For alkalinity, the resulting expression is called the alkalinity equation: $\text{Alk} = C_b - C_A = (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+]$. Alkalinity can be measured by titration to the H_2CO_3 endpoint, about pH 4.5 for most waters. Although alkalinity measures the ANC of a water to this endpoint, other types of alkalinity (e.g., phenolphthalein alkalinity) may be more important for other pH ranges of interest. Common units of alkalinity are eq/L and mg/L as CaCO_3 ; 1 meq/L = 50 mg/L as CaCO_3 .

In solving problems involving alkalinity, it is important to remember that knowing two of Alk, C_T , or pH allows you to calculate the third parameter. For the problem at hand, carefully decide whether the information you know allows you to more easily calculate Alk from $\text{Alk} = C_B - C_A$ or from $\text{Alk} = (\alpha_1 + 2\alpha_2)C_T + [\text{OH}^-] - [\text{H}^+]$. In addition, remember that alkalinity is conserved when waters are mixed (if no solids precipitate).

Weak acids and bases can influence alkalinity and acidity in certain waters. To include the effects of weak acids and bases, define their zero proton level as the species in highest concentration at the endpoint (about pH 4.5 for alkalinity). Then adjust the alkalinity equation to include species with excess or deficient protons compared to the zero proton level.

~~PART III CASE STUDY: ACID RAIN~~

~~From what you have learned in this chapter, it is apparent that the influence of acid rain on stream water pH can be determined much more easily by~~