Chapter 3 Acid-Base Equilibria

Acid–Base Equilibria

Acids and bases play a key role in a number of environmentally important chemical reactions, including weathering, transport of metals in solution, and CO_2 atmosphere–water equilibria. In this chapter we will develop the concept of an acid and a base, characterize strong and weak acids, develop the pH scale and the concept of buffers, and look at some of the important reactions that take place in the surface environment.
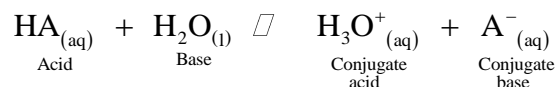
DEFINITION OF ACIDS AND BASES

Acids

According to the ***Arrhenius concept,*** *acids are substances that produce hydrogen ions (H^+) in aqueous solutions.* A more generalized view of acids is provided by the **Brönsted–Lowry model**. In this model *an acid is a proton donor.* Consider the following reaction

$$HCl_{(aq)} + H_2O_{(1)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$$
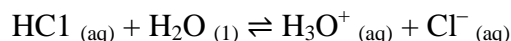
In this reaction a proton is transferred from the HCl molecule to the water molecule to form the hydronium ion (H_3O^+). A more general form of this type of reaction can be written

$$\underset{\text{Acid}}{HA_{(aq)}} + \underset{\text{Base}}{H_2O_{(1)}} \rightleftharpoons \underset{\substack{\text{Conjugate} \\ \text{acid}}}{H_3O^+_{(aq)}} + \underset{\substack{\text{Conjugate} \\ \text{base}}}{A^-_{(aq)}}$$

One way to view this reaction is that it represents a competition between two bases ($H_2O_{(1)}$ and $A^-_{(aq)}$) for the proton. If $H_2O_{(1)}$ is a much stronger base than $A^-_{(aq)}$ the equilibrium position will be far to the right and the $HA_{(aq)}$ will be completely broken down (dissociated). If $A^-_{(aq)}$ is a stronger base, then the reaction will not go far to the right and the $HA_{(aq)}$ will be only partially dissociated. As with any chemical reaction, we can calculate an equilibrium constant for the reaction. This is a particular type of equilibrium constant called an ***acid dissociation constant***, which represents the *degree to which the acid has dissociated.*

$$K_a = \frac{\left[H_3O^+\right][A^-]}{[HA]} = \frac{[H^+][A^-]}{[HA]} \qquad (3\text{–}1)$$

These types of reactions are often written using only the $H^+_{(aq)}$ species, rather than the $H_3O^+_{(aq)}$ species, and this is the convention we will use in this book. A ***strong acid*** is one that *undergoes significant dissociation and has a very large K_a*. A ***weak acid*** only *partially dissociates and has a relatively small K_a*.

Table 3–1 Dissociation Constants for Acids at 25°C*

Acid	Formula	pK_{a_1}	pK_{a_2}	pK_{a_3}
Hydrochloric	HCl	~ –3		
Sulfuric	H_2So_4	~ –3	1.99	
Nitric	HNO_3	0		
Oxalic	$H_2C_2O_4$	1.2	4.2	
Phosphoric	H_3PO_4	2.15	7.20	12.35
Hydrofluoric	HF	3.18		
Formic	HCOOH	3.75		
Acetic	CH_3COOH	4.76		
Carbonic	H_2CO_3	6.35	10.33	
Hydrosulfuric	H_2S	7.03	>14	
Boric	H_3BO3	9.27	>14	
Silicic	H_4SiO_4	9.83	13.17	

*Data from Drever (1997), Faure (1998), and Langmuir (1997).

Acids can contain more than one acidic proton. An example is the diprotic (contains two acidic protons) acid H_2SO_4 (sulfuric acid). This acid undergoes a two-step dissociation as follows:

$$H_2SO_4 \rightarrow H^+ + HSO_4^-$$

and

$$HSO_4^- \rightarrow H^+ + SO_4^{2-}$$
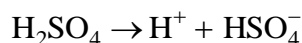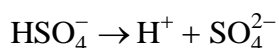
A triprotic acid has three acidic protons. An example is H_3PO_4 (phosphoric acid), which is a weak acid. If the acid contains more than one acidic proton, there will be more than one dissociation constant. These are listed in the order of the dissociation reactions. Table 3–1 lists dissociation

constants for a number of common and/or environmentally important acids. The dissociation constants are often reported as pK_a values, where $pK_a = -\log K_a$. This is the format used in Table 3–1. Acids that undergo significant dissociation have a negative pK_a, and acids that only partly dissociate have a positive pK_a.

Bases

Bases are defined similarly to acids. Thus, according to the ***Arrhenius concept***, *a base is a substance that produces OH⁻ ions in aqueous solution*, and according to the more general ***Brönsted–Lowry model***, *a base is a proton acceptor.* Let us consider two reactions. The first is the dissolution of NaOH $_{(s)}$ in water,

$$NaOH_{(s)} \rightleftharpoons Na^+_{(aq)} + OH^-_{(aq)}$$
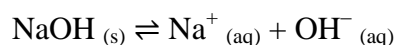
in which the OH⁻ ions are derived from the solid NaOH. The second reaction involves the aqueous ammonia molecule (NH_3),

$$NH_{3(aq)} + H_2O_{(1)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

In this reaction, the NH_3 molecule acts as a proton acceptor and water acts as an acid and provides the proton for the aqueous ammonia. ***Strong bases*** are those that *undergo essentially complete dissociation*, and ***weak bases*** only *undergo partial dissociation.* As was the case for acids, we can write a general equation for the dissociation of a base and define an equilibrium constant for the dissociation. The generalized equation is

$$\underset{\text{Base}}{B_{(aq)}} + \underset{\text{Acid}}{H_2O} \rightleftharpoons \underset{\substack{\text{Conjugate} \\ \text{acid}}}{BH^+_{(aq)}} + \underset{\substack{\text{Conjugate} \\ \text{base}}}{OH^-_{(aq)}}$$

Table 3–2   Dissociation Constants for Bases at 25°C*

Base (hydroxide)	Formula	pK_{b_1}	pK_{b_2}	pK_{b_3}
Methylamine	CH_3NH_2	3.36		
Ammonium	$NH_4(OH)$	4.7		
Magnesium	$Mg(OH)_2$	8.6	2.6	

Base (hydroxide)	Formula	pK_{b_1}	pK_{b_2}	pK_{b_3}
Pyridine	C_5H_5N	8.8		
Manganese	$Mn(OH)_2$	9.4	3.4	
Ferrous	$Fe(OH)_2$	10.6	4.5	
Al, amorphous	$Al(OH)_3$	12.3	10.3	9.0
Al, gibbsite	$Al(OH)_3$	14.8	10.3	9.0
Ferric, amorphous	$Fe(OH)_3$	16.5	10.5	11.8

*Data from Faure (1998) and Zumdahl (1989).

and the equilibrium constant for this reaction is

$$K_b = \frac{[BH^+][OH^-]}{[B]} \qquad (3\text{--}2)$$

A base such as $Al(OH)_3$ contains three OH molecules and, as was the case for acids that contain more than one H, there are multiple dissociation steps. As was done for acids, we define $pK_b = -\log K_b$. Dissociation constants for some common and/or environmentally important bases are given in Table 3–2.

THE DISSOCIATION OF WATER AND pH

pH is an important and fundamental concept. It arises from the dissociation of water as represented by the following equation:

$$H_2O \rightleftharpoons H^+ + OH^-$$

and

$$K_w = \frac{[H^+][OH^-]}{[H_2O]} = [H^+][OH^-] \qquad (3\text{--}3)$$

Note that the activity of $H_2O_{(1)} = 1$ in dilute solutions. For this reaction, at 25°C,

$$\Delta G_R^0 = (0) + (-157.2) - (-237.14) = 79.94 \qquad (3\text{--}4)$$

and

$$\log K_w = \frac{-79.94}{5.708} = -14.00$$

or

$$K_w = 10^{-14} = [H^+][OH^-] \text{ (3–5)}$$

This is the equilibrium constant for water at 25°C. The equilibrium constant varies as a function of temperature (Table 3–3), and at higher temperatures the equilibrium constant is greater than 10^{-14}. Thus, the pH of a neutral solution is a function of temperature. Also note that $K_w = 10^{-14}$ exactly at 24°C (Table 3–3), not at 25°C, but the difference is so minor that for simplicity $K_w = 10^{-14}$ is used at 25°C.

The pH scale is defined, at 25°C, using equation 3–3. By definition, pH $= -\log[H^+]$. When the activity of H^+ and OH^- are equal, the solution is neutral (i.e., the activity of both ions is 10^{-7}, pH $= 7$). When $[H^+] > 10^{-7}$, the pH is less than 7 and the solution is acidic. When $[H^+] < 10^{-7}$, the pH is greater than 7 and the solution is basic; i.e., there are more OH^- ions than H^+ ions. Remember that we are dealing with a negative exponent, so the larger the number the smaller the activity of the particular ion. pH is referred to as an ***environmental parameter***; that is, *pH is theoretically determined by all the equilibria reactions in the system.*

Table 3–3   Dissociation Constants (K_w) for Water as a Function of Temperature*

T (°C)	$-\log K_{eq}$	T (°C)	$-\log K_{eq}$
0	14.938	30	13.836
5	14.727	35	13.685
10	14.528	40	13.542
15	14.340	45	13.405
20	14.163	50	13.275
24	14.000	55	13.152
25	13.995	60	13.034

*Data from *CRC Handbook of Chemistry and Physics* (2000).

pH OF NATURAL WATERS

The majority of natural waters have pH values between 4 and 10 (Figure 3–1). For most natural waters the carbonic acid–carbonate system exerts the major control on pH. Waters in equilibrium with atmospheric CO_2 would have pH values of around 5.7. The controlling reaction involves the dissociation of the weak acid H_2CO_3. The presence of calcium carbonate, a salt of the weak acid H_2CO_3, results in a buffered system with a pH around 8.2. This buffer is the major control for ocean water pH. Because of its importance, the carbonic acid–carbonate system is discussed at some length in a subsequent section. Additionally, most minerals can be considered to be salts of weak acids and strong bases. For example, $CaAl_2Si_2O_8$ (plagioclase) contains the salt of a weak acid (H_4SiO_4) and two strong bases [$Ca(OH)_2$, $Al(OH)_3$]. The addition of powdered silicate and aluminosilicate minerals, with the exception of quartz, to pure water usually gives rise to a basic pH. pH values less than 4 are usually due to the weathering of sulfide minerals or acid rain. pH values greater than 10 are usually due to the presence of strong bases. The more important pH controlling reactions are discussed in the following sections.
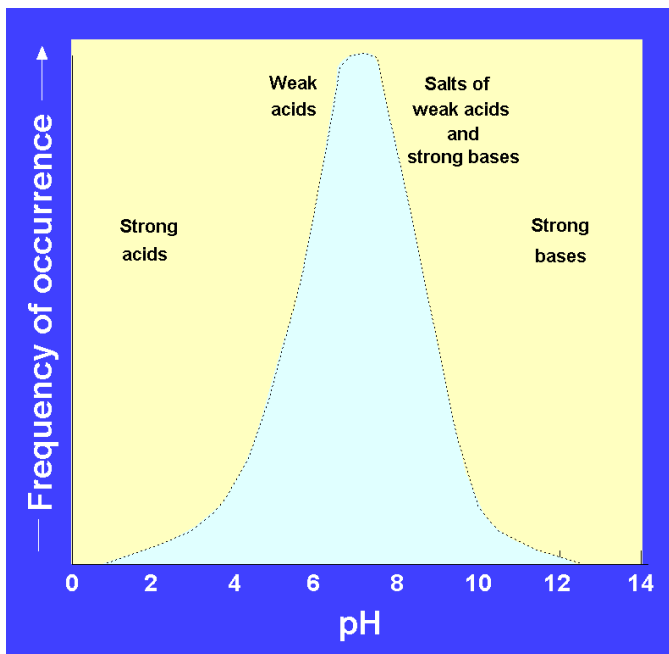

Figure 3–1 Schematic diagram showing the frequency of pH values in natural waters. The major controls for each pH range are indicated on the diagram. After Langmuir (1997).

Strong Acids

The principal strong acids in natural waters are hydrochloric (HCl), nitric (HNO$_3$), and sulfuric (H$_2$SO$_4$). The primary source of nitric acid is acid rain. The nitric acid is produced by the oxidation of various NO$_x$ compounds produced during combustion. The principal sources of sulfuric acid are the weathering of sulfide minerals and acid rain. The source of the sulfur in acid rain is the combustion of fossil fuel, which releases SO$_2$. Subsequent oxidation in the atmosphere results in sulfuric acid aerosols. The topic of acid rain is considered in Chapter 8, and acid mine drainage is considered in Chapter 9. The effect of strong acids on the pH of natural waters is controlled to some extent by mineral–water reactions. These buffering reactions will be considered in a subsequent section.

Weak Acids

The common weak acids are carbonic acid (H$_2$CO$_3$), silicic acid (H$_4$SiO$_4$), and various organic acids. The organic acids are discussed in Chapter 5. In addition to these *naturally occurring* acids, other organic acids can be produced by anthropogenic actions. These include acetic acid (CH$_3$COOH), often found in landfill leachates and sewage, and formic acid (HCOOH), often found in groundwater in association with hydrocarbons.

Acetic Acid Acetic acid is a weak monoprotic acid. The dissociation of acetic acid in water can be written
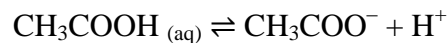
$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^- + H^+$$

and the equilibrium equation, at 25°C, is

$$K_a = \frac{\left[H^+\right]\left[CH_3COO^-\right]}{\left[CH_3COOH_{(aq)}\right]} = 10^{-4.76} \qquad (3\text{–}6)$$

Because acetic acid is a weak acid, as is evident from the small equilibrium constant, only a small amount of the dissolved acid will disassociate. Example 3–1 illustrates how to calculate the amount of H$^+$ in solution.

EXAMPLE 3–1 Calculate the concentration of H^+ ions in solution if 0.1 mol of acetic acid is dissolved in 1 L of water.

Because we start with only acetic acid and pure water, $[H^+] = [CH_3COO^-] = x$, and the amount of acetic acid left after dissociation is $0.1 - x$. We can now write the equilibrium equation (3–6) as

$$K_a = \frac{[x][x]}{[0.1-x]} = \frac{x^2}{0.1-x} = 10^{-4.76}$$

The student will recall from introductory algebra that this is a quadratic equation. If we put this equation into the standard form, we get

$$ax^2 + bx + c = 0 = x^2 + 10^{-4.76}x - 10^{-5.76}$$

Substituting the appropriate values, $a = 1$, $b = 10^{-4.76}$, and $c = -10^{-5.76}$, we get

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = \frac{-10^{-4.76} \pm \left[(10^{-4.76})^2 - 4(1)(-10^{-5.76})\right]^{1/2}}{(2)(1)}$$

$$= 1.32 \times 10^{-3}$$

We ignore the negative answer, which is clearly inappropriate. Thus, at equilibrium $[H^+] = [CH_3COO^-] = 1.32 \times 10^{-3}$ mol L^{-1} and $[CH_3COOH_{(aq)}] = 0.1 - 1.32 \times 10^{-3} = 0.0987$ mol L^{-1}. The degree of dissociation is

$$D = \frac{1.32 \times 10^{-3}}{0.0987} \times 100 = 1.34\%$$

a very small amount indicative of the weak acid character of acetic acid. Note that we could simplify the calculation, without introducing a significant error, by assuming that x is small relative to the amount of $CH_3COOH_{(aq)}$. This would immediately give

$$K_a = \frac{x^2}{0.1} = 10^{-4.76}, \quad x^2 = -10^{-5.76}, \quad x = 1.32 \times 10^{-3}$$

Carbonic Acid Carbonic acid (a diprotic acid) is the most abundant acid in natural waters. With its

salt, $CaCO_3$, it forms a buffer that plays an important role in regulating the pH of natural waters. Hence, an understanding of the carbonic acid system is essential to the understanding of the pH of natural waters. Three equilibrium relationships are required to describe this system. The first involves the equilibrium between atmospheric CO_2 and H_2CO_3 in solution, which is written

$$CO_{2\,(g)} + H_2O \rightleftharpoons H_2CO_{3\,(aq)}$$
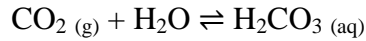
where $H_2CO_{3\,(aq)} = CO_{2\,(aq)} + H_2CO_3^0$ (the true concentration of H_2CO_3, which at 25°C is slightly less than 0.3%). For convenience, the convention is adopted that all the CO_2 in solution exists as $H_2CO_{3\,(aq)}$, and the equilibrium constants used are consistent with this convention. The amount of H_2CO_3 in solution in equilibrium with a particular CO_2 pressure in a coexisting gas phase can be calculated from Henry's law,

$$\left[H_2CO_{3\,(aq)}\right] = K_{CO_2} P_{CO_2} \qquad (3-7)$$

where K_{CO_2} is the Henry's law constant and P_{CO_2} is the partial pressure of CO_2 in atm. Henry's law constants for various temperatures can be found in Table 2–1.
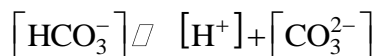
H_2CO_3 is a weak acid and undergoes a two-step dissociation. The first dissociation is
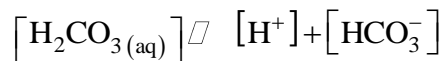
$$\left[H_2CO_{3\,(aq)}\right] \rightleftharpoons \left[H^+\right] + \left[HCO_3^-\right]$$

and the equilibrium equation is

$$K_{a_1} = \frac{\left[H^+\right]\left[HCO_3^-\right]}{\left[H_2CO_{3\,(aq)}\right]} \qquad (3-8)$$

The second dissociation is

$$\left[HCO_3^-\right] \rightleftharpoons \left[H^+\right] + \left[CO_3^{2-}\right]$$

and the equilibrium equation is

$$K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \qquad (3\text{--}9)$$

Equilibrium constants, as a function of temperature, for the carbonate system are listed in Table 3–4.

Let us rewrite equations 3–8 and 3–9 as follows, and insert the appropriate equilibrium constants for a solution at 25°C.

$$\frac{[H_2CO_{3\,(aq)}]}{[HCO_3^-]} = \frac{[H^+]}{K_{a_1}} = \frac{[H^+]}{10^{-6.35}} \qquad (3\text{--}10)$$

and

$$\frac{[HCO_3^-]}{[CO_3^{2-}]} = \frac{[H^+]}{K_{a_2}} = \frac{[H^+]}{10^{-10.33}} \qquad (3\text{--}11)$$

Table 3–4 Equilibrium Constants for the Carbonate System*

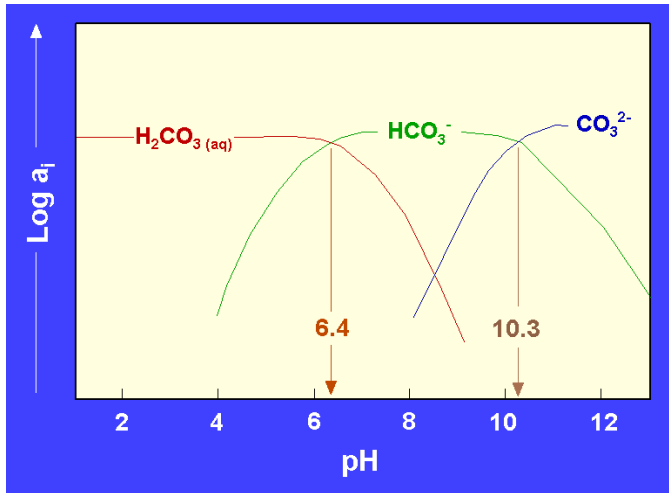|	Dissociation	constants	Solubility	products
T (°C)	pK_{a_1}	pK_{a_2}	pK_{cal}	pK_{arg}
0	6.58	10.63	8.38	8.22
5	6.52	10.55	8.39	8.24
10	6.46	10.49	8.41	8.26
15	6.42	10.43	8.43	8.28
20	6.38	10.38	8.45	8.31
25	6.35	10.33	8.48	8.34
30	6.33	10.29	8.51	8.37
45	6.29	10.20	8.62	8.49
60	6.29	10.14	8.76	8.64

*Data from Plummer and Busenberg (1982).

Figure 3–2 Relative activity of various carbonate species as a function of pH.

According to equation 3–10, when $[H^+] = 10^{-6.35}$ (pH = 6.35), the ratio $H_2CO_{3\,(aq)} / HCO_3^- = 1$; that is, these two species are present in equal abundance (or more precisely, they are of equal activity). Similarly, from equation 3–11, when pH = 10.33, HCO_3^- and CO_3^{2-} are present in equal abundance. These positions of equal abundance (activity) of species are determined solely by the dissociation constants, which vary only slightly with temperature. Returning to equation 3–10, if the pH is less than 6.35, $\left[H_2CO_{3\,(aq)}\right] > \left[HCO_3^-\right]$, and if the pH is greater than 6.35, $\left[HCO_3^-\right] > \left[H_2CO_{3\,(aq)}\right]$. Similarly, from equation 3–11, if pH < 10.33, $\left[HCO_3^-\right] > \left[CO_3^{2-}\right]$ and if pH > 10.33 $\left[CO_3^{2-}\right] > \left[HCO_3^-\right]$. These variations in the relative abundances (activities) of the different species are shown qualitatively on Figure 3–2. Note that in waters of intermediate pH, HCO_3^- is the dominant species. In relatively acidic waters $H_2CO_{3\,(aq)}$ is the dominant species, and only in very basic waters is CO_3^{2-} the dominant species.

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EXAMPLE 3–2 Calculate the relative activity, at 25°C, of H_2CO_3 to HCO_3^- in a water whose pH = 4.

$$\frac{\left[H_2CO_{3\,(aq)}\right]}{\left[HCO_3^-\right]} = \frac{\left[H^+\right]}{K_{a_1}} = \frac{10^{-4.0}}{10^{-6.35}} = 224$$

The activity of $[H_2CO_{3\,(aq)}]$ is 224 times greater than that of $\left[HCO_3^-\right]$

So far we have considered the abundances of the carbonate species in a qualitative way and have found that the relative abundance of the various species is controlled by pH. We will now consider quantitative solutions to the distribution of the species. There are two end-member cases, an ***open system*** when *the system is in equilibrium with atmospheric CO_2* and a ***closed system*** when the *system is isolated from atmospheric CO_2.*

We will first consider an open system, which is in equilibrium with atmospheric P_{CO_2} We need four equations to solve this problem: (1) equation 3–7, which relates the partial pressure of CO_2 to the concentration of $H_2CO_{3\,(aq)}$; (2) equation 3–8, which describes the dissociation of $H_2CO_{3\,(aq)}$; (3) equation 3–9, which describes the dissociation of HCO_3^-; and (4) a charge balance equation. ***A basic constraint of solution chemistry is that the positive and negative charges of the species in solution must be equal. This is an important concept and is used repeatedly in solving water-chemistry problems.*** For the system CO_2–H_2O, the charge balance equation is written

$$m_{H^+} = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{OH^-} \quad (3\text{–}12)$$

where *m* is the molar concentration of each species. We will make the assumption that measured molar concentrations are equal to activity. This is approximately true in very dilute solutions. For more precise calculations, activity coefficients can be calculated as described in Chapter 2 and the molar concentrations adjusted to take into account activity. CO_3^{2-} has two negative charges so the molar concentration of CO_3^{2-} is multiplied by 2 to get the electronic charge. From equation 3–12,

note that if there are any HCO_3^- or CO_3^{2-} ions in solution, $[H^+] > [OH^-]$ and the solution is acidic. From Figure 3–2, we see that at acidic pHs the dominant charged species in solution is HCO_3^-. Thus, we can make the simplifying assumption that the relative concentrations of CO_3^{2-} and OH^- are negligible and $m_{H^+} = m_{HCO_3^-}$. Example 3–3 illustrates a calculation of this type.

EXAMPLE 3–3 Calculate the pH of rainwater in equilibrium with atmospheric CO_2.

For the present-day atmosphere, $P_{CO_2} = 10^{-3.5}$ atm. At 25°C, the Henry's law constant is $10^{-1.47}$ (Table 2–1).

$$\left[H_2CO_{3\,(aq)}\right] = K_{CO_2}P_{CO_2} = \left(10^{-1.47}\right)\left(10^{-3.5}\right) = 10^{-4.97}$$

Rearranging equation 3–8 gives

$$[H^+][HCO_3^-] = K_{a_1}[H_2CO_{3\,(aq)}] = (10^{-6.35})[10^{-4.97}] = 10^{-11.32}$$

Making the simplifying assumption that $[H^+]^2 = [HCO_3^-]$,

$$\left[H^+\right]^2 = 10^{-11.32} \quad \text{and} \quad \left[H^+\right] = 10^{-5.66}$$

Therefore,

$$pH = -\log[H^+] = -\log[10^{-5.66}] = 5.66$$

Note that the pH of *pure* rainwater is acidic. The term ***acid rain*** is used to describe *rainwater that has a pH of less than 5.66.*

Returning to equation 3–12, note that the presence of any anions other than OH^- results in an acidic pH. There are a number of waters in equilibrium with atmospheric CO_2— ocean water, groundwater in contact with limestone, alkaline lake waters, etc.—that are basic. For this to be true, other cations must be present in the system.

In Example 3–3 we calculated the pH of waters in equilibrium with atmospheric CO_2. Changes

in the concentration of CO_2 will cause changes in pH. Table 3–5 lists some of the processes that can lead to changes in the pH and CO_2 content of surface and ground waters.

From previous calculations, as schematically summarized in Figure 3–2, we determined that at pH values of less than 10.3, HCO_3^- is the dominant anion in solution. Because this is the case, we can combine equations 3–7 and 3–8 to form an equation that relates the CO_2 partial pressure, pH, and bicarbonate ion activity. Substituting equation 3–7 into equation 3–8, we get

$$K_{a_1} = \frac{[H^+]\left[HCO_3^-\right]}{K_{CO_2} P_{CO_2}} \qquad (3\text{–}13)$$

Table 3–5 Examples of Processes That Control the CO_2 Content and pH of Surface and Ground Waters

Process	Reaction	pH
Temperature change	Increase T, decrease solubility of $CO_{2\,(g)}$	Increases
	Decrease T, increase solubility of $CO_{2\,(g)}$	Decreases
Photosynthesis	$6CO_{2\,(g)} + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_{2\,(g)}$	Increases
Respiration	$C_6H_{12}O_6 + 6O_{2(g)} \rightarrow 6CO_{2\,(g)} + 6H_2O$	Decreases
Anaerobic decay	$2CH_2O \rightarrow CH_{4(g)} + CO_{2\,(g)}$	Decreases
Denitrification	$5CH_2O + 4NO_3^- + 4H^+ \rightarrow 5CO_{2(g)} + 2N_{2(g)} + 7H_2O$	Increases
Dissolution of carbonate	$CaCO_{3\,calcite} + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_{2\,(g)}$	Increases
Precipitation of	$Ca^{2+} + H_2O + CO_{2\,(g)} \rightarrow CaCO_{3\,calcite} + 2H^+$	Decreases
Weathering of Al-silicate	$2KAISi_3O_{8\,fledspar} + 2CO_{2\,(g)} + 11H_2O \rightarrow$	Increases

$$Al_2Si_2O_5 (OH)_{4\,kaolinite} + 2K^+ + 2HCO_3^- + 4H_4SiO_{4(aq)}$$

Rearranging and solving for P_{CO_2} gives

$$P_{CO_2} = \frac{[H^+]\left[HCO_3^-\right]}{K_{a_1} K_{CO_2}} \qquad (3\text{–}14)$$

Taking the log, and remembering that pH = $-\log[H^+]$, results in the final form of the equation relating the partial pressure of CO_2, pH, and bicarbonate ion activity.

$$\log P_{CO_2} = -pH + \log\left(\frac{\left[HCO_3^-\right]}{K_{a_1}K_{CO_2}}\right) \quad (3\text{–}15)$$

See also Case Study 3–1.

EXAMPLE 3–4 A groundwater sample has a measured pH of 6.84 and HCO_3^- of 460 mg L^{-1}. We will assume that activity equals concentration. At 25°C, calculate the P_{CO_2} for this groundwater sample.

First, we need to convert the measured concentration of HCO_3^- to moles per liter. The atomic weight of $HCO_3^- = 61.0$ g. Therefore,

$$\left[HCO_3^-\right] = \frac{460\times10^{-3}\,g\,L^{-1}}{61.0\,g\,mol} = 7.54\times10^{-3}\,mol\,L^{-1}$$

Substituting into equation 3–15, and using the proper constants for $T = 25°C$,

$$\log P_{CO_2} = -6.84 + \log\left(\frac{\left[7.54\times10^{-3}\,mol\,L^{-1}\right]}{10^{-6.35}10^{-1.47}}\right) = -6.84 + \log\left(4.982\times10^5\right)$$
$$= -6.84 + 5.70 = -1.14$$

The calculated partial pressure for CO_2 is significantly greater than that for the atmosphere, hence the water is supersaturated in CO_2 with respect to the atmosphere and the groundwater is behaving as a closed system. The ground water sample was collected near a septic tank, and the elevated P_{CO_2} presumably due to aerobic and/or anaerobic decay of dissolved organic carbon in the water from the drain field.

Lastly, we will consider a system in which the total carbonate concentration remains constant. What we are interested in are the absolute abundances of the different species as a function of pH. Four equations are required to describe this system, one which represents the total amount of carbonate and the other three the absolute abundances of the three carbonate species. The equation for the total carbonate concentration is

$$C_T = H_2CO_{3\,(aq)} + HCO_3^- + CO_3^{2-} \qquad (3\text{--}16)$$

Rewriting equation 3–8 in terms of HCO_3^- gives

$$\left[HCO_3^- \right] = \frac{K_{a_1} \left[H_2CO_{3\,(aq)} \right]}{\left[H^+ \right]} \qquad (3\text{--}17)$$

Substituting in equation 3–9 for HCO_3^- gives

$$\left[CO_3^{2-} \right] = \frac{K_{a_1} K_{a_2} \left[H_2CO_{3\,(aq)} \right]}{\left[H^+ \right]^2} \qquad (3\text{--}18)$$

Equations 3–17 and 3–18 are combined with equation 3–16 to give

$$C_T = \left[H_2CO_{3\,(aq)} \right] \left(1 + \frac{K_{a_1}}{\left[H^+ \right]} + \frac{K_{a_1} K_{a_2}}{\left[H^+ \right]^2} \right) \qquad (3\text{--}19)$$

We now have an expression that relates total carbonate to the amount of $H_2CO_{3\,(aq)}$. As we will see, this is a very useful expression. In order to simplify subsequent equations, we will define a variable, α_H, that encompasses all of the terms inside the parentheses in equation 3–19. Note that this portion of equation 3–19 deals with the activity of the hydrogen ion, i.e., pH.

$$\alpha_H = \left(1 + \frac{K_{a_1}}{\left[H^+ \right]} + \frac{K_{a_1} K_{a_2}}{\left[H^+ \right]^2} \right) \qquad (3\text{--}20)$$

CASE STUDY 3–1

Relationship Between Concentration of Bicarbonate Ion, pH, and Partial Pressure of CO2

Langmuir (1997) summarizes the results of several studies that investigated the relationships between pH, HCO_3^-, and P_{CO_2} (Figure 3–Cl–1). The three investigations gave very different trends in terms of these variables, and the reasons for these trends are illustrative of the various factors that can effect the carbonate system. The NJ Coastal Plain is a sand aquifer. As the waters move downdip they react with alumino-silicate minerals. These reactions consume CO_2 (see Table

3–5), leading to an increase in pH, a decrease in CO_2, and an increase in HCO_3^-. In the case of the Floridian aquifer, traces of gypsum are present in the carbonate rock. The Ca released by the dissolution of gypsum causes the precipitation of additional calcite and an increase in CO_2, according to the reaction

$$CaSO_4 \cdot 2H_2O\,_{gypsum} + 2HCO_3^- \rightarrow CaCO_3\,_{clacite} + SO_4^{2-} + 3H_2O + CO_2$$
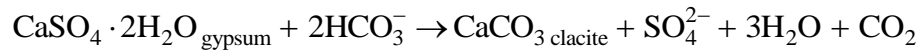
This is referred to as *common-ion driven precipitation*, because the dissolution of gypsum releases Ca^{2+}, which is also involved in the calcite precipitation reaction. Anaerobic decay of organic matter (Table 3–5) and sulfate reduction also occur, and both reactions release CO_2. The result is that CO_2 increases in the downdip direction and this increase is accompanied by both a decrease in pH and an increase in HCO_3^-. In the case of Slab Cabin Run, the HCO_3^- concentration in the stream remains essentially constant. The plotted data represent diurnal variations in the CO_2 content with concomitant changes in pH. CO_2 decreases during the day when photosynthesis is occurring (increasing pH) and increases at night when only respiration is taking place (decreasing pH). Plots such as that shown in Figure 3–C1–1 represent a useful way to summarize relations in the carbonate system and to investigate the factors that lead to variations in pH, P_{CO_2}, and HCO_3^-. *Source:* Langmuir (1997).
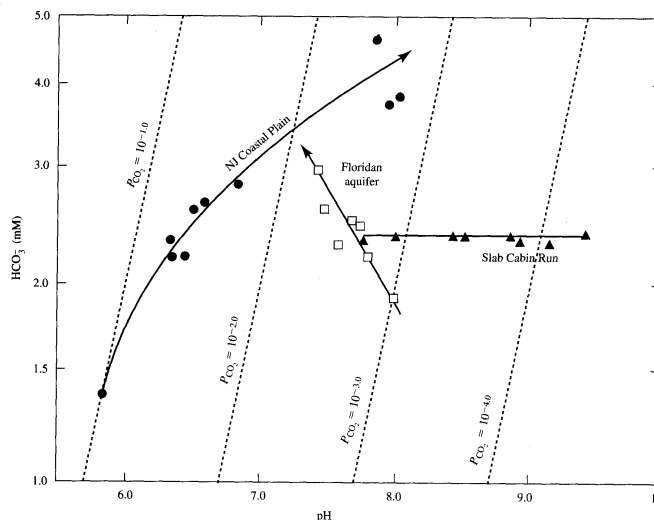

Figure 3–Cl–1 Variations in pH, HCO_3^-, and P_{CO_2} for two groundwater and one stream system. Arrows indicate the direction of groundwater flow. From Langmuir (1997).

We now write equation 3–19 in terms of α_H:

$$C_T = [H_2CO_{3\ (aq)}]\alpha_H \qquad (3–21)$$

Solving equation 3–21 for $[H_2CO_{3\ (aq)}]$ gives

$$\left[H_2CO_{3\,(aq)} \right] = \frac{C_T}{\alpha_H} \qquad (3–22)$$

Substituting equation 3–22 into equation 3–17 gives

$$\left[HCO_3^- \right] = \frac{C_T K_{a_1}}{[H^+]\alpha_H} \qquad (3–23)$$

Substituting equation 3–22 into equation 3–18 gives

$$\left[CO_3^{2-} \right] = \frac{C_T K_{a_1} K_{a_2}}{[H^+]^2 \alpha_H} \qquad (3–24)$$

EXAMPLE 3–5 Calculate the concentration of each carbonate species in solution at 25°C when
$$C_T = 1 \times 10^{-3}\ \text{mol L}^{-1} \text{ and pH} = 5.7.$$

Selecting the appropriate dissociation constants from Table 3–4 and setting $[H^+] = 10^{-5.7}$ mol L^{-1}.

$$\alpha_H = 1 + \frac{K_{a_1}}{[H^+]} + \frac{K_{a_1} K_{a_2}}{[H^+]^2} = 1 + \frac{\left(10^{-6.35}\right)}{\left[10^{-5.7}\right]} + \frac{\left(10^{-6.35}\right)\left(10^{-10.33}\right)}{\left[10^{-5.7}\right]^2} = 1.224$$

$$H_2CO_{3\,(aq)} = \frac{C_T}{\alpha_H} = \frac{1 \times 10^{-3}\,\text{mol L}^{-1}}{1.224} = 8.17 \times 10^{-4}\,\text{mol L}^{-1}$$

$$\left(HCO_3^- \right) = \frac{C_T K_{a_1}}{[H^+]\alpha_H} = \frac{\left(1 \times 10^{-3}\,\text{mol L}^{-1}\right)\left(10^{-6.35}\right)}{\left(10^{-5.7}\right)(1.224)} = 1.83 \times 10^{-4}\,\text{mol L}^{-1}$$

$$\left(CO_3^{2-}\right) = \frac{C_T K_{a_1} K_{a_2}}{[H^+]^2 \alpha_H} = \frac{(1 \times 10^{-3})(10^{-6.35})(10^{-10.33})}{[10^{-5.7}]^2 (1.224)} = 4.29 \times 10^{-9} \, mol \, L^{-1}$$

As expected, at pH = 5.7, $H_2CO_{3 \, (aq)}$ is the dominant species and the abundance of CO_3^{2-} is negligible.

Silicic Acid Silicic acid is produced during the weathering of silicate minerals (Chapter 9). Silicic acid is a tetraprotic acid and has four dissociation steps. Because of the very small dissociation constants (Table 3–1), in natural waters only the first two dissociation steps are important. The first dissociation is

$$H_4SiO_{4 \, (aq)} \rightleftharpoons H_3SiO_4^- + H^+$$

and the equilibrium equation, at 25°C, is

$$K_{a_1} = \frac{[H^+][H_3SiO_4^-]}{[H_4SiO_{4 \, (aq)}]} = 10^{-9.83} \qquad (3\text{–}25)$$

The second dissociation is

$$H_3SiO_4^- \rightleftharpoons H_3SiO_4^{2-} + H^+$$

and the equilibrium equation, at 25°C, is

$$K_{a_2} = \frac{[H^+][H_2SiO_4^{2-}]}{[H_3SiO_4^-]} = 10^{-13.17} \qquad (3\text{–}26)$$

Inspection of equation 3–25 reveals that at pH = 9.83, $[H_4SiO_{4(aq)}] = [H_3SiO_4^-]$. For pH values less than 9.83, the dominant species is $H_4SiO_{4 \, (aq)}$. Similarly, at pH = 13.17 (equation 3–26), $[H_3SiO_4^-] = [H_2SiO_4^{2-}]$. Only at pH values greater than 13.17, which are essentially never encountered in natural waters, is $H_2SiO_4^{2-}$ the dominant species. Thus, $H_4SiO_{4 \, (aq)}$ is the dominant species in all but relatively basic waters.

19

EXAMPLE 3–6 Calculate the relative abundance of $H_4SiO_{4\,(aq)}$ to $H_3SiO_4^-$ at pH = 7.0 and 25°C.

$$\frac{\left[H_4SiO_4\right]}{\left[H_3SiO_4^-\right]} = \frac{\left[H^+\right]}{K_{a_1}} = \frac{\left[10^{-7.0}\right]}{10^{-9.83}} = 676$$

H_4SiO_4 (aq) is 676 times more abundant in solution than $H_3SiO_4^-$. Note that we have ignored activities in this calculation. In dilute solutions the activity of the aqueous species, $H_4SiO_{4\,(aq)}$, would be 1, but the activity of $H_3SiO_4^-$ would be less than 1. More precise calculations require the calculation of the activity coefficient, and these more precise calculations would give a slightly lower ratio in terms of the absolute abundance of the two species in solution.

As we did for the carbonate system, we can calculate the total dissolved concentration of silica species as follows:

$$Si_T = H_4SiO_{4\,(aq)} + H_3SiO_4^- + H_2SiO_4^{2-} \qquad (3–27)$$

The second and third terms would only be significant in relatively basic solutions. We can rewrite equation 3–27 as follows:

$$Si_T = \left[H_4SiO_{4\,(aq)}\right]\left(1 + \frac{K_{a_1}}{\left[H^+\right]} + \frac{K_{a_1}K_{a_2}}{\left[H^+\right]^2}\right) \qquad (3–28)$$

As we did for the carbonates, we can solve for α_H and the concentrations of the various silicic acid species at a fixed pH and fixed total dissolved silica content.

Carbonic Acid–Carbonate System When we developed the equations for the carbonic acid system, it was pointed out, with reference to equation 3–12, that in order for natural waters to have a pH greater than 7, other cations in addition to H^+ must be present in solution. In mildly basic waters, the most important equilibria are those involving carbonic acid and the carbonate minerals calcite and aragonite. In this case, Ca^{2+} is the additional cation and waters in equilibrium with carbonate minerals are basic. These carbonate equilibrium reactions are important in determining the pH of the ocean and waters in contact with limestones. There are a number of possible cases

involving these equilibria, depending on whether or not we are dealing with an open system (P_{CO_2} constant) or a closed system ($\Sigma\ CO_2$ fixed) and when the system became closed. As an example, we will consider the pH of a system open to the atmosphere and saturated in calcite, for instance, water in a lake located in limestone. Other cases can be found in Garrels and Christ (1965), Drever (1997), and Langmuir (1997).

The following equations describe the system CO_2–$CaCO_3$. The solubility products for the $CaCO_3$ phases (the polymorphs calcite and aragonite) as a function of temperature are listed in Table 3–4. The following three equations were developed previously:

$$\left[H_2CO_{3\,(aq)} \right] = K_{CO_2} P_{CO_2} \qquad (3\text{–}29)$$

$$K_{a_1} = \frac{\left[H^+ \right]\left[HCO_3^- \right]}{\left[H_2CO_{3\,(aq)} \right]} \qquad (3\text{–}30)$$

$$K_{a_2} = \frac{\left[H^+ \right]\left[CO_3^{2-} \right]}{\left[HCO_3^- \right]} \qquad (3\text{–}31)$$

Because this system also involves calcite, an additional reaction representing the solubility of calcite is required.

$$CaCO_{3\text{ calcite}} \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

and

$$K_{sp} = \left[Ca^{2+} \right]\left[CO_3^{2-} \right] \qquad (3\text{–}32)$$

A final equation represents the charge balance and is written

$$m_H^+ + 2m_{Ca^{2+}} = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{OH^-} \qquad (3\text{–}33)$$

We now have five equations and six unknowns (P_{CO_2}, [$H_2CO_{3\,(aq)}$], $\left[HCO_3^- \right]$, $\left[CO_3^{2-} \right]$, [Ca^{2+}], and [H^+]). If we fix one of these variables, we can solve for the other variables. The exercise now becomes one of algebraic manipulation, although the manipulations may not always be obvious. In

this example, P_{CO_2} is fixed and we are going to solve for pH. We need to emphasize a significant point. In all of the equilibrium equations, we are dealing with the activities of the species. In the charge balance equation, we are dealing with the absolute concentrations. In order to solve this problem, we are going to assume that activity = concentration. A more exact solution requires the calculation of the activity coefficients. This can be done by an iterative technique, as was illustrated in Chapter 2.

EXAMPLE 3–7 Calculate the pH of a solution saturated with respect to calcite and in equilibrium with atmospheric CO_2. For the solution, $T = 25°C$.

As an initial assumption, we will anticipate that the final pH is going to be near neutrality, so equation 3–33 can be simplified to

$$2m_{Ca^{2+}} = m_{HCO_3^-}$$

Rewriting equation 3–31 in terms of CO_3^{2-} and substituting into equation 3–32,

$$K_{sp} = [Ca^{2+}] K_{a_2} \frac{[HCO_3^-]}{[H^+]}$$

Substituting HCO_3^- for Ca^{2+} using the simplified charge balance equation, $Ca^{2+} = 0.5 HCO_3^-$,

$$K_{sp} = 0.5 [HCO_3^-] K_{a_2} \frac{[HCO_3^-]}{[H^+]}$$

Combining equations 3–29 and 3–30 and solving for HCO_3^- gives

$$[HCO_3^-] = \frac{K_{a_1} K_{CO_2} P_{CO_2}}{[H^+]}$$

Combining this result with the previous equation for calcite solubility gives

$$K_{sp} = 0.5 \left(\frac{K_{a_1} K_{CO_2} P_{CO_2}}{[H^+]} \right)^2 \frac{K_{a_2}}{[H^+]}$$

Solve for [H$^+$] by inserting the appropriate constants and P_{CO_2}.

$$\left[H^+\right] = \left(\frac{K_{a_1}^2 K_{CO_2}^2 P_{CO_2}^2 K_{a_2}}{2K_{sp}}\right)^{1/3} = \left(\frac{\left(10^{-6.35}\right)^2 \left(10^{-1.47}\right)^2 \left(10^{-3.5}\right)^2 \left(10^{-10.33}\right)}{2\left(10^{-8.48}\right)}\right)^{1/3} = 10^{-8.26}$$

pH $= -\log[H^+]$, so the final pH is 8.26. Is our assumption that the dominant ionic carbonate species would be HCO_3^- correct? Rearranging equation 3–31 and solving for the CO_3^{2-} / HCO_3^- ratio gives

$$\frac{\left[CO_3^{2-}\right]}{\left[HCO_3^-\right]} = \frac{K_{a_2}}{\left[H^+\right]} = \frac{10^{-10.33}}{10^{-8.26}} = 10^{-2.07} = 0.009$$

The activity of CO_3^{2-} is less than 1% that of HCO_3^- so our simplification of the charge balance equation is acceptable.

Case Study 3–2 demonstrates how carbonate equilibria can be used to determine the source(s) of groundwater and the changes that occur along the flow path.

CASE STUDY 3–2

Groundwater Chemistry of a Plateau near Matsumoto City, Japan

Li and Misawa (1994) investigated the chemistry of groundwater seeping into the Matsumoto tunnel and the chemistry of well, spring, and river waters in the immediate vicinity of the tunnel. The purpose of the study was to determine the source of the groundwater seeping into the tunnel and the changes that occurred along the flow path of the groundwater.

The plateau consists of Miocene andesitic tuff breccia and sandstone overlain by Quaternary river terrace deposits. The plateau is forested and the source of the HCO_3^- ions in the groundwater was thought to be CO_2 gas derived from the soils. The reaction is

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+$$
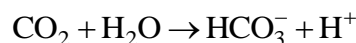
Solving equation 3–15 at $T = 25°C$,

$$\log P_{CO_2} = -pH + \log\left[HCO_3^-\right] + 7.81$$

The source of Ca^{2+} ions in the groundwater was inferred to be dissolution of calcite veins found in the rocks surrounding the tunnel, according to the reaction

$$CaCO_{3\,calcite} + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$$
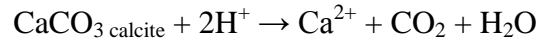
For this reaction at 25°C,

$$K_{eq} = 10^{9.8} = \frac{\left[Ca^{2+}\right]P_{CO_2}}{\left[H^+\right]^2}$$

and

$$\log P_{CO_2} = -2pH - \log\left[Ca^{2+}\right] + 9.8$$

Plots of HCO_3^- and Ca^{2+} versus pH are shown in Figure 3–C2–1. Calculated log P_{CO_2} varies from –1 to –4, with tunnel seepage showing the smaller values. P_{CO_2} values for waters calculated using both equations were generally in agreement. A number of groundwater samples had P_{CO_2} values that exceeded atmospheric P_{CO_2}, supporting the hypothesis that CO_2 had been added by the decay of organic material. The lower CO_2 pressures found in the tunnel seepage were ascribed to reactions between the groundwater and the silicate minerals of the andesitic tuffs as the groundwater flowed to the tunnel. These reactions are of the general type

$$CaAl_2Si_2O_{8\,anorthite} + 2CO_2 + 3H_2O \rightarrow Ca^{2+} + 2HCO_3^- + Al_2Si_2O_5(OH)_{4\,kaolinite}$$
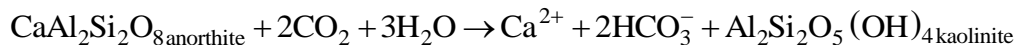
which consume CO_2.

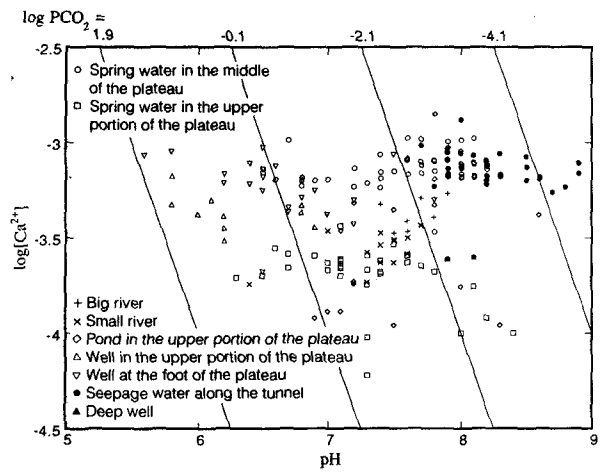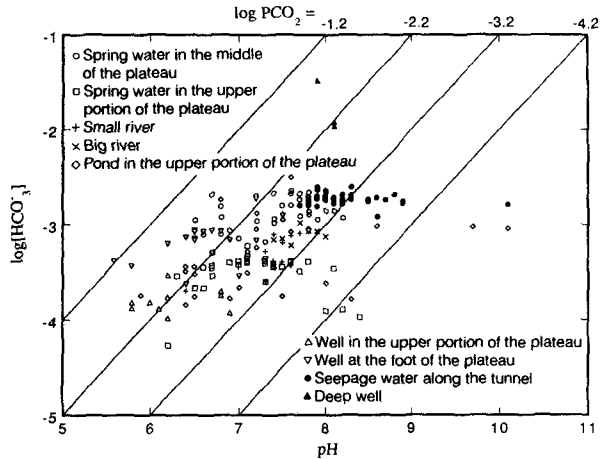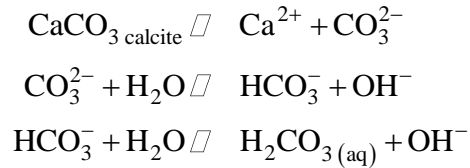*Source:* Li and Misawa (1994).

Figure 3–C2–1 The relationship between pH and $\log\left[HCO_3^-\right]$ and log [Ca^{2+}]. From Li and Misawa (1994).

Salts of Weak Acids and Strong Bases

Most, but not all, minerals can be considered to be salts of weak acids and strong bases. Waters in equilibrium with these minerals are normally basic. We will illustrate this by considering two examples, one involving our old friend calcite ($CaCO_3$), a common mineral in limestones, and the other natron ($Na_2CO_3 \cdot 10H_2O$), a mineral that forms in evaporative alkaline lakes, such as those found in the Rift Valley of East Africa.

EXAMPLE 3–8 An excess of pure calcite is placed in distilled water that has been purged of all gas phases—for example, by boiling. Therefore, for the purpose of this example we will assume

that $P_{CO_2} = 0$ atm. The following chemical reactions describe what happens in this system:

$$CaCO_{3 \, calcite} \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_{3 \, (aq)} + OH^-$$

All the carbon atoms in solution come from the dissolution of calcite, giving the mass balance equation

$$m_{Ca^{2+}} = m_{CO_3^{2-}} + m_{HCO_3^-} + m_{H_2CO_3}$$

We can also write a charge balance equation:

$$2m_{Ca^{2+}} + m_{H^+} = 2m_{CO_3^{2-}} + m_{HCO_3^-} + m_{OH^-}$$

We will once again assume that concentration equals activity, bearing in mind our standard warning about this simplification. We anticipate that the solution will be sufficiently basic so that [$H_2CO_{3 \, (aq)}$] is significantly smaller than $\left[HCO_3^- \right]$ and can be neglected in the following calculations. At 25°C (equilibrium constants from Table 3–4), the following equations describe this system:

$$\left[Ca^{2+} \right]\left[CO_3^{2-} \right] = 10^{-8.48}$$

$$\frac{\left[H^+ \right]\left[HCO_3^- \right]}{\left[H_2CO_{3 \, (aq)} \right]} = 10^{-6.35}$$

$$\frac{\left[H^+ \right]\left[CO_3^{2-} \right]}{\left[HCO_3^- \right]} = 10^{-10.33}$$

$$\left[H^+ \right]\left[OH^- \right] = 10^{-14}$$

We will write the mass balance equation substituting the activities of the various species for concentrations and ignoring $H_2CO_{3 \, (aq)}$.

$$\left[Ca^{2+} \right] + \left[CO_3^{2-} \right] + \left[HCO_3^- \right]$$

Similarly, for the charge balance equation, making the assumption that H^+ will be small relative to Ca^{2+},

$$2\left[Ca^{2+}\right]+2\left[CO_3^{2-}\right]+\left[HCO_3^-\right]+\left[OH^-\right]$$

Substituting from the mass balance equation for Ca^{2+} into the charge balance equation,

$$\left[HCO_3^-\right]+\left[OH^-\right]$$

What we are interested in is the pH of the solution. Therefore, it is more useful to solve this problem in terms of the H^+ rather than the OH^- ion. Hence, we want to write the equations in what is called the *proton condition.* As a first step we write OH^- in terms of H^+.

$$\left[OH^-\right]=\frac{K_w}{\left[H^+\right]}=\frac{10^{-14}}{\left[H^+\right]}$$

We can now write

$$\left[HCO_3^-\right]+\left[OH^-\right]=\frac{10^{-14}}{\left[H^+\right]}$$

We solve for CO_3^{2-} in terms of H^+ by rearranging the $HCO_3^- \ \square \ H^+ +CO_3^{2-}$ equilibrium equation and solving for CO_3^{2-}:

$$\left[CO_3^{2-}\right]=\frac{\left[HCO_3^-\right]10^{-10.33}}{\left[H^+\right]}=\frac{10^{-14}10^{-10.33}}{\left[H^+\right]\left[H^+\right]}=\frac{10^{-24.33}}{\left[H^+\right]^2}$$

Substituting for HCO_3^- in the calcite solubility equation,

$$\left[Ca^{2+}\right]=\frac{10^{-8.48}}{\left[CO_3^{2-}\right]}=\frac{10^{-8.48}\left[H^+\right]^2}{10^{-24.33}}=10^{15.85}\left[H^+\right]^2$$

Substituting into the modified mass balance equation, $\left[Ca^{2+}\right]+\left[CO_3^{2-}\right]+\left[HCO_3^-\right]$,

$$10^{-15.85} \left[H^+\right]^2 = \frac{10^{-24.33}}{\left[H^+\right]^2} + \frac{10^{-14}}{\left[H^+\right]}$$

Multiplying through by $[H^+]^2$ and rearranging,

$$10^{-15.85} \left[H^+\right]^4 - 10^{-14} \left[H^+\right] = 10^{-24.33}$$

This equation can be solved by successive approximations. The final value is $[H^+] = 10^{-9.9}$ and pH = 9.9. We can compare this result with the calculation we did in Example 3–7, in which the system was in equilibrium with atmospheric CO_2. In the case of the open system, pH = 8.26, a less basic pH than that calculated here, indicating the effect of P_{CO_2} on carbonate equilibria.

EXAMPLE 3–9 Evaporative alkaline lakes contain a number of strange and exotic minerals. One such mineral is natron, which dissolves according to the following reaction:

$$Na_2CO_3 \cdot 10H_2O_{natron} \rightarrow 2Na^+ + CO_3^{2-} + 10H_2O$$
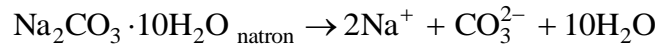
releasing Na^+ ions to solution and increasing the alkalinity of the lake water.

Calculate the pH for an alkaline lake in Tanzania in which the concentration of Na = 0.1 mol L^{-1}. The lake waters are in equilibrium with atmospheric CO_2, and the water temperature is 30°C.

We expect that this lake will have a very basic pH, hence we will ignore the H^+ ion. In addition, we will assume that Na^+ is the only other cation in the water. We can now write the combined mass balance and charge balance equation as follows:

$$m_{Na^+} = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{OH^-} = 10^{-1}$$

As we have done in the other examples, we now solve the various carbonate equilibria equations for the activity of HCO_3^- and CO_3^{2-}. The appropriate equilibrium constants are from Table 2–1 (Henry's law constants) and Table 3–4.

$$\left[HCO_3^-\right] = \frac{\left[H_2CO_{3\,(aq)}\right]K_{a_1}}{\left[H^+\right]} = \frac{K_{CO_2}P_{CO_2}K_{a_1}}{\left[H^+\right]} = \frac{10^{-1.53}10^{-3.5}10^{-6.33}}{\left[H^+\right]} = \frac{10^{-11.36}}{\left[H^+\right]}$$

$$\left[CO_3^{2-}\right] = \frac{\left[HCO_3^-\right]K_{a_2}}{\left[H^+\right]} = \frac{10^{-11.36}10^{-10.29}}{\left[H^+\right]^2} = \frac{10^{-21.65}}{\left[H^+\right]^2}$$

As in the case of Example 3–8, OH^- is replaced by $10^{-14}/[H^+]$. Substituting into the charge balance equation,

$$\frac{10^{-11.36}}{\left[H^+\right]} + (2)\left(\frac{10^{-21.65}}{\left[H^+\right]^2}\right) + \frac{10^{-14}}{\left[H^+\right]} = 10^{-1.0}$$

Multiplying through by $[H^+]^2$,

$$10^{-11.36}\left[H^+\right] + 10^{-21.35} + 10^{-14}\left[H^+\right] = 10^{-1.0}\left[H^+\right]^2$$

Rearranging and grouping terms,

$$\left[H^+\right]^2 - 10^{-10.36}\left[H^+\right] - 10^{-20.35} = 0$$

This is a quadratic equation and can be solved in the standard way (Example 3–1), giving pH = 10.04. In doing this problem we have once again made the simplifying assumption that activity equals concentration. The alkaline lake water has a significantly higher ionic charge than the solutions in the preceding examples, and a more precise calculation taking into account activity would give a slightly different pH value

Strong Bases

pH values greater than 10 are rarely found in nature, and when they are found they are inevitably due to the presence of strong bases such as $Ca(OH)_2$ and $Mg(OH)_2$. Possible natural sources for such bases are the weathering products of ultramafic rocks.

AMPHOTERIC HYDROXIDES

Amphoteric hydroxides are *hydroxides that can behave as either an acid or a base*. This behavior varies as a function of pH. As an example, consider the following reaction, which represents the dissolution of $Cd(OH)_{2\ (s)}$ when a hydroxyl ion is added:

$$Cd(OH)_{2\,(s)} + OH^- \;\rightleftharpoons\; Cd(OH)_3^-$$

The equilibrium equation for this reaction is

$$K_A = \frac{\left[Cd(OH)_3^-\right]}{\left[OH^-\right]} = 10^{-5.3} \quad (3\text{--}34)$$

where K_A is the equilibrium constant for the amphoteric reaction. Equilibrium constants for other amphoteric compounds are found in Table 3–6. When Cd(OH) is partially dissolved in water, OH^- ions are taken up to form $Cd(OH)_3^-$ and a hydrogen ion is released through the dissociation of water. In this case, $Cd(OH)_2$ acts as an acid because H^+ (protons) are released. Le Châtelier's principle predicts that in a basic solution the reaction will move to the right, using up OH^- ions, while in an acidic solution the reaction will move to the left, releasing OH^- ions. Thus, in basic solutions amphoteric compounds act as acids, and in acidic solutions they act as bases. If this does not seem obvious, consider the dissociation reaction for water. If OH^- ions are removed from solution, in order for the equilibrium constant to stay constant, the activity of H^+ ions must increase. The reverse is true for an acidic solution.

Table 3–6 Equilibrium Constants for Amphoteric Compounds*

| Hydroxide	Formula	$-\log K_A$
Aluminum, amorphous	$Al(OH)_3$	−1.1
Aluminum, gibbsite	$Al(OH)_3$	1.4
Cadmium	$Cd(OH)_2$	5.3
Cobalt	$Co(OH)_2$	5.2
Copper	$Cu(OH)_2$	2.9
Ferrous	$Fe(OH)_2$	5.1
Ferric	$Fe(OH)_3$	4.4
Manganese	$Mn(OH)_2$	5.1
Nickel	$Ni(OH)_2$	4
Thorium, amorphous	$Th(OH)_4$	5.8
Uranium	$UO_2(OH)_2$	3.6

| Zinc, amorphous | Zn(OH)$_2$ | 1.9 |

*Data from Krauskopf and Bird (1995).

ACIDITY AND ALKALINITY

Acidity is the *capacity of water to donate protons*; **alkalinity** is the *capacity of water to accept protons.* What do we mean by the capacity of water to donate or accept protons? Let us suppose we have an acidic solution whose acidity is due to the presence of hydrochloric acid. In this solution, HC1 will have dissociated to H$^+$ and Cl$^-$ ions. If we add hydroxyl ions to the solution, the following reaction will occur:

$$H^+ + OH^- \rightarrow H_2O$$

A hydronium ion in solution has donated a proton (i.e., an H$^+$), which combines with the OH$^-$ to produce H$_2$O. For a weak acid, such as H$_2$CO$_3$, the reaction would be

$$H_2CO_{3\,(aq)} + OH^- \rightarrow HCO_3^- + H_2O$$
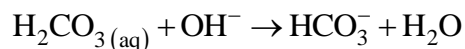
and once again an H$^+$ ion has combined with an OH$^-$ ion to produce water. The preceding are examples of acidity reactions. The acidity of a solution can be determined by titrating the solution with a strong base, such as NaOH. Examples of alkalinity reactions are those involving OH$^-$ or HCO$_3^-$ ions, such as

$$OH^- + H^+ \rightarrow H_2O \text{ and } HCO_3^- + H^+ \rightarrow H_2CO_{3\,(aq)}$$

Alkalinity is determined by titrating a solution with a strong acid, such as HCl.

Recall that a fundamental principle of aqueous chemistry is that solutions must be electrically neutral. Suppose that we have a solution of distilled water in equilibrium with atmospheric CO$_2$. For this solution we can write the following charge balance equation:

$$m_H^+ = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{OH^-}$$

Note, as we already know, this solution is acidic, because m_{H^+} must be greater than m_{OH^-}. If we

add acid to the solution, the H^+ ions will combine with OH^- to form H_2O, with CO_3^{2-} to form HCO_3^-, and with HCO_3^- to form $H_2CO_{3\,(aq)}$. During this set of reactions, the overall electrical neutrality of the solution must be maintained, but the concentration of the individual species will change. Hence, these species are considered to be **nonconservative species** because their *abundances vary as a function of pH or some other intensive variable (such as pressure or temperature).*

Now let us consider a more complicated solution in which other species occur. As an example, consider a typical groundwater. For this solution, an appropriate charge balance equation is

$$2m_{Ca^{2+}} + 2m_{Mg^{2+}} + m_{Na^+} + m_{K^+} + m_{H^+} = m_{Cl^-} + 2m_{SO_4^{2-}} + m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{OH^-}$$

If we add acid to this solution, the concentrations of HCO_3^-, CO_3^{2-}, and OH^- will change, but the concentrations of the other species (as long as precipitation or complex species formation doesn't occur) will remain constant. These species are referred to as **conservative species** because their *abundances do not vary as a function of pH or some other intensive variable (such as pressure or temperature).* Rearranging the equation so the conservative species are on the left and the nonconservative species are on the right (a reversal of the political spectrum) gives

$$2m_{Ca^{2+}} + 2m_{Mg^{2+}} + m_{Na^+} + m_{K^+} - m_{Cl^-} - m_{SO_4^{2-}} = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{OH^-} - m_{H^+}$$

The term on the right now represents the *excess of nonconservative bases with respect to hydrogen* and is a quantity known as **total alkalinity**. A final point with regard to conservative and nonconservative species is that during water mixing the total abundance of each conservative species will remain constant but the total abundance of each nonconservative species may change because of changes in pH, temperature, etc.

For waters in which acidity or alkalinity are largely determined by the carbonate system and completely dissociated acids or bases, we can define acidity (C_A) and alkalinity (C_B) as follows:

$$C_A = 2H_2CO_{3\,(aq)} + HCO_3^- + H^+ - OH^- \quad (3\text{–}35)$$

$$C_B = HCO_3^- + 2CO_3^{2-} + OH^- - H^+ \quad (3\text{–}36)$$

Systems in which other species are important contributors to the acidity or alkalinity would require additional terms. For example, weathering of pyrite and other sulfide minerals in coal leads to acid mine drainage that has pH values of 2 to 3. Under these conditions, sulfuric acid, bisulfate ion (HSO_4^-), and acid cations are produced. In this case, total acidity might be defined as

$$C_A = H^+ + HSO_4^- + 3Fe^{3+} + 2Fe(OH)^{2+} + Fe(OH)_2^+$$

Fe^{3+} is considered an acid cation because it can combine with OH^- to form Fe hydroxides.

Acidity and alkalinity are often reported in meq L^{-1}. Recall from Chapter 1 that a gram–equivalent weight is the molecular or atomic weight divided by the valence, or, in the case of acids and bases, the number of H^+ or OH^- ions that can be produced when the acid or base is dissolved in water. Hence, in the equation for total acidity, the number of moles of H_2CO_3 is multiplied by 2 because this acid can produce two H^+ ions. In the total alkalinity equation, the number of moles of CO_3^{2-} is multiplied by 2 because there are two gram–equivalents in one mole of CO_3^{2-}.

EXAMPLE 3–10 In Example 3–5 we calculated the abundances of the various carbonate species in a solution in equilibrium with the atmosphere at pH = 5.7. Calculate the total acidity and alkalinity of this solution.

From equation 3–35, total acidity is

$$\begin{aligned} C_A &= 2H_2CO_{3\,(aq)} + HCO_3^- + H^+ - OH^- \\ &= (2)(10^{-3.09}) + 10^{-3.74} + 10^{-5.7} - 10^{-8.3} \\ &= 1.81 \times 10^{-3}\,eq\ L^{-1} = 1.81\ meq\ L^{-1} \end{aligned}$$

From equation 3–36, the total alkalinity is

$$\begin{aligned} C_B &= HCO_3^- + 2CO_3^{2-} + OH^- - H^+ = 10^{-3.74} + (2)(10^{-8.37}) + 10^{-8.3} - 10^{-5.7} \\ &= 1.80 \times 10^{-4}\,eq\ L^{-1} = 0.18\ meq\ L^{-1} \end{aligned}$$

Another common way to report total alkalinity is as equivalent weight of calcium carbonate (in mg L^{-1}). In this calculation one must use the equivalent weight of calcium carbonate. The equation

is

$$\text{Total alkalinity} = \frac{C_A V_A \times \text{eq.wt CaCO}_3 \left(0.050\,\text{g/meq}\right) \times 1000\,\text{mg/g}}{V_s} \qquad (3\text{–}37)$$

where C_A is the concentration of the acid (in meq L^{-1}) used in the alkalinity titration, V_A is the volume (in L) of acid used in the alkalinity titration, and V_S is the volume (in L) of the solution.

Acidity and alkalinity are important environmental parameters for natural waters. Acidity affects the weathering of silicate and carbonate minerals, the transport of metal ions in solution, and the functioning of aquatic ecosystems. High–acidity waters are generally considered to be environmentally detrimental. Conversely, alkalinity is important in determining the capacity of a water to ameliorate acid additions and is generally considered to be a positive characteristic.

ACIDITY AND ALKALINITY TITRATIONS

If we know the concentrations of all the acidic (or basic) species in a solution, we can calculate the acidity (or alkalinity). This is generally a straightforward problem for very dilute (low ionic strength) solutions. However, in more concentrated (high ionic strength) solutions, uncertainties arise regarding the formation of complexes and the calculation of activity coefficients. Thus, total acidity or alkalinity is often determined by titrating the solution with a strong base (acidity determination) or a strong acid (alkalinity determination). At the endpoint pH (discussed next), the acidity (or alkalinity) can be calculated using the following equation:

$$C_t \times V_t = C_s \times V_s \qquad\qquad (3\text{–}38)$$

where C_t is the concentration (meq L^{-1}) of acid or base in the titrant, V_t is the volume of the titrant (L^{-1}), C_s is the acidity or alkalinity (meq L^{-1}) of the unknown solution, and V_S is the volume (L^{-1}) of the unknown solution.

We will first consider a solution that contains only a strong acid. We take a fixed volume of this solution and titrate with a strong base. As we add the base we monitor the change in the pH of the solution (Figure 3–3). In this case, we would find that there is an inflection in the curve at pH = 7.0, i.e., at neutrality. The reaction taking place in the solution is

$$H^+ + OH^- \rightarrow H_2O$$

and at neutrality all the excess H^+ has been consumed. If we repeat this experiment using a solution that contains only a strong base and titrate with an acid, we once again find that there is an inflection point at pH = 7.0. We are only dealing with strong acids and bases, so the definitions of acidity and alkalinity reduce to the following simple equations:

$$C_A = H^+ - OH^- \text{ and } C_B = OH^- - H^+$$

Because the activity of the OH^- ions in acidic solutions is negligible, and the activity of H^+ ions in basic solution is negligible, $C_A = H^+$ and $C_B = OH^-$.
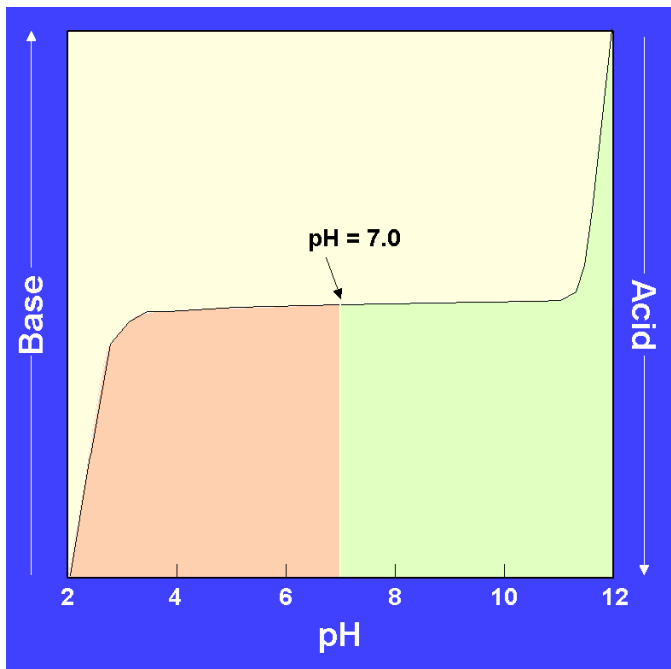
Figure 3–3 Schematic representation of an acid–base titration curve for a strong acid (base). The inflection point is at pH = 7.0, where all the excess H^+ (acid) or OH^- (base) has been consumed. Titrant is a base for an acidity determination; an acid for an alkalinity determination.

EXAMPLE 3–11 100 mL of an acidic solution is titrated with a 100 meq L^{-1} NaOH solution. Neutrality (pH = 7) is achieved after 50 mL of titrant have been added to the acid solution. Calculate the acidity of the solution.

From equation 3–38,

$$C_s = \frac{C_t \times V_t}{V_s} = \frac{\left(100 \text{ meq L}^{-1}\right)\left(50 \times 10^{-3} \text{L}\right)}{100 \times 10^{-3} \text{L}} = 50 \text{ meq L}^{-1}$$

Total acidity is 50 meq L^{-1}.

If both strong and weak acids are present in a solution, the titration curve is more complex. A schematic titration curve is shown in Figure 3–4 for a solution that contains a strong acid and carbonic acid. You will note that there are a number of inflection points on this curve, so the question arises as to what we are measuring at each inflection point. The total acidity of this solution is

$$C_A = 2H_2CO_{3\,(aq)} + HCO_3^- + H^+ - OH^-$$
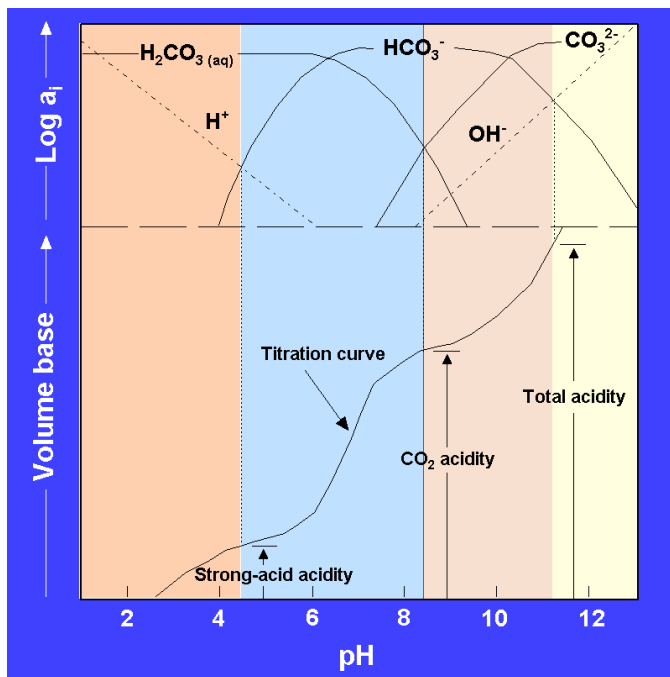
Figure 3–4 Schematic acidity titration curve for a solution that contains a strong acid and carbonic acid. See text for details.

We titrate this solution with a strong base and measure the pH changes. The first inflection point occurs at pH $\approx$ 4.5. This is the point at which the reaction $H^+ + OH^- \rightarrow H_2O$ is essentially complete

and $H^+ = HCO_3^-$. A point to note here is that while the position of the H^+ and OH^- curves on the top part of Figure 3–4 are fixed relative to pH, the positions of the curves representing the various carbonate equilibria change as a function of total carbonate content. Thus, the crossing points can vary by several tenths of a pH unit as a function of carbonate concentration. This first inflection point corresponds to the *strong–acid acidity*. The next segment of the titration curve is relatively steep; i.e., large additions of base result in only small changes in pH. In this region there is a buffer reaction involving $H_2CO_{3\ (aq)}$ and HCO_3^-, which tends to inhibit pH changes. Buffers will be discussed in the next section. At pH ≈ 8.35, there is another inflection point. At this point, 99% of the $H_2CO_{3\ (aq)}$ has been converted to HCO_3^-, as demonstrated by the following calculation, with which you should be very familiar:

$$\frac{\left[HCO_3^-\right]}{\left[H_2CO_{3\ (aq)}\right]} = \frac{K_{a_1}}{\left[H^+\right]} = \frac{10^{-6.35}}{10^{-8.35}} = 10^{-2.00}$$

This inflection point corresponds to the *CO₂ acidity*. The final inflection point occurs when $HCO_3^- = OH^-$. This inflection point corresponds to the *total acidity.*

If our solution contained a strong base and a weak acid, the titration curve would have the same shape as in Figure 3–4, except we would titrate with a strong acid and the pH would decrease as the titration proceeded. The point at which $OH^- = HCO_3^-$ represents the *caustic alkalinity* (the free OH^- ions from strong bases), the inflection point at pH ≈ 8.3 represents the *carbonate alkalinity*, and the inflection point at pH ≈ 4.5 represents the *total alkalinity.*

Alkalinity titrations are done using a strong acid and two endpoint indicators—phenolphthalein (pH = 8.3) and methyl orange (pH = 4.5). The first endpoint corresponds to the carbonate alkalinity and the second endpoint to the total alkalinity. Note from Figure 3–4 that near the two endpoints pH changes rapidly with small additions of acid. Hence, a precise determination of pH is not required. If a more precise measurement is desired, the pH change of the solution, as a function of the volume of acid added, can be monitored with a pH meter and a titration curve plotted from the data.

EXAMPLE 3–12 In Example 3–9 we calculated the pH of water from an alkaline lake in

Tanzania. A 100 mL water sample from the lake is titrated with 100 meq L^{-1} nitric acid. Inflection points are noted in the titration curve at about pH = 8.34 (after 54 mL of titrant have been added) and at about pH = 3.0 (after 102 mL of titrant have been added). Calculate the carbonate alkalinity and total alkalinity for this water sample in equivalent weight of calcium carbonate. Carbonate alkalinity corresponds to the inflection point at pH = 8.34.

$$\text{Carbonate alkalinity} = \frac{C_A V_A \times \text{eq.wt} \, CaCO_3 \, (0.050 \, g/meq) \times 1000 \, mg/g}{V_s}$$

$$= \frac{(100 \, \text{meq} \, L^{-1})(54 \times 10^{-3} L^{-1})(0.050)(1000)}{(100 \times 10^{-3} L^{-1})} = 2700 \, mg \, L^{-1} \quad \text{as} \quad CaCO_3$$

Total alkalinity corresponds to the inflection point at pH = 3.0.

$$\text{Total alkalinity} = \frac{C_A V_A \times \text{eq.wt} \, CaCO_3 \, (0.050 \, g/meq) \times 1000 \, mg/g}{V_s}$$

$$= \frac{(100 \, \text{meq} \, L^{-1})(102 \times 10^{-3} L^{-1})(0.050)(1000)}{(100 \times 10^{-3} L^{-1})} = 5100 \, mg \, L^{-1} \quad \text{as} \quad CaCO_3$$

BUFFERS

A weak acid and its salt (or a weak base and its salt) form what is known as a *buffer*. A ***buffered solution*** is *a solution that resists changes in pH when either hydrogen or hydroxyl ions are added to the solution.* Let us first illustrate what we mean by a buffer by considering once again the carbonic acid system. For all acidic waters, $H_2CO_{3 \, (aq)}$ and HCO_3^- (Figure 3–2) will be the dominant carbonate species. Equation 3–8 relates the activity of these carbonate species to the H^+ activity. We can rewrite equation 3–8 as follows:

$$\frac{1}{[H^+]} = \frac{1}{K_{a_1}} \frac{[HCO_3^-]}{[H_2CO_{3 \, (aq)}]} \qquad (3\text{–}39)$$

Taking the logs of both sides, and remembering that pH = –log $[H^+]$, gives

$$pH = -\log K_{a_1} + \log \frac{\left[HCO_3^-\right]}{\left[H_2CO_{3\,(aq)}\right]} \qquad (3\text{–}40)$$

We can use equation 3–40 to calculate the effect that the addition of hydrogen ions will have on the pH.

EXAMPLE 3–13 Let us suppose that we have 1 L of pure water with pH = 7.0. If we add 10^{-4} mol of H^+ ions to the pure water, the pH will drop to 4 (10^{-7} mol + 10^{-4} mol = 10^{-4} mol L^{-1} of H^+). If carbonic acid is present in the solution, what will be the change in pH when the H^+ ions are added? At pH = 7 and $T = 25°C$, assume that $\left[HCO_3^-\right] = 10^{-3}$ mol L^{-1}.

From equation 3–8 we get $[H_2CO_{3\,(aq)}] = 10^{-3.65}$ mol L^{-1}. When we add H^+ ions to the solution, the following reaction occurs:

$$H^+ + HCO_3^- \rightarrow H_2CO_{3\,(aq)}$$
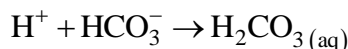
an example of LeChâtelier's principle. According to this reaction, the added H^+ ions combine with the HCO_3^- to form $H_2CO_{3\,(aq)}$. Thus, the activity of HCO_3^- decreases by 10^{-4} mol L^{-1} and the activity of $H_2CO_{3\,(aq)}$ increases by 10^{-4} mol L^{-1}. Solving equation 3–40 for pH gives

$$pH = -\log K_{a_1} + \log\left(\frac{\left[HCO_3^-\right]}{\left[H_2CO_{3\,(aq)}\right]}\right)$$

$$= 6.35 + \log\left(\frac{\left[10^{-3.0} - 10^{-4.0}\right]}{\left[10^{-3.65} + 10^{-4.0}\right]}\right) = 6.35 + 0.44 = 6.79$$

Due to the presence of carbonic acid, the pH only decreases by 0.21 units rather than 3.0 units.

The calculation we have just done used the ***Henderson–Hasselbalch equation.***

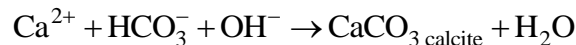Consider the following reaction:

$$H^+ + A^- \rightarrow HA$$

In this reaction, a H^+ ion has combined with the salt of a weak acid (a conjugate base) to form a weak acid. We can write equation 3–40 in a general form (the Henderson– Hasselbalch equation) as

$$pH = -\log K_a + \log\left(\frac{[A^-]}{[HA]}\right) \qquad (3\text{–}41)$$

Buffers are important in the natural environment because they control the impact of acid or base additions on natural waters. A widely discussed example of this type of impact is acid rain (see Chapter 8), which can lead to the acidification of streams and lakes. Even in the same geographic area, lakes can have widely different pH values, depending upon the available buffers. There are two types of reactions that can control pH—those due to dissolved species in water and those that require interactions between water and mineral species. The carbonic acid–bicarbonate ion reaction considered in Example 3–13 is illustrative of the first type of pH–controlling reaction. An example of the second type of pH–controlling reaction is the calcite–carbonate system, which controls the long–term pH of the oceans. If we add H^+ ions to the ocean, in addition to the carbonate equilibria illustrated in Example 3–13, the following reaction can occur, which will remove H^+ ions from solution:

$$CaCO_{3\,calcite} + H^+ \rightarrow Ca^{2+} + HCO_3^-$$
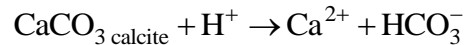
If we add OH^- ions, the following reaction may occur:

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_{3\,calcite} + H_2O$$

As a second example, consider the following reaction between the clay minerals illite and kaolinite:

$$2KAl_3Si_3O_{10}(OH)_{2\,illite} + 2H^+ + 3H_2O \rightarrow 3Al_2Si_2O_5(OH)_{4\,kaolinite} + 2K^+$$
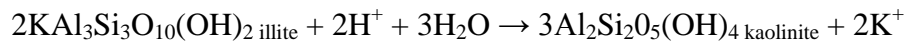
In this reaction, hydrogen ions are consumed during the conversion of illite to kaolinite.

The **buffering capacity** is *a measure of the amount of H^+ or OH^- ions a solution can absorb without a significant change in pH.* The capacity of a buffered solution is determined by the amount of [HA] and [A⁻] in the solution. For an acidity titration, the buffering index, *B,* is defined

as

$$B = \frac{dC_B}{dpH} \qquad (3\text{--}42)$$

where dC_B is the increment of strong base added in eq L^{-1} (or meq L^{-1}) and dpH is the corresponding change in solution pH. For an alkalinity titration, the buffering index is written

$$B = \frac{dC_A}{dpH} \qquad (3\text{--}43)$$

where dC_A is the incremental amount of strong acid added.

The ability of a particular system to buffer changes in pH varies as a function of pH. For weak acids and bases, the maximum buffering capacity occurs at pH values that equal the dissociation constants, pK_a or pK_b, of the weak acid or base. At $pH = pK_a$ (or pK_b), the ratio $[A^-]/[HA] = 1$ and is most resistant to change. The following example will illustrate this point.

EXAMPLE 3–14 We will return to Example 3–13, the carbonate buffer. In this case, the initial pH is 6.35, equivalent to the first dissociation constant for carbonic acid. The total carbonate content is 2×10^{-3} mol L^{-1}. At $pH = 6.35$, $H_2CO_{3\,(aq)}$ and HCO_3^- will be present in equal abundance. The activity of the CO_3^{2-} ion is negligible.

Hence, we can write

$$pH = -\log K_{a_1} + \log\left(\frac{\left[HCO_3^-\right]}{\left[H_2CO_{3\,(aq)}\right]}\right) = 6.35 + \log\left(\frac{\left[10^{-3.0}\right]}{\left[10^{-3.0}\right]}\right) = 6.35 + 0.0 = 6.35$$

We now add 10^{-5} mol of H^+ ions to 1 L of solution. After the addition we recalculate the pH:

$$pH = -\log K_{a_1} + \log\left(\frac{\left[HCO_3^-\right]}{\left[H_2CO_{3\,(aq)}\right]}\right)$$

$$= 6.35 + \log\left(\frac{\left[10^{-3.0} - 10^{-5.0}\right]}{\left[10^{-3.0} + 10^{-5.0}\right]}\right) = 6.35 + (-0.009) = 6.34$$

Because of the buffering capacity of the system, the pH has only changed by –0.01 units. Let us continue to add acid until the pH of the solution is reduced to 5.35. At this pH, $H_2CO_{3\,(aq)}$ is 10 times more abundant in the solution than HCO_3^-. Under these conditions, what is the effect of a 10^{-5} mol addition of H^+?

$$pH = -\log K_{a_1} + \log\left(\frac{\left[HCO_3^-\right]}{\left[H_2CO_{3\,(aq)}\right]}\right)$$

$$= 6.35 + \log\left(\frac{\left[1.818\times10^{-4.0} - 10^{-5.0}\right]}{\left[1.818\times10^{-3.0} + 10^{-5.0}\right]}\right) = 6.35 + (-1.03) = 5.32$$

In this case, the pH has changed by –0.03 pH units. Although not a large difference from the previous calculation, we can see that there has been a decrease in the buffering capacity of the solution. Repeating the calculation when pH = 4.35, with the same addition of acid, gives pH = 4.04, a change of –0.31 pH units, clearly showing the declining effectiveness of the buffer.

The derivation of the buffering index for various systems is not always straightforward. Several examples will be considered next. A more complete discussion can be found in Langmuir (1997). We will start with the simple system H_2O and then extend our analysis to include weak acids.

Buffering Index for H_2O

We start with pure water, which we titrate with a NaOH solution; i.e., we are determining the total acidity of water. In this example, and all the following examples, we will assume that activity equals concentration. The charge balance equation is

$$Na^+ + H^+ = OH^-$$

and $C_B = Na^+$, which represents the total amount of base added to the solution. Substituting into the charge balance equation we can write

$$C_B = OH^- - H^+ = \frac{K_w}{H^+} - H^+ \qquad (3\text{–}44)$$

Taking the derivative of both sides gives

$$dC_B = \left[-\frac{K_w}{(H^+)^2} - 1 \right] dH^+ \qquad (3\text{–}45)$$

pH = $-\ln(H^+)/2.3$, so $dH^+ = d$pH$[-2.3(H^+)]$. Substituting for dH^+ gives the final form of the equation:

$$B_{H_2O} = \frac{dC_B}{d\text{pH}} = 2.3 \left[\frac{K_w}{H^+} + H^+ \right] \qquad (3\text{–}46)$$

Equation 3–46 is easily solved on a spreadsheet for a range of pH values, and the result of such a computation is shown graphically in Figure 3–5. The buffering capacity of water is greatest at very low and very high pHs and quickly declines to essentially zero at intermediate pH values. Hence, in most natural waters, H_2O is not an important pH buffer.
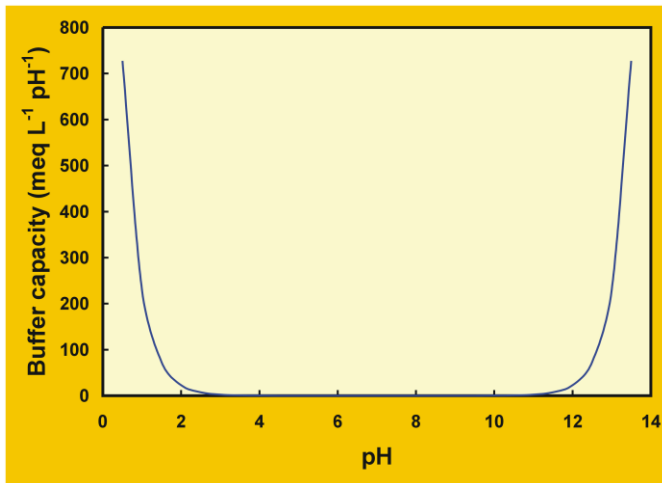

Figure 3–5 Variations in buffer capacity as a function of pH for water. Only at very low and very high pH values is water an important buffer.

Buffering Index for a Weak Monoprotic Acid

We start with a solution that contains a weak monoprotic acid (HA) and we determine its acidity by titrating with NaOH. The total acidity due to the weak acid is

$$C_A = HA + A^-$$

The charge balance equation for the system monoprotic weak acid plus water plus NaOH is

$$Na^+ + H^+ = A^- + OH^-$$

Because $C_B = Na^+$, we can write the charge balance equation as

$$C_B = A^- + OH^- - H^+$$

What we now want to do is express A^- in terms of hydrogen ions and the acidity (C_A). We do this by rearranging the equation for total acidity to give

$$HA = C_A - A^-$$

and then substituting for HA in the equilibrium equation:

$$K_a = \frac{(H^+)(A^-)}{(HA)} = \frac{(H^+)(A^-)}{(C_A - A^-)} \qquad (3-47)$$

Solving equation 3–47 for A^- gives

$$A^- = \frac{K_a C_A}{(K_a + H^+)} \qquad (3-48)$$

We now substitute into the charge balance equation:

$$C_B = A^- + OH^- - H^+ = \frac{K_a C_A}{(K_a + H^+)} + \frac{K_w}{H^+} - H^+ \qquad (3-49)$$

Taking the derivative of both sides,

$$dC_B = \left[-\frac{K_a C_A}{(K_a + H^+)^2} - \frac{K_w}{(H^+)^2} - 1 \right] dH^+ \qquad (3-50)$$

and rearranging gives

$$-\frac{dC_B}{dH^+} - \left[-\frac{K_a C_A}{\left(K_a + H^+\right)^2} + \frac{K_w}{\left(H^+\right)^2} - 1 \right] \tag{3-51}$$

Recalling that $dR^+ = dpH[-2.3(H^+)]$ and substituting for dH^+ gives the final form of the buffering index equation for a weak monoprotic acid:

$$B = \frac{dC_B}{dpH^+} = 2.3 \left[\frac{K_a C_A (H^+)}{\left(K_a + H^+\right)^2} + \frac{K_w}{H^+} + H^+ \right] \tag{3-52}$$

The first term in this equation describes the buffering index for the weak monoprotic acid; the second and third terms describe the buffering index for water. This equation is plotted for acetic acid in Figure 3–6 with $C_A = 1$ mol. As noted previously, acetic acid has its maximum buffering capacity at a pH equal to the pK_a for acetic acid.
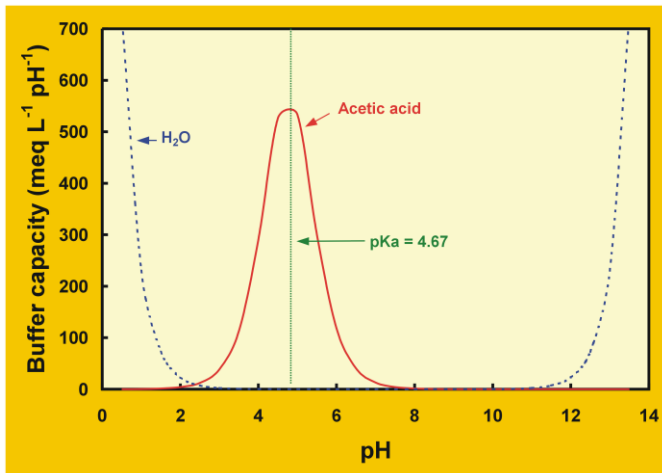

Figure 3–6 Variations in buffering capacity as a function of pH for water and acetic acid when C_A = 1 mol.

Buffering Index for Weak Polyprotic Acids

As long as the dissociation constants differ by a factor of 20 or more, the solution for the buffering index of polyprotic acids is analogous to equation 3–52. Additional terms are added to represent the additional dissociation steps. Equation (3–53) is for a diprotic acid. Note that there are now two terms at the beginning of the equation that describe the first and second dissociation for the

diprotic acid.

$$B = \frac{dC_B}{d\text{pH}^+} = 2.3\left[\frac{K_{a_1}C_A\left(\text{H}^+\right)}{\left(K_{a_1}+\text{H}^+\right)^2} + \frac{K_{a_2}C_A\left(\text{H}^+\right)}{\left(K_{a_2}+\text{H}^+\right)^2} + \frac{K_w}{\text{H}^+} + \text{H}^+ \right] \tag{3-53}$$

As previously mentioned, carbonic acid is one of the most important acids in the natural waters. Because carbonic acid is a diprotic acid, it will have two pH regions in which it acts as a buffer. The equation for carbonic acid is plotted in Figure 3–7 for $C_A = 1 \times 10^{-3}$ mol L^{-1}. Note the two regions of highest buffering capacity corresponding to $pK_{a_1} = 6.35$ and $pK_{a_2} = 10.33$, the first and second dissociation constants, respectively, of carbonic acid. At pH values less than 4.7 and greater than 10.4, the buffering capacity of water is greater than that of carbonic acid.
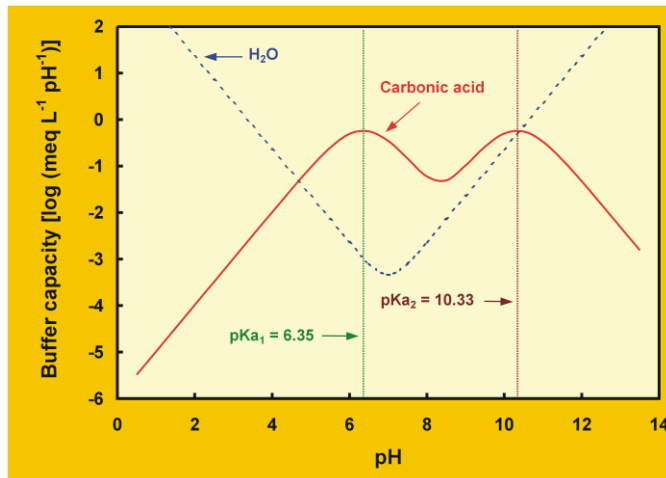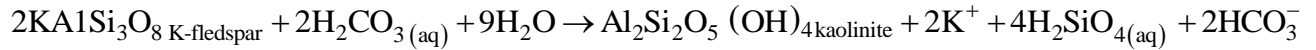

Figure 3–7 Variations in buffering capacity as a function of pH for the system carbonic acid–water when $C_A = 1 \times 10^{-3}$ mol L^{-1}.

MINERAL–WATER REACTIONS

So far we have considered buffering reactions that utilize dissolved species. On a longer time frame, we are also interested in acidity and alkalinity due to interactions between minerals and water. Most minerals can be considered to be salts of weak acids and strong bases, so these interactions contribute to the alkalinity of the water. There are several exceptions to this generality, particularly in the case of acid mine drainage, where minerals may be present that are salts of a

weak base and a strong acid. Such minerals would contribute to the acidity of the water.

Consider what happens when acidic waters come in contact with K-feldspar. This reaction can be written as follows:

$$2KAlSi_3O_8 \text{ K-fledspar} + 2H_2CO_3{}_{(aq)} + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 \text{ kaolinite} + 2K^+ + 4H_2SiO_4{}_{(aq)} + 2HCO_3^-$$

In the course of this reaction, carbonic acid is consumed and bicarbonate ion $\left(HCO_3^-\right)$ is formed. Also formed is silicic acid, but this acid is essentially undissociated in acidic waters. The net result of this reaction is the consumption of carbonic acid and an increase in bicarbonate ion. Thus, the weathering of feldspar tends to offset acid additions (reduces acidity). Carbonate minerals play a significant role in buffering acid additions, particularly because they react with water much more quickly than do the silicate minerals. A representative reaction is

$$CaCO_3 \text{ calcite} + H_2CO_3{}_{(aq)} \rightarrow Ca^{2+} + 2HCO_3^-$$
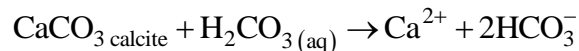
in which the carbonic acid reacts with calcite to form Ca^{2+} and bicarbonate ions. As in the case of the silicate minerals, carbonic acid is consumed and there is an increase in the bicarbonate ion.

Buffering Index for the Calcite–Carbonic Acid System

As has been noted, this important system controls the long-term pH of the ocean. It also exerts a significant influence on the pH of fresh waters in contact with limestone or in soils containing carbonate minerals. The full derivation will not be done here (it can be found in Langmuir, 1997). This calculation is for a calcite-saturated solution with fixed total carbonate. The solution is titrated with HCl; therefore, $C_A = Cl^-$. The charge balance equation is

$$2Ca^{2+} + H^+ = HCO_3^- + 2CO_3^{2-} + Cl^- + OH^-$$
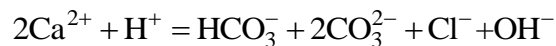
Substituting C_A for Cl^- and rearranging the charge balance equation in terms of C_A gives

$$C_A = H^+ - OH^- + 2Ca^{2+} - HCO_3^- - 2CO_3^{2-}$$
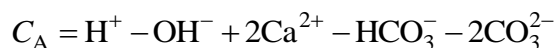
As we have done in the previous cases, we now carry out a set of substitutions so that the equation

is written in terms of the H$^+$ ion and then differentiate the resulting equation. After completion of these operations, the equation becomes

$$B = 2.3\left[(H^+) + \frac{K_w}{(H^+)}\right] + 2.3\left[\frac{C_T K_{a_2}^{-1}(H^+)\left[K_{a_1}^{-1}K_{a_2}^{-1}(H^+)^2 + 4K_{a_2}^{-1}(H^+) + 1\right]}{\left[K_{a_1}^{-1}K_{a_2}^{-1}(H^+)^2 + K_{a_2}^{-1}(H^+) + 1\right]^2}\right]$$

$$+ 2.3\left[\frac{(H^+)}{K_{cal}C_T}\left[2(H^+) + K_{a_1}\right]\right]$$
(3–54)

where C_T is the total carbonate concentration, K_{a_1} and K_{a_2} are the first and second dissociation constants for carbonic acid, and K_{cal} is the solubility constant for calcite. If we wanted to solve this equation for aragonite, we would use the aragonite solubility constant, K_{arag}. The equation has been written in three parts to illustrate the various components of the calculation. The first part represents the buffering capacity of water, the second the buffering capacity of carbonic acid, and the third the buffering capacity due to the dissolution of calcite. This system reacts relatively rapidly to changes in pH because calcite readily dissolves in acidic waters. Note that the dissolution of calcite tends to offset pH decreases. The precipitation of calcite is more difficult, so this system would not be as effective in mitigating pH increases. The buffering curve for the system calcite–carbonic acid, at 25°C and $C_T = 1 \times 10^{-3}$ mol L^{-1}, is shown in Figure 3–8.

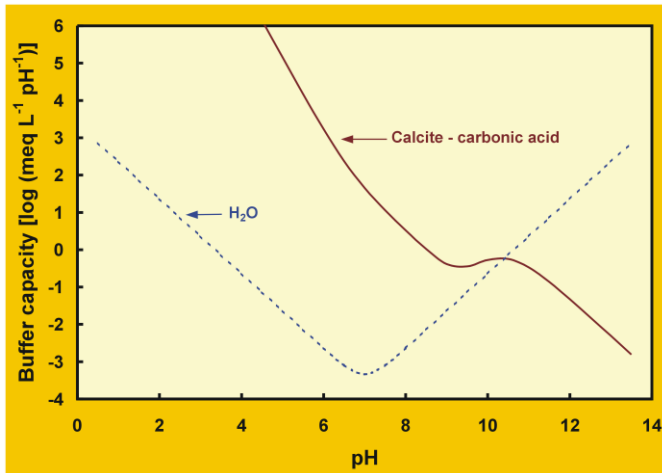**Figure 3–8** Variations in buffering capacity as a function of pH for the calcite–carbonic acid system. $C_T = 1 \times 10^{-3}$ mol L^{-1}.

EXAMPLE 3–15 Calculate the buffering index for the system calcite–carbonic acid at pH = 6, total carbonate $= 1 \times 10^{-2}$ mol L^{-1}, and $T = 25°C$. Select the appropriate equilibrium constants from Table 3–3 (for water) and Table 3–4 (for the carbonates). Solve for the buffering index using equation 3–54.
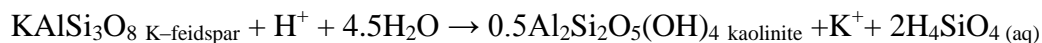
$$
\begin{aligned}
B &= 2.3\left[\left(H^+\right)+\frac{K_w}{\left(H^+\right)}\right]+2.3\left[\frac{C_T K_{a_2}^{-1}\left(H^+\right)\left[K_{a_1}^{-1}K_{a_2}^{-1}\left(H^+\right)^2+4K_{a_1}^{-1}\left(H^+\right)+1\right]}{\left[K_{a_1}^{-1}K_{a_2}^{-1}\left(H^+\right)^2+K_{a_2}^{-1}\left(H^+\right)+1\right]^2}\right] \\
&\quad +2.3\left[\frac{\left(H^+\right)}{K_{cal}C_T}\left[2\left(H^+\right)+K_{a_1}\right]\right] \\
&= 2.3\left[10^{-6}+\frac{10^{-13.995}}{10^{-6}}\right] \\
&\quad +2.3\left[\frac{10^{-2}10^{10.33}10^{-6}\left[10^{6.35}10^{-10.33}\left(10^{-6}\right)^2+4\times10^{6.35}10^{-6}+1\right]}{\left[10^{6.35}10^{10.33}\left(10^{-6}\right)^2+10^{10.33}10^{-6}+1\right]^2}\right] \\
&\quad +2.3\left[\frac{10^{-6}}{10^{-8.48}10^{-2}}\left[2\times10^{-6}+10^{-6.35}\right]\right] \\
&= 2.32\times10^{-6}+4.91\times10^{-3}+0.16994=0.17485\,\text{eq}\,L^{-1}\,\text{pH}^{-1} \\
&= 174.9\,\text{meq}\,L^{-1}\,\text{pH}^{-1}
\end{aligned}
$$

Buffering Index for Water–Silicate Mineral Systems

Various water-silicate mineral reactions can occur that tend to mitigate the effect of the acid addition. These reactions proceed much more slowly than those just discussed because of kinetic constraints. As examples of these types of buffers, consider the following reactions:

$$KAl_3Si_3O_{10}(OH)_2 \text{ muscovite} + H^+ + 1.5H_2O \rightarrow 1.5Al_2Si_2O_5(OH)_4 \text{ kaolinite} + K^+$$

and

$$KAlSi_3O_8 \text{ K–feidspar} + H^+ + 4.5H_2O \rightarrow 0.5Al_2Si_2O_5(OH)_4 \text{ kaolinite} + K^+ + 2H_4SiO_4 \text{ (aq)}$$

In the first reaction, hydrogen ions are consumed in the conversion of muscovite to the clay mineral kaolinite. In the second reaction, a common weathering reaction in humid temperate

climates, hydrogen ions are consumed when K-feldspar is weathered to kaolinite. Both reactions are essentially irreversible, so they will only buffer hydrogen ion additions, i.e., pH decreases. We start by calculating the equilibrium constants (at 25°C) for both reactions. In each case,

$$K_{eq} = \frac{\left[K^+ \right]}{\left[H^+ \right]}$$

because activity = 1 for the other species in both equations. We calculate the equilibrium constants as was done in Chapter 2. For this set of calculations, we will use the free–energy values of Robie et al. (1978) (Appendix II, source 3), an internally consistent set of thermodynamic data for calculations involving common minerals. For the muscovite–kaolinite reaction, $\Delta G_R^0 = -25.25 \text{ kJ mol}^{-1}$ and log K_{eq} = 4.42. For the K-feldspar–kaolinite reaction, $\Delta G_R^0 = 11.05 \text{ kJ mol}^{-1}$ and log $K_{eq} = -1.94$.

The buffering index will have the same form for both mineral pairs. Here we will derive the buffering index equation for the muscovite–kaolinite pair. We start by assuming that we are titrating a water–mineral mixture with HCl ($C_A = Cl^-$). The charge balance equation is

$$H^+ + K^+ = OH^- + Cl^-$$

The total acidity equation is

$$C_A = H^+ + K^+ - OH^-$$

Because $[K^+] = K_{eq}[H^+]$, substitution into the total acidity equation for K^+ and OH^- gives

$$C_A = K_{eq} \left[H^+ \right] + \left[H^+ \right] - \frac{K_w}{H^+} \qquad (3\text{–}55)$$

Taking the derivative and substituting for dH^+, as in previous examples, gives

$$B = 2.3 \left[\left(H^+ \right) + \frac{K_w}{\left(H^+ \right)} + K_{eq} \left(H^+ \right) \right] = 2.3 \left[\left(H^+ \right) + \frac{10^{-14}}{\left(H^+ \right)} + 10^{4.42} \left(H^+ \right) \right] \qquad (3\text{–}56)$$

For the K-feldspar–kaolinite reaction, we have a similar equation—the only difference is the value for the equilibrium constant. Silicic acid is not included in the buffer calculation because

only at very basic pH values would there be any significant dissociation to $H_3SiO_4^-$ (first dissociation constant $= 10^{-9.9}$). The buffering index equation for the K-feldspar–kaolinite pair is

$$B = 2.3\left[\left(H^+\right) + \frac{10^{-14}}{\left(H^+\right)} + 10^{-1.94}\left(H^+\right)\right] \qquad (3\text{--}57)$$

Equations 3–56 and 3–57 are plotted in Figure 3–9.

Buffering Capacities of Natural Waters

Figure 3–9 summarizes the results of our calculations of buffering reactions for natural waters. Several important generalizations can be made from this diagram. Except at very low or very high pH, water has little buffering capacity. In most natural waters carbonic acid is the most important system for buffering pH at intermediate values. If calcite is present in the system, there is a significant increase in buffering capacity. Hence, waters in contact with limestone, or soils containing carbonate minerals, will be very resistant to pH changes, particularly decreasing pH changes. Although they operate more slowly because of kinetic factors, clay– type minerals have significant buffering capacity for acid additions. Conversely, weathering reactions involving feldspar have very low buffering capacity (note from Figure 3–9 that the buffering capacity of the feldspar–kaolinite reaction is less than that of water). These are important observations in terms of the effect of acid additions on natural waters. In terrains where carbonates (and/or clay minerals) are present, there will be significant buffering of acid additions. In terrains underlain by rocks such as granite (quartz and feldspar minerals), buffering capacity will be nil. Hence, we would expect that lakes and streams draining limestones areas would be much less affected by acid rain than those draining granitic terrains.
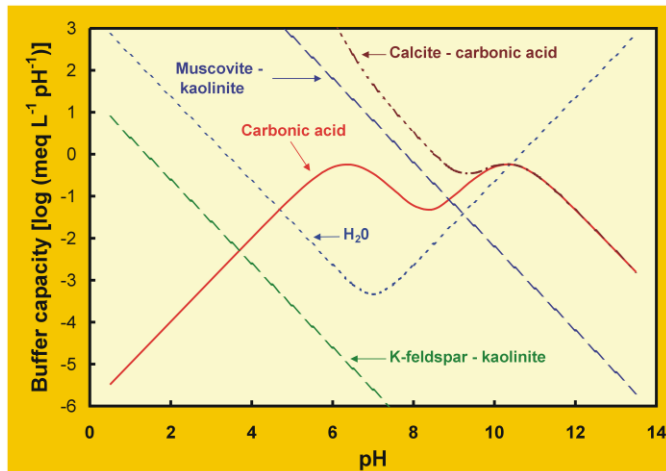
Figure 3–9 Summary of buffering reactions for natural waters containing carbonic acid and/or in contact with various minerals. Note the importance of the carbonate and clay minerals for buffering acid additions to natural waters

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Mineral Reactivity

A final factor to consider is the rate at which buffering reactions will occur. Carbonate minerals are generally considered to be highly reactive, particularly when present as minute grains. Using the reactivity of carbonate minerals as a reference point, Table 3–7 lists the relative reactivity, at pH = 5, for a number of common minerals. What is meant by relative reactivity is, under the given set of conditions, compared to calcite, how readily the mineral will react with the fluid. For minerals with low relative reactivity, there is little interaction between the fluid and the mineral. Even if these minerals were effective buffers, we would not expect them to have a significant effect on pH.

Table 3–7 Relative Reactivity of Common Minerals at pH = 5*

Mineral group	Typical minerals	Relative reactivity at pH 5
Dissolving	Calcite, aragonite, dolomite, magnesite, brucite	1.00
Fast weathering	Anorthite, nepheline, forsterite, olivine, garnet, jadeite, leucite, spodumene, diopside, wollastonite	0.40

Mineral group	Typical minerals	Relative reactivity at pH 5
Slow weathering	Plagioclase feldspars (albite, oligoclase, labradorite), clays (vermiculite, montmorillonite)	0.01
Very slow weathering	K-feldspars (orthoclase, microcline), muscovite	0.01
Inert	Quartz, rutile, zircon	0.004

*From Lawrence and Scheske (1997).

Lawrence and Scheske (1997) used relative reactivities to calculate the neutralization potential of mining wastes. This was done by using the normative mineralogy (weight abundance of ideal end-member minerals calculated from the chemical composition of the rock) and the relative reactivity of the various minerals to calculate a neutralization potential for the rock that could be compared to that of limestone. From a strictly kinetic point of view, rocks composed of reactive minerals would be more effective at neutralizing acid waters than those containing minerals of low relative reactivity.

EXAMPLE 3–16 A rock contains 24% (24 g/100 g) normative forsterite (Mg_2SiO_4). Calculate the contribution of the forsterite to the neutralization potential (NP) of the rock. NP values are expressed as kg $CaCO_3$-equivalent per 1000 kg of rock (1 ton).

In doing the calculation, we must take account of the differences in molecular weights.

$$
\begin{aligned}
\text{NP contribution} &= \frac{\text{Normative wt mineral}\,(g)}{100\,g} \times \frac{\text{mol wt calcite}}{\text{mol wt mineral}} \\
&\quad \times \frac{1000\,g}{\text{ton}} \times \text{relative reactivity} \\
&= \frac{24}{100} \times \frac{100.1}{140.7} \times 1000\,\text{kg ton}^{-1} \times 0.4 \\
&= 68.3\,\text{kg CaCO}_3\text{-equivalent ton}^{-1}
\end{aligned}
$$

ACID–BASE EQUILIBRIA CASE STUDIES

We conclude our discussion of acid–base equilibria with two case studies that illustrate the application of several concepts developed in this chapter to "real-world" problems. In Case Study 3–3, a model is developed for the attenuation of acid mine drainage by natural processes. In Case Study 3–4, the potential of deep saline aquifers as disposal sites for carbon dioxide and other acid gases is investigated.

CASE STUDY 3–3

A Process Model for the Natural Attenuation of Acid Mine Drainage

Berger et al. (2000) investigated the chemistry of acid mine drainage from an abandoned Cu-Pb-Zn mine located in the southern Sangre de Cristo mountains in New Mexico. Waste rock from the mining operation was piled on top of an existing drainage channel, and acid waters discharged directly from this waste pile. The waste rock is largely composed of quartz- chlorite and biotite schists. The underlying bedrock consists of a Pennsylvanian-age conglomeratic unit composed of siliclastic and carbonate components. Flow through the waste pile is essentially vertical, and atmospheric O_2 + rainwater react with the waste pile to produce acid waters and metal ions in solution. In the immediate vicinity of the waste pile, waters have a pH of 4.1 to 4.2. Willow Creek runs along the western edge of the site, and the contaminated waters enter this creek. Upstream from the site, Willow Creek waters have pH = 7.2. Given the relatively high pH of Willow Creek, simple mixing with Willow Creek water would lead to a pH increase and a dilution in the concentrations of the dissolved metals in the acid mine drainage. This pH increase may also cause the precipitation of metal ions as insoluble hydroxides, oxides, and sulfates. An additional factor affecting pH and the precipitation of metals is the interaction between the acid mine drainage and the carbonate component of the underlying bedrock. Field observations indicated that there had been acid water–carbonate interactions, as shown by the cracked and discolored nature of the limestone. The calcite dissolution reaction can be written

$$CaCO_{3\ calcite} + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_{2\ (aq)}$$
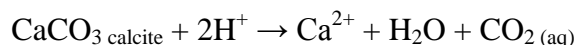
This reaction will lead to an increase in pH and will release Ca^{2+} ions to the water.

The authors investigated these questions by collecting water samples from several drainage channels and measuring the change in chemistry of the water samples. The assumption was made that SO_4^{2-} was a conservative component; i.e., its concentration was not affected by processes occurring in the water. Thus, sulfate concentration varies simply as a function of the ratio of contaminated water to uncontaminated water. For example, contaminated waters from the site had maximum sulfate concentrations of approximately 8400 mg L^{-1}, while uncontaminated Willow Creek water had sulfate concentrations on the order of 120 mg L^{-1}. A 50/50 mixture of contaminated and uncontaminated water would have a sulfate concentration of approximately 4260 mg L^{-1}. Plots of various components versus sulfate showed that Zn, Mg, and Mn behaved conservatively; Fe, Al, Pb, and to some degree Cu showed concentrations less than that expected by simple mixing. Ca concentrations exceeded those due to simple mixing. The elevated Ca concentrations led the authors to conclude that the dissolution of limestone was a factor in determining the pH of the acid mine drainage. The authors developed a reaction path model, illustrated in Figure 3–C3–1, to explain the variations in Ca^{2+}. In this model, calcite dissolution and mixing lead to an increase in pH to a value of 6; mixing alone leads to a final pH value of 7.2. Under these conditions Al, Cu, and Fe precipitate directly from solution. The authors concluded that the chemistry of the acid mine drainage was controlled by two processes: mineral buffering and mixing with ambient waters.
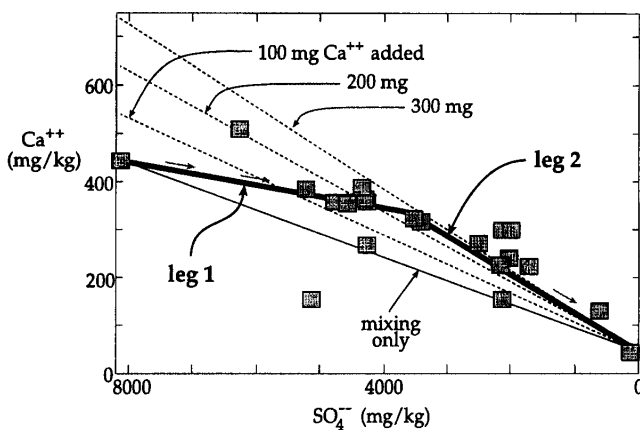

Figure 3–C3–1 Trend in Ca concentration predicted by the reaction path model. Dashed lines show simple mixing for fluids with different amounts of added Ca. Filled squares represent individual water samples. The reaction pathway is shown by the heavy line. In leg 1, Ca is added by dissolution of limestone. In leg 2, Ca concentrations change only by simple dilution. In leg 1,

2.5 kg of uncontaminated water and 250 mg of Ca are added to the solution. In leg 2, 12.5 kg of uncontaminated water is added. From Berger et al. (2000).
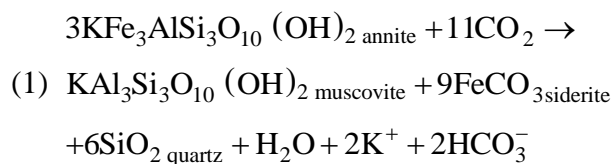
Source: Berger et al. (2000).
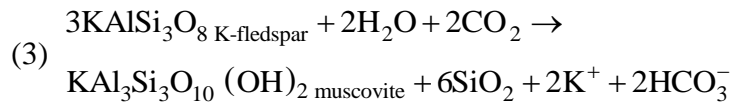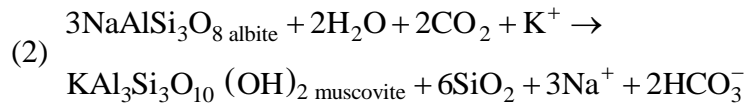

CASE STUDY 3–4

Aquifer Disposal of Acid Gases

Gunter et al. (2000) investigated the possibility of disposing of acid gases (CO_2, H_2SO_4 and H_2S) in deep saline aquifers in the Alberta sedimentary basin. Models were developed for the chemical reactions that would occur between these acid gases and two sedimentary reservoirs: the Glauconitic Sandstone aquifer, consisting of 87% quartz, 2% K-feldspar, 1% plagio-clase, 5% glauconite, 2% kaolinite, 1% calcite, 1% dolomite, and 1% siderite; and the Nisku carbonate aquifer, consisting predominantly of dolomite and/or calcite with or without accessory anhydrite, quartz, pyrite, and illite. The modeling was done using the reaction path computer model PATHARC.94 and a single injection of acid gases. The reaction between the acid gases and the carbonate aquifer was essentially instantaneous, while reactions with the Glauconitic Sandstone took hundreds of years to run to completion (Figure 3–C4–1). In the carbonate aquifer, the reaction involving CO_2 is

$$CaCO_{3\ calcite} + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^-$$

This reaction quickly reaches equilibrium (Figure 3–C4–1), but little CO_2 is removed from solution. In the model calculation, the reduction in CO_2 pressure is from 87 to 86 bars. Thus, carbonate rocks have little trapping capacity for CO_2. For the Glauconitic Sandstone, hundreds of years were required to reach equilibrium (Figure 3–C4–1), but in this case essentially all of the CO_2 is trapped by mineral reactions of the following types. In the calculations, muscovite was used as a proxy for illite.

$$3KFe_3AlSi_3O_{10}(OH)_{2\ annite} + 11CO_2 \rightarrow$$
$$(1)\quad KAl_3Si_3O_{10}(OH)_{2\ muscovite} + 9FeCO_{3\ siderite}$$
$$+6SiO_{2\ quartz} + H_2O + 2K^+ + 2HCO_3^-$$

$$(2) \quad 3NaAlSi_3O_{8\,albite} + 2H_2O + 2CO_2 + K^+ \rightarrow$$
$$KAl_3Si_3O_{10}(OH)_{2\,muscovite} + 6SiO_2 + 3Na^+ + 2HCO_3^-$$

$$(3) \quad 3KAlSi_3O_{8\,K\text{-}fledspar} + 2H_2O + 2CO_2 \rightarrow$$
$$KAl_3Si_3O_{10}(OH)_{2\,muscovite} + 6SiO_2 + 2K^+ + 2HCO_3^-$$

The calculations showed that the carbonate aquifer would not be a good trap for CO_2, but the Glauconitic Sandstone would be an effective trap.

Similar calculations were done for the disposal of SO_2 (as H_2SO_4). In the carbonate aquifer, the reaction is

$$CaCO_{3\,calcite} + H_2SO_4 \rightarrow CaSO_{4\,anhydrite} + H_2O + CO_2$$
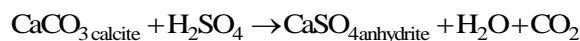
In this process CO_2 pressure builds up to substantial levels, in the model run to 80 bars. This is a significant overpressure that can fracture the rocks, thus permitting the escape of CO_2. Because the Glauconitic Sandstone also contained carbonate minerals, a similar reaction would occur. However, in this case reactions 1–3 would also occur, leading to the reduction of the CO_2 pressure to ambient values. Thus, the Glauconitic Sandstone is a potential trap for sulfuric acid.
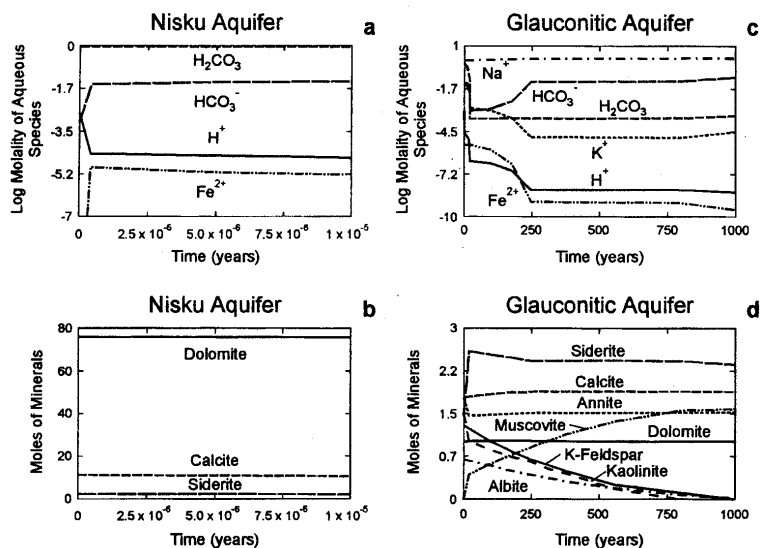
Source: Gunter et al. (2000).

Figure 3–C4–1 Water–rock reactions as a function of time. Initial input is 1 mol of CO_2 into 1 kg

of formation water.

(a) Variation in amounts of aqueous species and (b) minerals for the Nisku carbonate aquifer. (c) Variation in amounts of aqueous species and (d) minerals for the Glauconitic Sandstone aquifer. From Gunter et al. (2000).

QUESTIONS AND PROBLEMS

1. Distinguish between the *Arrhenius concept* and the *Brönsted–Lowry model* of acids and bases.

2. How does a strong acid differ from a weak acid?

3. Does a pH of 7 always indicate neutrality? Explain.

4. At 250°C, the equilibrium constant for the dissociation of water is $10^{-11.16}$ (Ohmoto et al., 1994). At this temperature, what is the pH of a neutral solution?

5. pH is referred to as an *environmental parameter*. What does this mean?

6. Most minerals can be considered to be salts of weak acids and strong bases. Identify the weak-acid and strong-base components in each of the following minerals:

   a. Olivine [Mg_2SiO_4]

   b. K-feldspar [$KAlSi_3O_8$]

   c. Diopside [$CaMgSi_2O_6$]

   d. Kaolinite [$Al_2Si_2O_5(OH)_4$]

7. In terms of the carbonic acid system, distinguish between an *open* system and a *closed* system.

8. Explain why the pH of surface waters increases when green plants in the water are actively photosynthesizing.

9. With reference to Case Study 3–1, explain the trends shown by waters from the NJ Coastal Plain and Floridian aquifers.

10. With reference to Case Study 3–2, explain why interactions between groundwaters and silicate

minerals would lead to a reduction in P_{CO_2}.

11. What is an *amphoteric hydroxide*?

12. Define *acidity* and *alkalinity.*

13. Why do titration curves for weak acids show regions in which large additions of base result in very small pH changes while in other regions small additions of base lead to large pH changes?

14. What is a *buffer?*

15. Define *buffering capacity.*

16. Refer to Figure 3–9 to answer this question. For waters of pH 4, 5.7, 7, 8.5, and 10, identify the most important buffer(s). Why did you choose these particular buffers?

17. What is meant by *mineral reactivity*?

18. In Case Study 3–3, the authors assumed that SO_4^{2-} was a conservative component. What does this mean?

19. With reference to Case Study 3–4, why would a limestone formation be a poor choice as a disposal site for CO_2? Why would a siliciclastic unit be a better choice?

20. With reference to Case Study 3–4, in terms of the various chemical reactions explain the observed variations in the mineral abundances with time (Figure 3–C4–1).

21. At 60°C, the pH of a water sample is 5.1. Calculate the concentration of the hydroxyl ion.

22. Calculate the concentration of H^+ ions in solution if 0.2 mol of formic acid (Table 3–1) is dissolved in 1 L of pure water. The water temperature is 25°C.

23. Calculate the concentration of OH^- ions in solution if 0.1 mol of ammonium (Table 3–2) is dissolved in 1 L of pure water. The water temperature is 25°C.

24. Water from a septic tank drainage field enters an aquifer. The water contains a significant amount of dissolved organic carbon. Oxidation of this dissolved organic carbon adds CO_2 to the groundwater. The system is effectively isolated from the atmosphere and after the

breakdown of the dissolved organic carbon, $P_{CO_2} = 10^{-2.5}$ atm. The temperature of the groundwater is 15°C. Calculate the pH of the groundwater.

25. A sandstone aquifer underlies an agricultural area. Extensive use of nitrogen fertilizer has led to a significant nitrogen burden in the groundwater of the sandstone aquifer. Denitrification has caused an increase in dissolved CO_2 in the groundwater. The measured $P_{CO_2} = 10^{-2}$ atm. The temperature of the groundwater is 20°C. Calculate the pH of the groundwater.

26. A water sample from a lake has a measured pH = 8.0 and $HCO_3^- = 22\,mg\,L^{-1}$. The water temperature is 15°C. Is the lake water in equilibrium with atmospheric CO_2 (a calculation is required)? What type of rock serves as the basin for the lake, and why did you chose this type of rock?

27. Calculate the concentration of each carbonate species in a solution at 20°C when $C_T = 3 \times 10^{-3}\,mol\,L^{-1}$ and pH = 6.2.

28. Water samples were collected from a series of wells drilled into a sandstone aquifer. Bicarbonate ion concentration and pH were measured for each water sample. The following table lists the data for the wells measured in the downdip (1 → 7) direction. Plot pH versus HCO_3^- in millimoles L^{-1}. You will first have to convert the concentration of HCO_3^- to millimoles L^{-1}. Draw a smooth curve through the data. For each water sample, calculate the P_{CO_2} Assume the water temperature is 25°C. Interpret the data. You may want to refer to Case Study 3–1 when you do this problem.

Well	pH	$HCO_3^- \left(mg\,L^{-1} \right)$	$HCO_3^- \left(1 \times 10^{-3}\,mol\,L^{-1} \right)$	P_{CO_2} (atm)
1	5.7	92		
2	6.0	122		
3	6.4	171		
4	6.9	220		
5	7.3	244		
6	7.7	262		

Well	pH	$HCO_3^-\ (mg\ L^{-1})$	$HCO_3^-\ (1 \times 10^{-3}\ mol\ L^{-1})$	$P_{CO_2}\ (atm)$
7	8.0	275		

29. Calculate the relative abundance of $H_4SiO_{4\ (aq)}$ to $H_3SiO_4^-$ at pH $= 8.2$. $T\ =\ 25°C$.

30. A river contains 10.5 mg L^{-1} of dissolved silica (as SiO_2). The measured pH $= 6.5$ and the water temperature is 25°C. Calculate the concentration of each silica species in solution.

31. Calculate the pH of a solution saturated in calcite and in equilibrium with atmospheric CO_2. The temperature of the solution is 5°C.

32. A water sample collected from a well has $T\ =\ 25°C$, pH $=\ 7.9$, $Ca^{2+}\ =\ 96$ mg L^{-1} and $HCO_3^-\ =\ 30$ mg L^{-1}. With reference to Case Study 3–2, calculate the P_{CO_2} for the water sample using both the HCO_3^- and Ca^{2+} concentrations. Do the calculations agree? Is this sample in equilibrium with atmospheric CO_2?

33. A water sample collected from a well has $T\ =\ 12°C$, pH $=\ 7.9$, $Ca^{2+}\ =\ 61$ mg L^{-1}, and $HCO_3^-\ =\ 48$ mg L^{-1}. With reference to Case Study 3–2, calculate the P_{CO_2} for the water sample using both the HCO_3^- and Ca^{2+} concentrations. Note that the equations in Case Study 3–2 are for 25°C. These will have to be modified because of the temperature difference. The equation for the bicarbonate ion can be modified using Henry's law (Table 2–1) and the carbonate equilibria constants in Table 3–4. The equation for the Ca ion can be modified by using Henry's law (Table 2–1) and the solubility products for calcite from Table 3–4. Do the calculations agree? Is this sample in equilibrium with atmospheric CO_2?

34. $CU(OH)_{2\ (s)}$ is an amphoteric compound and dissolves according to the following reaction:

$$Cu(OH)_{2\ (s)} + OH^- \rightarrow Cu(OH)_3^-$$

For the following calculations assume that the water temperature is 25°C.

a. Excess copper hydroxide is added to beaker of water; i.e., solid copper hydroxide is present in the water. Using a base, the solution pH is adjusted to 10. Calculate the concentration of

$Cu(OH)_3^-$ in the solution at equilibrium. Equilibrium constants for amphoteric compounds are found in Table 3–6.

b. A strong acid is added to the solution until the pH is reduced to 4. At this pH, calculate the concentration of $Cu(OH)_3^-$ in the solution. Will the amount of $Cu(OH)_{2\ (S)}$ in the beaker increase or decrease? Explain.

35. Calculate the total acidity and total alkalinity of a carbonic acid solution for which $C_T = 3 \times 10^{-3}$ mol L^{-1}, $T = 20°C$, and pH = 6.2. If you did problem 27 you have already calculated the abundance of the various carbonate species.

36. Calculate the buffering index for a solution containing 1×10^{-2} mol L^{-1} of acetic acid when the solution pH = 5 and $T = 25°C$.

37. Calculate the buffering index, as a function of pH, for an aqueous solution containing 1×10^{-2} mol L^{-1} of acetic acid at 25°C. This problem is easily done on a spreadsheet.

38. Calculate the buffering index for a solution containing 1×10^{-2} mol L^{-1} of silicic acid at pH = 7, $T = 25°C$. Assume that only the first two dissociation steps are significant.

39. Calculate the buffering index, as a function of pH, for an aqueous solution containing 1×10^{-2} mol L^{-1} silicic acid at 25°C. Assume that only the first two dissociation steps are significant. This problem is easily done on a spreadsheet.

40. Calculate the buffering index for the system calcite–carbonic acid at pH = 8.2, total carbonate $= 1 \times 10^{-2}$ mol L^{-1}, and $T = 15°C$. Select the appropriate equilibrium constants from Table 3–3 (for water) and Table 3–4 (for the carbonates).

41. Calculate the buffering index, as a function of pH, for the system calcite–carbonic acid with total carbonate $= 1 \times 10^{-2}$ mol L^{-1} and $T = 15°C$. Select the appropriate equilibrium constants from Table 3–3 (for water) and Table 3–4 (for the carbonates). This problem is easily done on a spreadsheet.

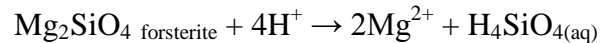**42.** Calculate the buffering index for the reaction

$$KAl_3Si_3O_{10}(OH)_{2\ muscovite} + H^+ + 1.5H_2O \rightarrow 1.5Al_2Si_2O_5(OH)_{4 kaolinite} + K^+$$

at pH = 5.7. $T = 25°C$.

43. Derive the buffering index equation for the reaction

$$Al_2Si_2O_5(OH)_{4 \text{ kaolinite}} + 6H^+ \rightarrow 2Al^{3+} + 2H_4SiO_{4(aq)} + H_2O$$
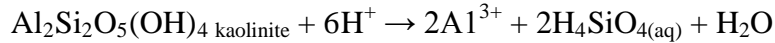
and at pH = 3.5, calculate the buffering index for the reaction. Use the thermodynamic data from Appendix II, source 3. $T = 25°C$.

44. Derive the buffering index equation for the reaction

$$Mg_2SiO_{4 \text{ forsterite}} + 4H^+ \rightarrow 2Mg^{2+} + H_4SiO_{4(aq)}$$

and at pH = 5.0, calculate the buffering index for the reaction. Use the thermodynamic data from Appendix II, source 3. $T = 25°C$.

45. Use the model of Lawrence and Scheske (1997) to calculate the acid neutralization potential of waste rock from a sulfide ore deposit that has the following mineralogical composition:

Quartz (SiO_2)—26%

Orthoclase ($KAlSi_3O_8$)— 10%

Albite ($NaAlSi_3O_8$)—13%

Anorthite ($CaAl_2Si_2O_8$)—11%

Diopside ($CaMgSi_2O_6$)—4%

Hypersthene ($MgSiO_3$)—26%

Calcite ($CaCO_3$)—10%