

**STATE OF NEW MEXICO
BEFORE THE WATER QUALITY CONTROL COMMISSION**

In the Matter of:)
)
)
)
PROPOSED AMENDMENT)
TO 20.6.2 NMAC (Copper Rule))
)
_____)

No. WQCC 12-01(R)

EXHIBIT FINLEY - 5

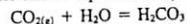
4

The Carbonate System and pH Control

CARBONIC ACID SYSTEM

The pH of most natural waters is controlled by reactions involving the carbonate system. The carbonate system is also used here as an example of acid-base systems in general; the relationships developed for carbonate equilibria can be used with little modification for equilibria involving such species as phosphate, sulfide, and silicic acid.

When CO₂ gas is brought into contact with water, the CO₂ will dissolve until equilibrium is reached. At equilibrium, the concentration (or, more strictly, activity) of dissolved carbon dioxide will be proportional to the pressure (or, more strictly, fugacity) of CO₂ in the gas phase. At earth-surface conditions, the difference between partial pressure and fugacity can be ignored. The normal convention is to refer to all dissolved carbon dioxide as H₂CO₃ (carbonic acid), and thus the dissolution of carbon dioxide in water can be represented by the equation



for which an equilibrium constant can be written

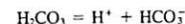
$$K_{\text{CO}_2} = \frac{a_{\text{H}_2\text{CO}_3}}{P_{\text{CO}_2} a_{\text{H}_2\text{O}}} \quad (4-1)$$

For dilute solutions, $a_{\text{H}_2\text{O}}$, the activity of water, is very close to 1 (in seawater, it is 0.98, for example); deviations from 1 will be ignored here. In fact, most of the dissolved carbon dioxide is in the form of solvated CO₂ rather than H₂CO₃, but provided that equilibrium is established, the exact chemical form of dissolved carbon dioxide does not affect the equilibrium relationships presented here. It is convenient to adopt the convention that dissolved carbon dioxide is all H₂CO₃, and to use equilibrium constants consistent with this convention. Equation (4-1) thus simplifies to

$$a_{\text{H}_2\text{CO}_3} = K_{\text{CO}_2} P_{\text{CO}_2} \quad (4-2)$$

Thus for every P_{CO_2} , there is a corresponding $a_{\text{H}_2\text{CO}_3}$, and for every $a_{\text{H}_2\text{CO}_3}$, there is a corresponding P_{CO_2} . In the literature, it is quite common to report $a_{\text{H}_2\text{CO}_3}$, as the corresponding P_{CO_2} , even when no gas phase is present.

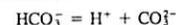
Since H₂CO₃ is an acid, it will tend to dissociate into hydrogen and bicarbonate ions:



An equilibrium constant can be written for this reaction:

$$K_1 = \frac{a_{\text{H}^+} a_{\text{HCO}_3^-}}{a_{\text{H}_2\text{CO}_3}} \quad (4-3)$$

Bicarbonate ion itself dissociates also:



$$K_2 = \frac{a_{\text{H}^+} a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}} \quad (4-4)$$

Numerical values for K_{CO_2} , K_1 , and K_2 are listed in Table 4-1.

From Eqs. (4-3) and (4-4), the ratios $a_{\text{H}_2\text{CO}_3}/a_{\text{HCO}_3^-}$ and $a_{\text{HCO}_3^-}/a_{\text{CO}_3^{2-}}$ depend on the pH of the solution. When we talk about pH as an independent variable, we are no longer talking about the system CO₂-H₂O. To obtain a pH above 7, for example, it is necessary to introduce some cation other than H⁺. If we consider a solution containing a total activity of dissolved carbonate species of 10⁻², we can calculate the activity of each individual species as a function of pH:

$$10^{-2} = a_{\text{H}_2\text{CO}_3} + a_{\text{HCO}_3^-} + a_{\text{CO}_3^{2-}}$$

TABLE 4-1 EQUILIBRIUM CONSTANTS* FOR THE CARBONATE SYSTEM
($pK = -\log_{10} K$) (after Plummer and Busenberg, 1982)

T (°C)	pK_{CO_2}	pK_1	pK_2	pK_{cal}	pK_{org}	$pK_{\text{CaHCO}_3^+}$ ^b	$pK_{\text{CaCO}_3^0}$ ^c
0	1.11	6.58	10.63	8.38	8.22	-0.82	-3.13
5	1.19	6.52	10.55	8.39	8.24	-0.90	-3.13
10	1.27	6.46	10.49	8.41	8.26	-0.97	-3.13
15	1.34	6.42	10.43	8.43	8.28	-1.02	-3.15
20	1.41	6.38	10.38	8.45	8.31	-1.07	-3.18
25	1.47	6.35	10.33	8.48	8.34	-1.11	-3.22
30	1.52	6.33	10.29	8.51	8.37	-1.14	-3.27
45	1.67	6.29	10.20	8.62	8.49	-1.19	-3.45
60	1.78	6.29	10.14	8.76	8.64	-1.23	-3.65
80	1.90	6.34	10.13	8.99	8.88	-1.28	-3.92
90	1.94	6.38	10.14	9.12	9.02	-1.31	-4.05

* based on the infinite dilution standard state

^b $K_{\text{CaHCO}_3^+} = a_{\text{CaHCO}_3^+} / (a_{\text{Ca}^{2+}} a_{\text{HCO}_3^-})$

^c $K_{\text{CaCO}_3^0} = a_{\text{CaCO}_3^0} / (a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}})$

From Eq. (4-3),

$$\frac{a_{\text{H}_2\text{CO}_3}}{a_{\text{HCO}_3^-}} = \frac{a_{\text{H}^+}}{K_1} = 10^{+6.35} a_{\text{H}^+} \quad \text{at } 25^\circ\text{C}$$

Ignoring CO_3^{2-} for the moment and rounding the value of K_1 to $10^{-6.4}$, at a pH of 6.4 the activity of H_2CO_3 will equal that of HCO_3^- :

$$\frac{a_{\text{H}_2\text{CO}_3}}{a_{\text{HCO}_3^-}} = \frac{10^{-6.4}}{10^{-6.4}} = 1$$

$$a_{\text{H}_2\text{CO}_3} + a_{\text{HCO}_3^-} = 10^{-2}$$

$$a_{\text{H}_2\text{CO}_3} = a_{\text{HCO}_3^-} = 0.5 \times 10^{-2} = 10^{-2.3}$$

Similarly, at pH 5.4,

$$\frac{a_{\text{H}_2\text{CO}_3}}{a_{\text{HCO}_3^-}} = \frac{10^{-5.4}}{10^{-6.4}} = 10^{+1}$$

$$a_{\text{H}_2\text{CO}_3} + a_{\text{HCO}_3^-} = 10^{-2}$$

$$a_{\text{H}_2\text{CO}_3} = 0.9 \times 10^{-2} = 10^{-2.05}$$

$$a_{\text{HCO}_3^-} = 0.1 \times 10^{-2} = 10^{-3}$$

The same procedure at pH 4.4 gives

$$a_{\text{H}_2\text{CO}_3} = 10^{-2.004}$$

$$a_{\text{HCO}_3^-} = 10^{-4}$$

At pH 7.4,

$$a_{\text{H}_2\text{CO}_3} = 10^{-3}$$

$$a_{\text{HCO}_3^-} = 10^{-2.05}$$

and at pH 8.4,

$$a_{\text{H}_2\text{CO}_3} = 10^{-4}$$

$$a_{\text{HCO}_3^-} = 10^{-2.004}$$

Thus it is only at pH values close to 6.4 that both species are present at comparable activities (and hence concentrations). Below pH 6, essentially all the dissolved carbonate species are in the form of H_2CO_3 , and above pH 7 essentially all are in the form of HCO_3^- .

For the $\text{HCO}_3^-/\text{CO}_3^{2-}$ pair, Eq. (4-4) gives

$$\frac{a_{\text{HCO}_3^-}}{a_{\text{CO}_3^{2-}}} = \frac{a_{\text{H}^+}}{10^{-10.33}}$$

This equation is exactly analogous to the one for $\text{H}_2\text{CO}_3/\text{HCO}_3^-$, except that the crossover point is at pH 10.33 rather than 6.4. Above pH 10.33, the activity of HCO_3^- rapidly becomes small, and below pH 10.33 the activity of CO_3^{2-} rapidly becomes small. These relationships are displayed in Fig. 4-1. This type of graph is sometimes called a *Bjerrum plot*. Since the crossover points are far apart, we were quite justified in ignoring CO_3^{2-} when discussing the $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ pair and in ignoring H_2CO_3 when discussing the $\text{HCO}_3^-/\text{CO}_3^{2-}$ pair.

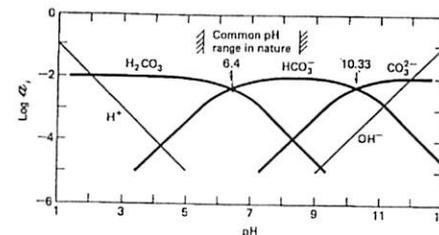


Figure 4-1 Activities of different species in the carbonate system as a function of pH, assuming $\Sigma\text{CO}_3 = 10^{-2}$, temperature = 25°C . Activities of H^+ and OH^- are defined by pH. This diagram is an example of a Bjerrum plot.

An important conclusion from Fig. 4-1 is that in most natural waters the CO_3^{2-} concentration is small compared to the HCO_3^- concentration. It is only in unusual, generally saline, waters that pH values above 9 are encountered.

ALKALINITY AND TITRATION CURVES

We mentioned in the preceding section that solutions with pH values greater than 7 must contain cations other than H^+ . This can be seen from considerations of charge balance. It is a fundamental principle of solution chemistry that solutions are electrically neutral, that is, that the total number of positive charges carried by cations must equal the total number of negative charges carried by anions:

$$\sum m_i z_i = 0$$

where m is the concentration and z the charge of the i th ion.

For the system $\text{H}_2\text{O}-\text{CO}_2$, the charge balance equation is

$$m_{\text{H}^+} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-}$$

At pH 7, $m_{\text{H}^+} = m_{\text{OH}^-}$ (the dissociation constant of water, K_w , is 10^{-14} at 25°C). Thus, if $m_{\text{HCO}_3^-}$ or $m_{\text{CO}_3^{2-}}$ has any finite value, m_{H^+} must be correspondingly greater than m_{OH^-} , and the solution will have a pH lower than 7. If we introduce sodium into the system, the charge balance equation becomes

$$m_{\text{H}^+} + m_{\text{Na}^+} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-}$$

and there are no immediate constraints on the value of m_{H^+} and hence pH. For solutions that are approximately neutral, m_{H^+} , m_{OH^-} , and $m_{\text{CO}_3^{2-}}$ are generally negligible compared to m_{Na^+} and $m_{\text{HCO}_3^-}$. In this case the charge balance equation simplifies to

$$m_{\text{Na}^+} = m_{\text{HCO}_3^-}$$

Equations (4-2) and (4-3) can be combined to give

$$a_{\text{H}^+} a_{\text{HCO}_3^-} = K_1 K_{\text{CO}_2} P_{\text{CO}_2}$$

Thus, at constant P_{CO_2} , hydrogen ion activity is inversely related to bicarbonate concentration. In the absence of other anions such as Cl^- and SO_4^{2-} , the total cation concentration (weighted according to charge) will approximately equal the bicarbonate concentration, and hence pH and salinity in bicarbonate-rich waters are inversely related.

The charge balance equation can be extended to cover all dissolved species:

$$\begin{aligned} m_{\text{Na}^+} + m_{\text{K}^+} + 2m_{\text{Ca}^{2+}} + 2m_{\text{Mg}^{2+}} + \dots \\ = m_{\text{Cl}^-} + 2m_{\text{SO}_4^{2-}} + m_{\text{NO}_3^-} + m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-} \\ + m_{\text{B(OH)}_4^-} + m_{\text{H}_2\text{SiO}_4} + m_{\text{HS}^-} + m_{\text{organic anions}} + \dots \end{aligned} \quad (4-5)$$

Ions such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , and NO_3^- can be regarded as "conservative" in the sense that their concentrations are unaffected by changes in pH, pressure, or temperature (within the ranges normally encountered near the earth's surface and assuming no precipitation or dissolution of solid phases, or biological transformations). Complex formation (Chapter 2) will not affect the charge balance equation provided that total analytical concentrations of each species are used.

Equation (4-5) can be written

$$\begin{aligned} \sum \text{conservative cations (in equivalents)} - \sum \text{conservative anions (in equivalents)} \\ = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{B(OH)}_4^-} + m_{\text{H}_2\text{SiO}_4} + m_{\text{HS}^-} \\ + m_{\text{organic anions}} + m_{\text{OH}^-} - m_{\text{H}^+} \end{aligned} \quad (4-6)$$

The expression on the right side of Eq. (4-6) is the *total alkalinity*, which is formally defined as the equivalent sum of the bases that are titratable with strong acid (Stumm and Morgan, 1981). If the pH of the solution is progressively lowered by addition of a strong acid (HCl, for example), all the anions on the right will be converted to uncharged species [H_2CO_3 , B(OH)_3 , H_2SiO_4 , H_2S , organic acids, H_2O]. The amount of acid required to complete the conversion can easily be measured (see below), so that total alkalinity can easily be measured. Also, since the terms on the left side of Eq. (4-6) are not affected by changes in P or T , total alkalinity must also be unaffected by changes in P and T . Total alkalinity is thus a conservative quantity. Note that the individual terms on the right side of Eq. (4-6) are not conservative. A change in T , for example, will cause a change in K_2 , which will cause a change in the ratio $m_{\text{HCO}_3^-}/m_{\text{CO}_3^{2-}}$.

In most natural waters, borate, ionized silicic acid, bisulfide, organic anions, hydrogen ion, and hydroxyl ion are present in concentrations that are very small compared to bicarbonate and carbonate. Under these circumstances

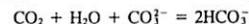
$$\text{Alkalinity} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}}$$

The expression $(m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}})$ is the *carbonate alkalinity*. In most natural waters

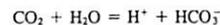
$$\text{Carbonate alkalinity} \cong \text{total alkalinity}$$

and hence carbonate alkalinity is generally conservative. Alkalinity is independent

of P_{CO_2} , because P_{CO_2} is not involved directly in the charge balance equation. Although an increase in P_{CO_2} will cause an increase in $m_{\text{HCO}_3^-}$, the reaction is either



or



In the first case, the alkalinity gained by increasing $m_{\text{HCO}_3^-}$ is exactly balanced by the alkalinity lost by decreasing $m_{\text{CO}_3^{2-}}$. In the second case, the increased HCO_3^- is balanced by increased H^+ , so the net effect on alkalinity is zero.

Total dissolved carbonate species, ΣCO_2 , is also a conservative quantity, provided that the solution cannot exchange with a gas phase.

$$\Sigma\text{CO}_2 = m_{\text{H}_2\text{CO}_3} + m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}}$$

ΣCO_2 simply represents the sum of all dissolved oxidized carbon species. It can change only if oxidized carbon is added to or removed from the solution. It could also change by oxidation-reduction reactions involving organic carbon, but such reactions are in a different class from those considered in defining conservative species.

Alkalinity Titration

The alkalinity titration is an important analytical procedure in natural-water chemistry. The titration curve also provides insights into pH stability and buffering, so we shall consider it in some detail.

Problem. Suppose that we have 1 l of a 5×10^{-3} m solution of Na_2CO_3 in a closed container with no gas phase present, and add ν ml of 1M HCl. How does the pH vary with ν , assuming that activity coefficients are all unity, no gas phase forms, and the total volume remains effectively 1 l?

Starting conditions (before addition of any acid):

$$m_{\text{Na}^+} = 10^{-2}, \quad \Sigma\text{CO}_2 = 5 \times 10^{-3} \text{ m}$$

The charge balance equation is

$$m_{\text{Na}^+} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-} - m_{\text{H}^+}$$

Until HCl is added, m_{H^+} will be negligible compared to the other terms; therefore,

$$m_{\text{Na}^+} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-} \quad (4-7)$$

$$\Sigma\text{CO}_2 = m_{\text{H}_2\text{CO}_3} + m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}} \quad (4-8)$$

Since a solution of Na_2CO_3 will be alkaline, we can provisionally assume that $m_{\text{H}_2\text{CO}_3}$ will be small compared to $m_{\text{HCO}_3^-}$ and $m_{\text{CO}_3^{2-}}$. Equation (4-8) then becomes

$$\Sigma\text{CO}_2 = m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}} \quad (4-9)$$

Multiplying Eq. (4-9) by 2 and subtracting from Eq. (4-7) gives

Since $m_{Na^+} = 2 \Sigma CO_2$ (there are two Na atoms per CO_3 in Na_2CO_3),

$$(4-10) \quad m_{Na^+} = m_{OH^-} - m_{HCO_3^-} + m_{OH^-}$$

The result of Eq. (4-10) can also be deduced intuitively; if any CO_3^{2-} is converted to HCO_3^- , there will be a net loss of one negative charge per molecule converted. Since HCO_3^- solution must remain electrically neutral, an additional unit of charge must come from somewhere. The only possibility is formation of OH^- , so one OH^- ion must be formed for each HCO_3^- that is formed from CO_3^{2-} .

Equation (4-4) is (assuming that activities equal concentrations)

$$K_2 = \frac{m_{H^+} m_{CO_3^{2-}}}{m_{HCO_3^-}}$$

Substituting Eq. (4-10) gives

$$(4-11) \quad K_2 = \frac{K_w}{m_{H^+} m_{CO_3^{2-}}}$$

Substituting Eq. (4-11) into (4-7) gives

$$m_{Na^+} = \frac{K_w}{K_a} + \frac{m_{H^+}}{2K_2 K_a} + \frac{K_w}{m_{H^+}}$$

Substituting numerical values for m_{Na^+} and the equilibrium constants and solving the resulting quadratic gives

$$m_{H^+} = 10^{-10.96}$$

The pH of the solution before adding any acid would be 10.96. At this pH the assumption that $m_{HCO_3^-}$ could be ignored in the expression for ΣCO_2 is obviously justified. When we start to add acid, the H^+ in the acid will be involved in reaction, and the Cl^- will simply accumulate. After v ml of acid has been added, the charge balance equation will be

$$(4-12) \quad m_{Na^+} - m_{Cl^-} = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{OH^-} - m_{H^+}$$

$$10^{-2} - 10^{-3} v = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{OH^-} - m_{H^+}$$

Equations (4-3) and (4-4) can be rewritten as

$$(4-13) \quad m_{HCO_3^-} = \frac{m_{H^+}}{K_1 m_{H_2CO_3}}$$

$$(4-14) \quad m_{CO_3^{2-}} = \frac{m_{H^+}}{K_2 m_{HCO_3^-}}$$

Substituting Eq. (4-13) in (4-14) gives

$$(4-15) \quad m_{CO_3^{2-}} = \frac{m_{H^+}}{K_1 K_2 m_{H_2CO_3}}$$

Substituting (4-13) and (4-15) and the expression for K_a in (4-12) gives

$$(4-16) \quad 10^{-2} - 10^{-3} v = \frac{K_1 m_{H_2CO_3}}{K_1 m_{H_2CO_3}} + \frac{m_{H^+}}{10^{-14}} + 10^{-14} - m_{H^+}$$

and substituting (4-13) and (4-15) in (4-8) gives

$$(4-17) \quad 5 \times 10^{-3} = m_{H_2CO_3} + \frac{K_1 m_{H_2CO_3}}{K_1 m_{H_2CO_3}} + \frac{m_{H^+}}{K_1 K_2 m_{H_2CO_3}}$$

Elimination of $m_{H_2CO_3}$ between (4-16) and (4-17) gives

$$(4-18) \quad 10^{-2} v = 10^{-2} - \frac{5 \times 10^{-3} K_1 (1 + 2K_2/m_{H^+})}{10^{-14}} - \frac{m_{H^+}}{10^{-14}} + m_{H^+}$$

Values for m_{H^+} can be substituted directly into (4-18) to give the graph shown in Fig. 4-2. Figure 4-2 also includes the Bjerrum plot discussed earlier.

The titration curve contains two inflections, or end points, at pH values of 8.35 and 4.32. The corresponding volumes of acid are 5 and 10 ml. At the first end point, we have added just enough acid to convert all the CO_3^{2-} to HCO_3^- , and at the second end point, we have converted all the HCO_3^- (derived from CO_3^{2-}) to H_2CO_3 . The expression "converted all the CO_3^{2-} to HCO_3^- " is confusing at first, as some CO_3^{2-} remains at all pH values. The actual equivalence condition is that

$$m_{CO_3^{2-}} = m_{H_2CO_3}$$

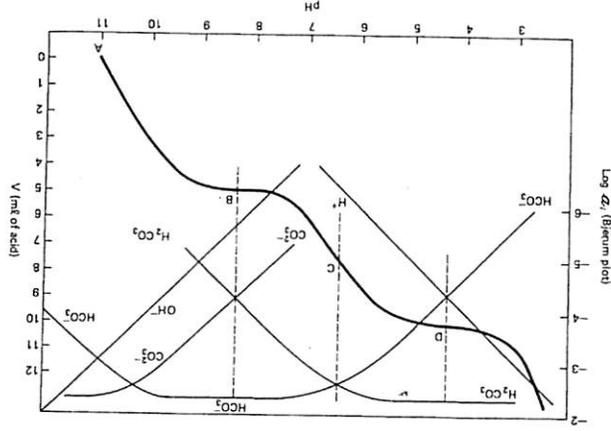


Figure 4-2. Titration curve (heavy line ABCD) for 5×10^{-3} M Na_2CO_3 with acid, and Bjerrum plot for $\Sigma CO_2 = 5 \times 10^{-3}$. B is carbonate end point, C is region of strong buffering, and D is bicarbonate end point.

In terms of proton balance, 1 unit of CO_3^{2-} plus 1 unit of H_2CO_3 is equivalent to 2 units of HCO_3^- , so that, at the equivalence point, all the dissolved carbonate species are effectively HCO_3^- . Note that on Fig. 4-2 the inflection point on the titration curve corresponds to the point on the Bjerrum plot where $m_{\text{CO}_3^{2-}} = m_{\text{H}_2\text{CO}_3}$. By similar reasoning, the second end point corresponds to the condition $m_{\text{H}^+} = m_{\text{HCO}_3^-}$, so all the dissolved carbonate species are effectively H_2CO_3 .

For purposes of chemical analysis, the carbonate concentration and alkalinity can be determined by titration to the two end points. At the end points, the pH changes rapidly with small additions of acid, so that determination of the exact equivalence pH is not critical unless a high degree of accuracy is required. Traditionally, the carbonate concentration has been measured by titration to the point where the indicator phenolphthalein changes color (pH approximately 9), and alkalinity by the indicator methyl orange end point (pH approximately 4). More accurate analyses use a pH electrode rather than indicators, and either the titration curve is drawn out in full, or the titration is performed to a particular pH that is known to be close to the correct end point. For the highest accuracy, a special graphical technique, the *Gran plot*, is used to determine the end points (Stumm and Morgan, 1981; Edmond, 1970). The principle of a Gran plot is illustrated by the following example: well below point *D* on the titration curve (Fig. 4-2), the shape of the curve is determined simply by the buildup of H^+ in solution from the added acid. The curvature results from the logarithmic relationship between pH and hydrogen ion activity/concentration. If $10^{-\text{pH}}$ is plotted against v for the region around the end point (Fig. 4-3), a straight line results in the pH region below the end point. Extrapolation of the straight line to $m_{\text{H}^+} = 0$ locates the end point with great precision. Conceptually, added hydrogen ion during the titration is used first to convert HCO_3^- to H_2CO_3 , and when that is "complete," it builds up in solution. The Gran plot identifies the point at which stoichiometrically all the alkalinity has been titrated and the buildup of free hydrogen ions begins.

The Gran plot can also be used to locate an end point when the titration curve is incomplete. It would be very difficult (Fig. 4-3) to identify visually the end point for a sample whose initial pH was below about 5. With the Gran plot this is no problem, and it can even be used to locate the "end point" of a sample with a slightly negative alkalinity. In Fig. 4-2 we ignored the change in volume of the system resulting from the added acid. To allow for this, we would plot $(V + v)10^{-\text{pH}}$ instead of $10^{-\text{pH}}$ against v (V is the initial volume of sample, v the volume of acid added). Analogous Gran functions can be formulated for the first end point in the alkalinity titration.

In determining Eq. (4-18) and Fig. 4-2, a necessary input was the value of ΣCO_2 (here 5×10^{-3}). Thus the titration curve can be used to measure ΣCO_2 as well as alkalinity. The procedure is explained in detail by Edmond (1970). When alkalinity and ΣCO_2 are known, in situ values for P_{CO_2} , pH, bicarbonate, and carbonate concentrations can be calculated. The titration can be used to measure ΣCO_2 only if CO_2 does not exchange with a gas phase (the system is closed to CO_2 exchange). In the particular example given, P_{CO_2} would increase from about 10^{-14} atm in the pure Na_2CO_3 solution to about 0.15 atm at the end point. If the titration was done in contact with the atmosphere ($P_{\text{CO}_2} = 10^{-3.5}$), CO_2 would have entered the solution

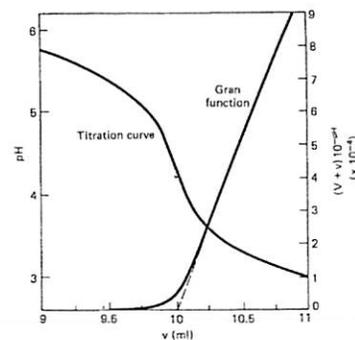


Figure 4-3 Titration curve and Gran function for the alkalinity titration of Fig. 4-2. Note that the straight-line portion of the Gran function extrapolates to 10.00 ml, which corresponds to the inflection point on the titration curve.

from the atmosphere at the beginning of the titration and would have diffused out of the solution into the atmosphere at the end of the titration. Alkalinity can be measured whether the solution is open or closed to CO_2 exchange, but ΣCO_2 can be measured only if the system is closed.

At a pH of about 6.4 (Fig. 4-2), the pH of the solution changes very slowly as acid is added. In this region the solution is strongly buffered with respect to pH change. Buffering occurs when a protonated species (here H_2CO_3) and an unprotonated species (here HCO_3^-) are both present in significant concentrations. When acid is added, the protons combine with HCO_3^- to form H_2CO_3 , and the net change in pH is small. Similar buffering by the $\text{HCO}_3^-/\text{CO}_3^{2-}$ pair occurs around pH 10.3.

In deriving Eq. (4-18) and Fig. 4-2, we assumed that activities and concentrations were equal, which is obviously not true. Equation (4-18) is correct in this regard, however, if the K values represent apparent equilibrium constants (Chapter 2) rather than thermodynamic constants. The titration curve can thus be used to determine apparent constants in natural waters, although the apparent constants may be slightly changed by the addition of HCl. The change is likely to be significant only if carbonate species are the major anions in solution. This information is important in determining the stabilities of various complexes and in determining the state of saturation of a water with respect to carbonate minerals. Equation (4-18) can be modified to include the change in total volume as acid is added.

Organic anions present both conceptual and practical problems for the definition of alkalinity. If the corresponding organic acid had the same pK_a value as H_2CO_3 (6.35), there would be no problem, and the measured alkalinity would be the sum of the carbonate alkalinity and the concentration of the organic anion. Most organic acids, however, have pK_a values around 4 or 5 (Fig. 3-1). At the pH of the bi-

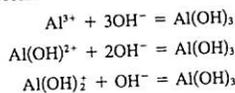
carbonate end point (about 4.5), some fraction of the organic anions will be converted to undissociated acid, and some will remain as anions. If the concentration of organic anions is much less than that of bicarbonate, the titration curve will show an inflection at the bicarbonate end point, and the measured alkalinity (defined by the bicarbonate end point) will equal the sum of carbonate alkalinity and that fraction of the organic anions that has been titrated by the pH of the carbonate end point. As the concentration of organic anions increases relative to carbonate species, the inflection at the bicarbonate end point gradually disappears and cannot be used to define the pH corresponding to zero alkalinity. One approach is to define a certain pH (say 5.0) arbitrarily as the zero point of alkalinity; the alkalinity would then be the amount of acid required to bring the sample to that pH. This definition is convenient, but the alkalinity so defined is not conservative. Another approach is to include all organic anions in the definition of alkalinity. The problem with this approach is that some organic acids are quite strong (e.g., oxalic acid has a pK_a of 1.2, which makes it a stronger acid than HSO_4^-). It is impossible to measure anions of such strong "weak" acids by acid-base titrations; thus, although alkalinity so defined is conservative, it is not directly measurable.

Acidity (equivalent to the terms *mineral acidity* or *strong acidity* of other authors) can be defined as the negative of alkalinity, that is, as the amount of base required to raise the pH of the sample to the bicarbonate end point. If acidity is positive,

$$m_{\text{H}^+} > m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-}$$

which means, from charge balance considerations, that an anion of an acid stronger than carbonic acid must be present. In nature, the anion is commonly sulfate.

Hydrolyzable cations such as aluminum also contribute to acidity, because they are titratable by base. If a solution containing Al^{3+} is titrated with strong base, the following reactions will occur:



The acidity (the negative alkalinity) thus becomes (ignoring CO_3^{2-} and OH^-)

$$\text{Acidity} = m_{\text{H}^+} - m_{\text{HCO}_3^-} + 3m_{\text{Al}^{3+}} + 2m_{\text{Al}(\text{OH})_3} + m_{\text{Al}(\text{OH})_4^-} - m_{\text{Al}(\text{OH})_5^{2-}}$$

The contribution of Al species to the titration acidity is called the *aluminum acidity*. The solubility of $\text{Al}(\text{OH})_3$ at around pH 5 is small, so the presence of dissolved Al species does not in practice complicate the definition of the pH corresponding to zero acidity/alkalinity. The behavior of Fe^{3+} is analogous to that of Al^{3+} .

CALCIUM CARBONATE SOLUBILITY

The solubility of calcium carbonate can be understood by adding one more equation to the equations for the carbonate system discussed in the preceding section. The solubility products of calcite and aragonite are defined by the equations

$$K_{\text{cal}} = a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} = 10^{-8.48} \quad \text{at } 25^\circ\text{C}$$

$$K_{\text{arr}} = a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} = 10^{-8.34} \quad \text{at } 25^\circ\text{C}$$

Values for the solubility product at other temperatures are listed in Table 4-1. Aragonite is the less stable polymorph of calcium carbonate at 1 atm pressure, and hence it is more soluble than calcite.

Garrels and Christ (1965) discuss at length calculations involving calcite solubility, and only a few examples will be given here. Most problems reduce to setting up a set of equations consisting of equilibrium conditions (the expressions for K_{CO_2} , K_1 , K_2 , K_w , and K_{cal}), a charge balance equation, and some other condition. The other condition is usually either a fixed value of P_{CO_2} if an open system is being considered, or a fixed value of ΣCO_2 if a closed system is being considered. This set of equations usually describes the system completely, and all that remains is algebraic manipulation to get the desired answer.

Example 1

Express the solubility product of calcite in terms of bicarbonate activity and P_{CO_2} instead of carbonate activity.

$$K_{\text{CO}_2} = \frac{a_{\text{H}_2\text{CO}_3}}{P_{\text{CO}_2}} \quad (4-19)$$

$$K_1 = \frac{a_{\text{H}^+} a_{\text{HCO}_3^-}}{a_{\text{H}_2\text{CO}_3}} \quad (4-20)$$

$$K_2 = \frac{a_{\text{H}^+} a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}} \quad (4-21)$$

$$K_{\text{cal}} = a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} \quad (4-22)$$

Rearranging Eq. (4-20) gives

$$a_{\text{H}^+} = \frac{K_1 a_{\text{H}_2\text{CO}_3}}{a_{\text{HCO}_3^-}} \quad (4-23)$$

Rearranging (4-21) gives

$$a_{\text{CO}_3^{2-}} = \frac{K_2 a_{\text{HCO}_3^-}}{a_{\text{H}^+}} \quad (4-24)$$

Substituting (4-23) in (4-24) gives

$$a_{\text{CO}_3^{2-}} = \frac{K_2 a_{\text{HCO}_3^-}}{K_1 a_{\text{H}_2\text{CO}_3}}$$

Substituting this in (4-22) gives

$$K_{\text{cal}} = a_{\text{Ca}^{2+}} \frac{K_2 a_{\text{HCO}_3^-}}{K_1 a_{\text{H}_2\text{CO}_3}}$$

or

$$\frac{a_{\text{Ca}^{2+}} a_{\text{HCO}_3^-}}{a_{\text{H}_2\text{CO}_3}} = \frac{K_{\text{cal}} K_1}{K_2}$$

or, from (4-19),

$$\frac{a_{\text{Ca}^{2+}} a_{\text{HCO}_3^-}}{P_{\text{CO}_2}} = \frac{K_{\text{cal}} K_1 K_2}{K_2} \quad (4-25)$$

Equation (4-25) is useful in understanding natural waters, since the controlling variables in many natural systems are CO_2 and HCO_3^- . Carbonate concentration and pH can often be thought of as consequences of P_{CO_2} and $m_{\text{HCO}_3^-}$. For example, photosynthesis decreases dissolved CO_2 , which will increase the state of saturation. Respiration and aerobic decay, on the other hand, increase dissolved CO_2 and decrease saturation. Anaerobic decay with sulfate reduction (see Chapter 14) may be represented in a simplified way by the equation



Where C_{org} represents carbon in organic matter. Thus anaerobic decay will increase saturation with respect to carbonate minerals, the opposite of aerobic decay.

Example 2

How do the pH and calcium concentration of pure water in equilibrium with calcite vary as a function of P_{CO_2} ?

$$a_{\text{H}_2\text{CO}_3} = K_{\text{CO}_2} P_{\text{CO}_2} \quad (4-26)$$

$$K_1 = \frac{a_{\text{H}^+} a_{\text{HCO}_3^-}}{a_{\text{H}_2\text{CO}_3}} \quad (4-27)$$

Rearranging Eq. (4-27) and substituting (4-26) gives

$$a_{\text{HCO}_3^-} = \frac{K_1 K_{\text{CO}_2} P_{\text{CO}_2}}{a_{\text{H}^+}} \quad (4-28)$$

$$K_2 = \frac{a_{\text{H}^+} a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}} \quad (4-29)$$

Rearranging (4-29) and substituting (4-28) gives

$$a_{\text{CO}_3^{2-}} = \frac{K_1 K_2 K_{\text{CO}_2} P_{\text{CO}_2}}{a_{\text{H}^+}^2} \quad (4-30)$$

$$K_{\text{cal}} = a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} \quad (4-31)$$

Substituting (4-30) in (4-31) gives

$$K_{\text{cal}} = \frac{a_{\text{Ca}^{2+}} K_1 K_2 K_{\text{CO}_2} P_{\text{CO}_2}}{a_{\text{H}^+}^2} \quad (4-32)$$

The charge balance equation is

$$m_{\text{H}^+} + 2m_{\text{Ca}^{2+}} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-} \quad (4-33)$$

If we restrict our attention to the pH region below 9, m_{H^+} , m_{OH^-} , and $2m_{\text{CO}_3^{2-}}$ will be small compared to $2m_{\text{Ca}^{2+}}$ and $m_{\text{HCO}_3^-}$ in the charge balance equation (small quantities can be neglected when they are added to or subtracted from large quantities; they may not be neglected when they multiply large quantities). Equation (4-33) then simplifies to

$$2m_{\text{Ca}^{2+}} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} \quad (4-34)$$

or

$$\frac{2a_{\text{Ca}^{2+}}}{\gamma_{\text{Ca}^{2+}}} = \frac{a_{\text{HCO}_3^-}}{\gamma_{\text{HCO}_3^-}} + \frac{2a_{\text{CO}_3^{2-}}}{\gamma_{\text{CO}_3^{2-}}}$$

or

$$a_{\text{Ca}^{2+}} = \frac{1}{2} a_{\text{HCO}_3^-} \frac{\gamma_{\text{Ca}^{2+}}}{\gamma_{\text{HCO}_3^-}} = \frac{L}{2} \frac{K_1 K_2 K_{\text{CO}_2} P_{\text{CO}_2}}{a_{\text{H}^+}^2} \frac{\gamma_{\text{Ca}^{2+}}}{\gamma_{\text{HCO}_3^-}} \quad (4-35)$$

Substituting (4-28) in (4-35) and then substituting the result in (4-32) gives

$$K_{\text{cal}} = \frac{\frac{1}{2} K_1 K_2 K_{\text{CO}_2} P_{\text{CO}_2} \frac{K_1 K_2 K_{\text{CO}_2} P_{\text{CO}_2}}{a_{\text{H}^+}^2} \frac{\gamma_{\text{Ca}^{2+}}}{\gamma_{\text{HCO}_3^-}}}{a_{\text{H}^+}^2} \frac{\gamma_{\text{Ca}^{2+}}}{\gamma_{\text{HCO}_3^-}}$$

which rearranges to

$$a_{\text{H}^+} = P_{\text{CO}_2}^{1/2} \frac{K_1^2 K_2 K_{\text{CO}_2} \gamma_{\text{Ca}^{2+}}}{2K_{\text{cal}} \gamma_{\text{HCO}_3^-}} \quad (4-36)$$

which is the desired relationship.

The relationship is shown graphically in Fig. 4-4, assuming 25°C and a total pressure of 1 atm. The calculation of the activity coefficients can be done by an iteration procedure similar to that used in Example 5 of Chapter 2. For each value of P_{CO_2} , a preliminary calculation is made assuming that $\gamma_{\text{Ca}^{2+}} = \gamma_{\text{HCO}_3^-}$; the concentrations of all species are calculated on this assumption, and these concentrations are used to calculate $\gamma_{\text{Ca}^{2+}}$ and $\gamma_{\text{HCO}_3^-}$ by the Debye-Hückel equation. These γ values are then used in Eq. (4-36) to give better values for pH and hence the concentrations of other dissolved species, and the cycle is repeated until consistent results are achieved.

In most surface waters, the P_{CO_2} lies between 10^{-2} atm and the atmospheric value of $10^{-3.5}$ atm. Waters with P_{CO_2} values in this range in equilibrium with calcite would have pH values between 7.3 and 8.4. The majority of surface waters do have

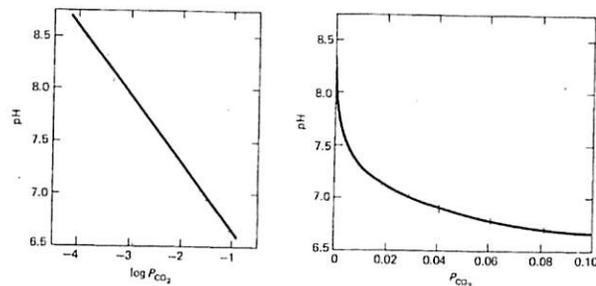


Figure 4-4 Relationship between pH and P_{CO_2} for pure water in equilibrium with calcite at 25°C and 1 atm total pressure. Note the difference of form when P_{CO_2} is plotted as a logarithm.

pH values in this range; lower pH values occur in waters that are undersaturated with respect to calcite.

To derive a relationship between $m_{\text{Ca}^{2+}}$ and P_{CO_2} , we can manipulate the same set of equations. Dividing Eq. (4-27) by (4-29) gives

$$\frac{K_1}{K_2} = \frac{a_{\text{HCO}_3^-}}{a_{\text{CO}_3^{2-}} a_{\text{H}_2\text{CO}_3}}$$

Substituting (4-26) and (4-31) in this yields

$$\frac{K_1}{K_2} = \frac{a_{\text{HCO}_3^-} a_{\text{Ca}^{2+}}}{K_{\text{cal}} K_{\text{CO}_2} P_{\text{CO}_2}} \quad (4-37)$$

From (4-34)

$$\begin{aligned} m_{\text{HCO}_3^-} &= 2m_{\text{Ca}^{2+}} \\ a_{\text{HCO}_3^-} &= 2m_{\text{Ca}^{2+}} \gamma_{\text{HCO}_3^-} \end{aligned}$$

Substituting this in (4-37) and substituting $a_{\text{Ca}^{2+}} = m_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}}$ gives

$$\frac{K_1}{K_2} = \frac{4m_{\text{Ca}^{2+}}^2 \gamma_{\text{Ca}^{2+}} \gamma_{\text{HCO}_3^-}}{K_{\text{cal}} K_{\text{CO}_2} P_{\text{CO}_2}}$$

or

$$m_{\text{Ca}^{2+}}^2 = P_{\text{CO}_2} \frac{K_1 K_{\text{cal}} K_{\text{CO}_2}}{4 K_2 \gamma_{\text{Ca}^{2+}} \gamma_{\text{HCO}_3^-}} \quad (4-38)$$

This relationship is plotted in Fig. 4-5. It is interesting to note that the relationship between $m_{\text{Ca}^{2+}}$ and P_{CO_2} is not linear. For example, if a water in equilibrium with calcite at $P_{\text{CO}_2} = 0.05$ atm (A in Fig. 4-5) is mixed with a water in equilibrium with calcite at $P_{\text{CO}_2} = 0.005$ atm (B in Fig. 4-5), the resulting water (C in Fig. 4-5) is *not* in equilibrium with calcite. In fact, it is undersaturated and could cause dissolution

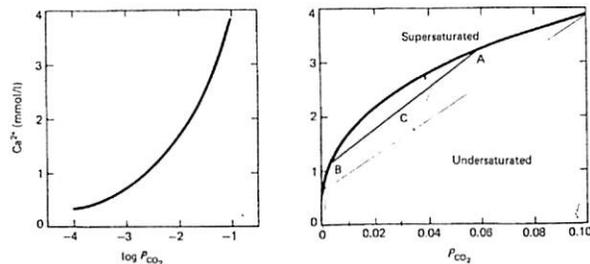


Figure 4-5 Concentration of calcium in equilibrium with calcite as a function of P_{CO_2} in the system $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ at 25°C and 1 atm total pressure. For explanation of points A, B, and C, see text.

of calcite. In general, mixing of two waters of different compositions, both of which are in equilibrium with calcite, is likely to result in a water that is not in equilibrium with calcite. It may be supersaturated or undersaturated, depending on the particular compositions or the waters involved (Runnells, 1969; Wigley and Plummer, 1976). Supersaturation would occur if, for example, a water with high calcium concentration and low alkalinity mixed with a water of high alkalinity and low calcium concentration.

Example 3

How does the presence of dissolved sodium bicarbonate affect the concentration of dissolved calcium in equilibrium with calcite at different CO_2 pressures?

The equations for solving this problem are identical with those for Example 2 except that the charge balance equation becomes (for pH values below 9)

$$m_{\text{Na}^+} + 2m_{\text{Ca}^{2+}} = m_{\text{HCO}_3^-}$$

Substituting this equation for Eq. (4-34) in Example 2 and following the same derivation, Eq. (4-38) becomes

$$m_{\text{Ca}^{2+}} (m_{\text{Na}^+} + 2m_{\text{Ca}^{2+}})^2 = P_{\text{CO}_2} \frac{K_1 K_{\text{cal}} K_{\text{CO}_2}}{K_2 \gamma_{\text{Ca}^{2+}} \gamma_{\text{HCO}_3^-}} \quad (4-39)$$

This relationship is shown graphically in Fig. 4-6. The presence of excess NaHCO_3 decreases the concentration of Ca^{2+} in equilibrium with calcite. This is the familiar common-ion effect in solution chemistry. In alkaline brines where the Na^+ concentration is very high, the dissolved Ca^{2+} concentration is often vanishingly small (see Chapter 11).

Example 4

How does the presence of dissolved calcium chloride affect the concentration of dissolved calcium in equilibrium with calcite at different CO_2 pressures?

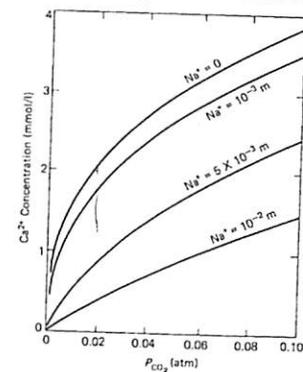


Figure 4-6 Concentration of calcium in equilibrium with calcite as a function of P_{CO_2} and Na^+ concentration in the system $\text{CaCO}_3\text{-Na}_2\text{CO}_3\text{-CO}_2\text{-H}_2\text{O}$ at 25°C and 1 atm total pressure.

Again, the basic equations are the same as in Example 2, except that the charge balance equation is now

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

By the same procedure as in Examples 2 and 3, this gives the final equation

$$m_{Ca^{2+}}^2 (2m_{Ca^{2+}} - m_{Cl^-})^2 = \frac{K_1 K_{a1} K_{CO_2}}{K_2 \gamma_{Ca^{2+}} \gamma_{HCO_3^-}} \quad (4-40)$$

This relationship is shown in Fig. 4-7. The concentration of calcium equivalent to chloride is not affected by changes in P_{CO_2} . The additional Ca^{2+} balanced by carbonate species is related to P_{CO_2} in a way that is rather similar to that of the simple system without Cl^- or Na^+ .

These three examples cover all the possibilities in common natural-water systems. The general charge balance equation is

$$m_{Na^+} + m_{K^+} + 2m_{Mg^{2+}} + 2m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{Cl^-} + 2m_{SO_4^{2-}} + m_{MnO_4^-} + m_{MnO_2} = m_{HCO_3^-} + 2m_{CO_3^{2-}}$$

This can be rewritten as (ignoring minor species)

$$\frac{m_{Na^+} + m_{K^+} + 2m_{Mg^{2+}} - m_{Cl^-} - 2m_{SO_4^{2-}}}{M} = m_{HCO_3^-} + 2m_{CO_3^{2-}}$$

If the expression M is positive, then M is exactly analogous to Na^+ in Example 3, and M can be substituted for m_{Na^+} in Eq. (4-39). If M is negative, then M will be analogous to Cl^- in Example 4, and M may be substituted for m_{Cl^-} in Eq. (4-40). Seawater is a good example of a water in which M is negative.

Some general relationships among species in the carbonate system are shown in Fig. 4-8. In constructing Fig. 4-8, it was assumed that, when $m_{Ca^{2+}}$ was less than

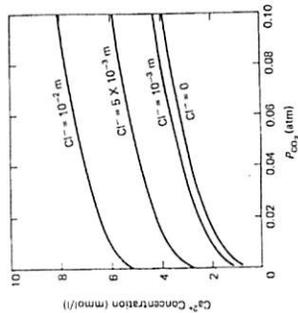
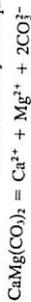


Figure 4-7 Concentration of calcium in equilibrium with calcite as a function of P_{CO_2} and Cl^- concentration in the system $CaCO_3-CaCl_2-CO_2-H_2O$ at 25°C and 1 atm total pressure.

alkalinity, the difference was made up by Na^+ ; when $m_{Ca^{2+}}$ was greater than alkalinity, the difference was made up by Cl^- .

DOLomite

Dolomite has a chemical formula $CaMg(CO_3)_2$, and a crystallographic structure similar to that of calcite, except that the Ca and Mg atoms are arranged in separate planes. The ordering of the Ca and Mg atoms distinguishes dolomite from a high-magnesium calcite of the same composition. Protodolomite is a partially disordered form of dolomite; it usually contains more Ca and less Mg than the ideal formula. The solubility of dolomite can be represented by the equation



$$K_{sol} = a_{Ca^{2+}} a_{Mg^{2+}} a_{CO_3^{2-}}^2$$

There has been considerable disagreement in the literature as to the correct value of K_{sol} . The disagreement results from the fact that dolomite is very unreactive at low temperatures. At 25°C it is almost impossible to make dolomite grow in the laboratory, and dolomite dissolves only slowly in solutions that are strongly undersaturated with respect to it. The most accepted value for K_{sol} is about 10^{-17} , which is deduced from the compositions of groundwaters that have spent a long time in dolomite aquifers (Hsi, 1967).

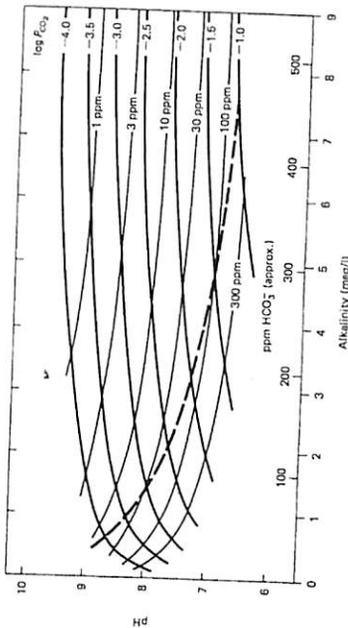
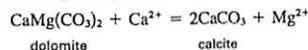


Figure 4-8 Relation among pH, alkalinity, P_{CO_2} , and calcium concentration in waters saturated with respect to calcite at 25°C and 1 atm total pressure. Heavy lines are contours of equal P_{CO_2} , light lines are contours of equal calcium concentration, and the dashed line is the locus of compositions where the calcium concentration exactly balances the alkalinity. For assumptions, see text (after Drever, 1972).

In nature, dolomite is generally formed by alteration of calcite or aragonite:



$$K_{\text{cd}} = \frac{a_{\text{Mg}^{2+}}}{a_{\text{Ca}^{2+}}}$$

In solutions in which the ratio $a_{\text{Mg}^{2+}}/a_{\text{Ca}^{2+}}$ is higher than K_{cd} , dolomite is more stable than calcite, and vice versa. K_{cd} is related to K_{dol} by the equation

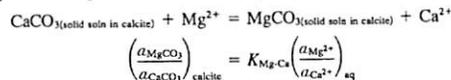
$$\begin{aligned} K_{\text{cd}} &= \frac{K_{\text{dol}}}{K_{\text{calcite}}} \\ &= \frac{10^{-17}}{10^{-16.8}} = 10^{-0.2} \\ &= 0.6 \end{aligned}$$

There is a large uncertainty associated with this number, but calcite is probably unstable with respect to dolomite in surface waters in which the $a_{\text{Mg}^{2+}}/a_{\text{Ca}^{2+}}$ ratio is greater than 1. Because dolomite is so inert, calcite is rarely converted to dolomite at low temperatures unless the $a_{\text{Mg}^{2+}}/a_{\text{Ca}^{2+}}$ ratio is considerably higher than 1. The conversion is more rapid in the absence of sulfate (Baker and Kastner, 1981).

HIGH-MAGNESIUM CALCITE

Magnesium can substitute for calcium in the calcite structure. The calcite formed in modern shallow-marine environments commonly contains 11 to 19 mole percent MgCO_3 and is called high-magnesium calcite. Calcite containing 5 percent or less MgCO_3 is referred to as low-magnesium calcite. In discussing the stability of high-magnesium calcites, it is important to define what is meant by stability. All high-magnesium calcites are unstable with respect to low-magnesium calcite plus dolomite. This is of little importance in surface-water chemistry because dolomite is so kinetically inert.

Equilibrium between high-magnesium calcite and a solution can be defined in terms of a cation displacement reaction and in terms of a solubility reaction. For cation displacement equilibrium between a high-magnesium calcite and solution,



In general, the Ca-Mg carbonate solid solution will be highly nonideal, so no simple linear relationship will exist between the concentration ratio in the solid and the concentration ratio in solution. However, for any particular ratio in solution, there is a corresponding unique ratio in the solid, and when the ratio in solution varies, so should the ratio in the solid.

Solubility equilibrium or, more strictly, *stoichiometric saturation* can be defined by the equations

$$\begin{aligned} \text{Mg}_x\text{Ca}_{(1-x)}\text{CO}_3 &= x\text{Mg}^{2+} + (1-x)\text{Ca}^{2+} + \text{CO}_3^{2-} \\ K_{\text{sp}} &= a_{\text{Mg}^{2+}}^x a_{\text{Ca}^{2+}}^{(1-x)} a_{\text{CO}_3^{2-}} \\ &= \left(\frac{a_{\text{Mg}^{2+}}}{a_{\text{Ca}^{2+}}} \right)^x a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} \end{aligned} \quad (4-41)$$

Measurement of K_{sp} is complicated by the fact that, when high-magnesium calcites are placed in water, they initially dissolve congruently,* but as the concentration of ions in solution increases, dissolution becomes incongruent. During incongruent dissolution, a low-magnesium calcite precipitates as the high-magnesium calcite dissolves. Plummer and Mackenzie (1974) and Bischoff et al. (1987) estimated the solubility of high-magnesium calcites by measuring the rate of dissolution when dissolution was constant and extrapolating the results to infinite time. This approach has been criticized by Lafon (1978) and by Garrels and Wollast (1978). Mucci and Morse (1984) measured the solubility of magnesian calcites in seawater by precipitating them as overgrowths on calcite. The detailed results of these various studies differ somewhat, but there is a consensus that calcites containing *some* magnesium, probably up to at least 5 mole percent MgCO_3 , are more stable than pure calcite in seawater. Biogenic (magnesian) calcites tend to be less stable/more soluble than synthetic materials of the same Mg/Ca ratio (Bischoff et al., 1987).

For true equilibrium, the equations describing cation displacement and stoichiometric saturation must both be satisfied. Stoichiometric saturation is commonly attained much more rapidly than cation displacement equilibrium.

GROUND AND SURFACE WATERS IN CARBONATE TERRAINS

The equations derived in this chapter provide a good framework for understanding the chemistry of waters in limestone aquifers. Rainwater is in equilibrium with atmospheric carbon dioxide, which has a partial pressure of $10^{-3.5}$ atm. The gases in soils commonly contain much more CO_2 than the atmosphere as a consequence of respiration and decay of organic matter. As rain percolates through soil, its CO_2 content increases, typically to an equivalent P_{CO_2} of 10^{-2} or so. The additional CO_2 from the soil greatly increases the amount of CaCO_3 the water can dissolve. The amount of CaCO_3 dissolved per liter of percolating water (and hence the Ca^{2+} concentration in the water) depends on the initial CO_2 concentration and on the extent to which the CO_2 in the water can be replenished by exchanging with a gas phase. If CO_2 is not replenished (the system is *closed* to exchange of CO_2 gas), the amount of calcite that a water can dissolve is essentially limited by the amount of CO_2 present initially, since dissolution follows the equation



* Congruent solution means that the entire solid dissolves; incongruent solution occurs when part of the solid dissolves, leaving behind a solid phase different in composition from the original.

If the system is open to CO_2 , the P_{CO_2} of the water will remain constant, and CO_2 will be transferred from the gas phase to replace the CO_2 consumed by dissolution of calcite. In this case, the dissolution of calcite is not limited by the availability of CO_2 ; more calcite will dissolve under open-system conditions than under closed-system conditions.

Example 5 Pure water at 25°C is in equilibrium with CO_2 at a partial pressure of 10^{-2} atm. How much calcite can the water dissolve, assuming (a) a closed system (no exchange of CO_2 with a gas phase); (b) an open system (P_{CO_2} remains constant)? In case (a), what will be the final P_{CO_2} of the system? Assume that all activity coefficients are unity.

The equilibrium equations for the carbonate system are

$$K_{\text{CO}_2} = \frac{a_{\text{H}_2\text{CO}_3}}{P_{\text{CO}_2}} \quad (4-42)$$

$$K_1 = \frac{a_{\text{H}^+} a_{\text{HCO}_3^-}}{a_{\text{H}_2\text{CO}_3}} \quad (4-43)$$

$$K_2 = \frac{a_{\text{H}^+} a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}} \quad (4-44)$$

$$K_{\text{sat}} = a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} \quad (4-45)$$

The charge balance equation is

$$m_{\text{H}^+} + 2m_{\text{Ca}^{2+}} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-}$$

If the final pH is less than about 9, m_{H^+} , m_{OH^-} , and $2m_{\text{CO}_3^{2-}}$ will all be small compared to $2m_{\text{Ca}^{2+}}$ and $m_{\text{HCO}_3^-}$. Assuming that these terms can be neglected, and introducing the assumption $\alpha = m$, the charge balance equation becomes

$$2\alpha_{\text{Ca}^{2+}} = \alpha_{\text{HCO}_3^-} \quad (4-46)$$

We now have five equations in six unknowns. The other equation necessary to solve the system in case (b) is simply

$$P_{\text{CO}_2} = \text{constant} = 10^{-2}$$

In case (a) the condition is conservation of carbonate species; that is,

$$\begin{aligned} \Sigma \text{CO}_2 &= \Sigma \text{CO}_2^{\text{initial}} + \Sigma \text{CO}_2^{\text{from dissolution of CaCO}_3} \\ &= (m_{\text{H}_2\text{CO}_3})_{\text{initial}} + m_{\text{Ca}^{2+}} \end{aligned} \quad (4-47)$$

where ()_{initial} means before any CaCO_3 dissolves ($10^{-2} \times 10^{-1.47}$ m), and $m_{\text{Ca}^{2+}}$ comes from the fact that each mole of CaCO_3 that dissolves adds 1 mol of Ca^{2+} and 1 mol of CO_3^{2-} . If $m_{\text{CO}_3^{2-}}$ can be neglected in the expression for ΣCO_2 , Eq. (4-47) becomes

$$\begin{aligned} m_{\text{H}_2\text{CO}_3} + m_{\text{HCO}_3^-} &= (m_{\text{H}_2\text{CO}_3})_{\text{initial}} + m_{\text{Ca}^{2+}} \\ (m_{\text{H}_2\text{CO}_3})_{\text{initial}} &= m_{\text{H}_2\text{CO}_3} + m_{\text{HCO}_3^-} - m_{\text{Ca}^{2+}} \end{aligned} \quad (4-48)$$

All that remains now is algebraic manipulation. Dividing Eq. (4-43) by (4-44) gives

$$\frac{K_1}{K_2} = \frac{a_{\text{H}^+} a_{\text{CO}_3^{2-}}}{a_{\text{H}_2\text{CO}_3} a_{\text{CO}_3^{2-}}}$$

Substituting (4-45), (4-48), and (4-46) in this gives

$$\frac{K_1}{K_2} = \frac{4\alpha_{\text{Ca}^{2+}}}{K_{\text{sat}}(m_{\text{H}_2\text{CO}_3})_{\text{initial}} - m_{\text{Ca}^{2+}}}$$

which, assuming that $\alpha = m$, rearranges to

$$m_{\text{Ca}^{2+}} + \frac{K_1 K_{\text{sat}}}{4K_2} m_{\text{Ca}^{2+}} - \frac{K_1 K_{\text{sat}} K_{\text{CO}_2}}{4K_2} (P_{\text{CO}_2})_{\text{initial}} = 0$$

This cubic equation is solved to give

$$m_{\text{Ca}^{2+}} = 3.34 \times 10^{-4} \text{ m}$$

The equations for case (b) were derived in Example 2. Substituting the appropriate numerical values in Eq. (4-38) gives

$$m_{\text{Ca}^{2+}} = 1.39 \times 10^{-3}$$

Thus the amount of CaCO_3 dissolved under open-system conditions is approximately four times that dissolved under closed-system conditions. The factor of 4 applies only to the example of $P_{\text{CO}_2} = 10^{-2}$; other factors apply at other P_{CO_2} values.

To calculate the final P_{CO_2} in the closed system, we can rearrange Eq. (4-38) to:

$$P_{\text{CO}_2} = \frac{m_{\text{Ca}^{2+}} \cdot 4K_2}{K_1 K_{\text{sat}} K_{\text{CO}_2}}$$

$$P_{\text{CO}_2} = 10^{(4-46)}$$

Substituting the value we calculated for $m_{\text{Ca}^{2+}}$ gives

Thus the dissolution of calcite in a closed system has reduced the P_{CO_2} from the relatively high value of 10^{-2} to the below-atmospheric value of $10^{-4.46}$. Finally, we can calculate the pH from Eq. (4-43). The result is 8.50; at this pH our assumption that m_{H^+} , m_{OH^-} , and $m_{\text{CO}_3^{2-}}$ could all be neglected in the charge balance equation and the equation for ΣCO_2 is justified.

The conclusion from Example 5 is that the amount of CaCO_3 dissolved by a percolating water depends critically on whether the water is in communication with a gas phase while the mineral is dissolving (Fig. 4-9). Measured P_{CO_2} values in groundwaters in limestone aquifers are almost always above atmospheric (e.g., Back and Hanshaw, 1970; Holland et al., 1964; Langmuir, 1971), suggesting that dissolution takes place largely under open-system conditions. Plummer (1977) showed that the main Floridan aquifer (a limestone aquifer underlying most of Florida) was receiving soil-derived CO_2 over a significant distance "downstream" from its recharge area.

In summary, waters in limestone aquifers generally have Ca^{2+} and HCO_3^- as the major dissolved species and are generally close to equilibrium with calcite. The

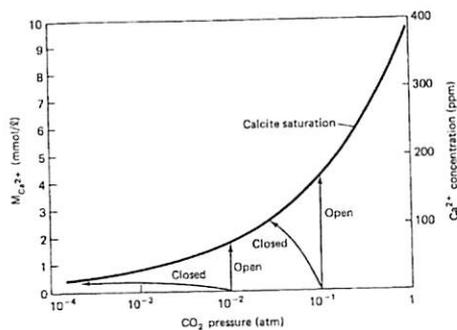


Figure 4-9 Changes in composition of carbonated water as it equilibrates with calcite when the system is either open or closed to exchange of CO_2 gas. Initial P_{CO_2} values of 10^{-2} and 10^{-1} atm. (After Holland et al., 1964. Reprinted from *Journal of Geology* by permission of the University of Chicago Press.)

Ca^{2+} concentration (and TDS) depends on the P_{CO_2} of the water, which is generally controlled by the soil atmosphere in the recharge area. The main exceptions to these generalizations are waters in deeper aquifers which have received solutes by mixing with waters from other sources or which have received solutes by dissolution of gypsum or halite.

Two examples of groundwaters from limestone aquifers are shown in Table 4-2. The first, from central Florida, shows the typical dominance of calcium and bicarbonate. Some magnesium is also present, derived from either magnesian calcite or dolomite, but other species are generally minor. The silica was probably derived from siliceous microfossils in the rock. The water is close to equilibrium with calcite at a P_{CO_2} of about $10^{-3.1}$ atm. The second analysis shows several differences. The calcium and bicarbonate concentrations are higher and the pH is lower because the water is in equilibrium with calcite at a higher P_{CO_2} value ($10^{-2.0}$ atm). The strikingly higher nitrate concentration is an indication of contamination by sewage, agricultural wastes, or fertilizers. Indeed, Langmuir (1971) concluded that the nitrate, sulfate, chloride, potassium, and sodium were all largely derived from human activities—sewage, fertilizer, and salting of roads in winter. Near-surface carbonate aquifers are particularly vulnerable to contamination because water commonly moves rapidly both vertically and horizontally in relatively large openings and because the aquifer material has little sorptive capacity.

Groundwaters in Dolomite

The weathering of dolomite is closely analogous to that of calcite, except that rates are slower, and half the HCO_3^- in the water is balanced by Mg^{2+} rather than Ca^{2+} .

TABLE 4-2 CHEMICAL ANALYSES (mg/l) OF GROUNDWATERS IN CARBONATE AQUIFERS FROM CENTRAL FLORIDA (from Back and Hanshaw, 1970) AND CENTRAL PENNSYLVANIA (from Langmuir, 1971)

	Florida	Pennsylvania
Ca^{2+}	34	83
Mg^{2+}	5.6	17
Na^+	3.2	8.5
K^+	0.5	6.3
HCO_3^-	124	279
SO_4^{2-}	2.4	27
Cl^-	4.5	17
NO_3^-	0.1	38
SiO_2	12	—
pH	8.00	7.36

Dolomite normally dissolves congruently. In a rock containing both calcite and dolomite, the water should ultimately come to equilibrium with calcite and dolomite, in which case

$$\frac{a_{\text{Mg}^{2+}}}{a_{\text{Ca}^{2+}}} = 0.6$$

$$a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} = 10^{-8.3}$$

In practice, establishment of equilibrium with dolomite is slow. Such waters usually contain more calcium than magnesium near the recharge area because calcite dissolves more rapidly than dolomite. Over time periods of thousands of years, however, the magnesium/calcium ratio of the water rises to the "equilibrium" value (e.g., Plummer 1977). "Equilibrium" is in quotation marks because, as mentioned earlier, the equilibrium solubility of dolomite is calculated from analyses of groundwaters from dolomite aquifers, which are presumed to have had sufficient time to reach equilibrium.

CARBONATE CHEMISTRY IN THE OCEANS

The carbonate system in seawater has been studied in great detail by many workers. For precise calculations on the state of saturation of seawater with respect to calcite, either activity-concentration corrections must be made with great accuracy (e.g., Millero, 1974) or apparent constants must be measured empirically (Edmond and Gieskes, 1970). Most oceanographers use the apparent-constant approach, which is well suited to seawater because the major element composition (which largely determines activity coefficients) is almost constant.

Most surface seawater is supersaturated with respect to calcite, and deep water is undersaturated. The reasons for the undersaturation are increased pressure, de-

creased temperature, and increased CO_2 concentrations in the deeper water (see Chapter 12). There is a dramatic change in the abundance of calcite in marine sediments at a depth of about 3.5 km (Pacific) or 5 km (Atlantic). Below these depths, calcite is essentially absent because planktonic shells that fall to greater depths are dissolved before they can be buried. The depth at which the dramatic decrease in the calcite content of sediments occurs is called the *calcite compensation depth* (CCD), because the rate of dissolution of calcite compensates for the supply. At some depth above the CCD, there is a marked change in the dissolution behavior of calcite, called the *lysocline*. Above the lysocline, calcite shells (or, more properly, tests) show almost no evidence of dissolution. Below the lysocline, the thinner tests and the more delicate structures have disappeared, and the only calcite tests found in the sediment are the more massive types, which resist dissolution longer. (Massive is a relative term; the tests are essentially all under 1 mm in diameter.)

There have been long-standing arguments in the literature as to whether the CCD (and, more recently, the lysocline) represents a transition from supersaturated to undersaturated conditions or whether it is controlled by kinetic factors. Chemical measurements (see, e.g., Edmond and Gieskes, 1970; Edmond, 1974; Takahashi, 1975) suggest that the transition from supersaturation occurs at much shallower depths (perhaps 500 m), and the compensation depth represents the depth at which undersaturation is sufficient for dissolution to be more rapid than burial. This conclusion is supported by laboratory experiments on calcite dissolution (Morse and Berner, 1972), and by experiments in which samples of calcite were exposed to seawater at various depths and monitored for dissolution or precipitation (Peterson, 1966; Berger, 1967; Honjo and Erez, 1978). Both laboratory and in situ experiments show that dissolution of calcite is very slow in slightly undersaturated seawater, but dissolution is rapid once a critical degree of undersaturation is reached (Fig. 4-10).

Because aragonite is more soluble than calcite, it has a shallower compensation depth. The aragonite compensation depth is a few hundred meters in the tropical north Pacific and has a maximum depth of 2 to 3 km in the north Atlantic (Berger, 1976). The only significant carbonate mineral in deep-sea sediments is thus low-magnesium calcite.

ACID WATERS

Waters that contain zero carbonate alkalinity and contain free strong acids ($m_{\text{H}^+} > m_{\text{HCO}_3^-}$; pH generally less than 4.5) are referred to as acid. Acid waters cause environmental problems because most organisms (other than certain algae and bacteria) are adapted to waters buffered by the carbonate system and cannot tolerate strong acidity, and because many toxic trace elements are mobilized under strongly acidic conditions. Acid deposition from the atmosphere is discussed in Chapter 10.

Acid Mine Drainage

The waters draining from many coal mines in the eastern United States are strongly acidic as a consequence of oxidation of pyrite in the coal. The stoichiometry of the oxidation can be represented by the equations

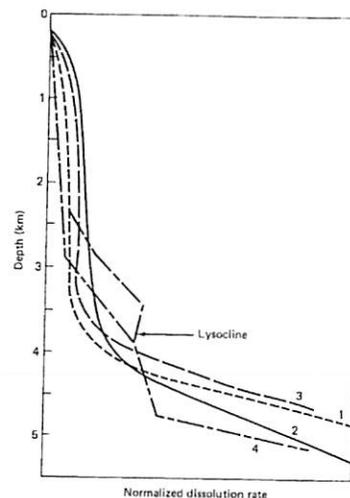
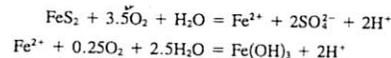


Figure 4-10 Dissolution rate of calcite in seawater as a function of depth. Curve 3 is calcite spheres suspended in the ocean (Peterson, 1966); curve 4 is foraminifera suspended in the ocean (Berger, 1967); curves 1 and 2 were calculated from experimental data of Morse and Berner (1972); the rate plotted is that which corresponds to the degree of undersaturation in the water at each depth. Position of lysocline is from examination of sediment cores (Bramlette, 1961). The horizontal scales for each set of experiments have been normalized to bring out the similar form of each curve (after Morse and Berner, 1972).



When streams become contaminated by acid mine drainage, adjacent vegetation dies and precipitation of ferric hydroxide occurs over long distances. Although the oxidation reactions are bacterially mediated and complex (Singer and Stumm, 1970; Stumm-Zollinger, 1971; U.S. Environmental Protection Agency, 1971), the balance of acidity and alkalinity can be visualized in terms of a simple model (Fig. 4-11). Rain penetrates overburden and acquires a certain alkalinity, usually by dissolution of calcite (Caruccio and Geidel, 1978). The amount of alkalinity acquired is determined by the P_{CO_2} of the water and the solubility of calcite. As the water moves through the coal seam, oxidation of pyrite occurs, generating acidity, which at first is neutralized by the alkalinity in the groundwater. If the acidity generated is greater than the initial alkalinity of the water, all the alkalinity will be consumed and an acid water will result. If sufficient oxygen is present, the amount of acidity generated is determined by the amount of reactive pyrite in the coal. Only very fine-grained pyrite is reactive, so the total sulfur content of a coal may be a poor predictor of potential acidity problems (Caruccio, 1975). Usually, the underclay below the coal seam is impermeable, so water exits to the surface before interacting with any other rock type.

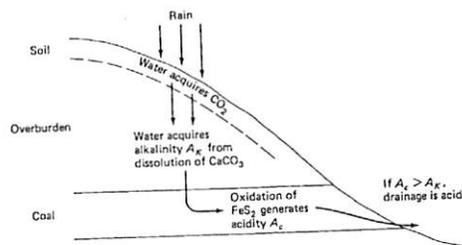


Figure 4-11 Schematic balance between acidity and alkalinity in generation of acid mine drainage, as discussed by Caruccio and Geidel (1978).

In the absence of mining, acid waters are uncommon because dissolved oxygen in the groundwater is insufficient to produce acidity greater than the alkalinity of the groundwater. Approximately 1 mol of O_2 is required to generate 1 mol of acidity, and soil waters generally contain less than 0.6 mmol O_2 per liter. When mining occurs, additional O_2 is introduced, and water movement through the system is accelerated. Oxidation is no longer limited by groundwater transport of oxygen, and acidity may result. The bacteria that catalyze the acidity-producing reactions thrive only under acid conditions, so once acidity is initiated, acid production becomes more rapid and the acidity problem increases rapidly.

REVIEW QUESTIONS

In the following problems assume activities equal concentrations and ignore complexing unless instructed otherwise.

1. What is the pH of pure water in equilibrium with atmospheric P_{CO_2} ($10^{-3.5}$ atm) at $25^\circ C$?
2. What is the pH and calcium concentration of pure water in equilibrium with calcite and atmospheric P_{CO_2} at $25^\circ C$?
3. What is the calcium concentration in a water in equilibrium with calcite at a P_{CO_2} of $10^{-2.5}$ atm at $5^\circ C$?
4. The water in question 3 is warmed from 5° to $25^\circ C$. How much calcite should precipitate, assuming chemical equilibrium and (a) constant P_{CO_2} ; (b) no loss or gain of CO_2 gas? In case (b), what will be the final pH and P_{CO_2} ?
5. A 0.01-m $NaHCO_3$ solution is allowed to equilibrate with calcite at a P_{CO_2} of 10^{-1} atm at $25^\circ C$. How much Ca^{2+} (in ppm) will the solution contain, and what will be its pH?
6. A 0.01-m $CaCl_2$ solution is allowed to equilibrate with calcite at a P_{CO_2} of $10^{-3.5}$ atm and $25^\circ C$. What will be the resulting pH and HCO_3^- concentration?
7. What should be the pH of a puddle of rain on an outcrop of dolomite at $25^\circ C$? (Assume chemical equilibrium.)

8. An "ideal" rain consists of pure water in equilibrium with CO_2 at a partial pressure of $10^{-3.5}$ atm. By how many millimeters per century should limestone exposed to this rain be dissolved if equilibrium is attained? Assume a rainfall of 1 m/year, $25^\circ C$, a system open to CO_2 , and a density for calcite of 2.7 g/cm^3 .
9. If the rain in question 8 were "acid," containing 0.1 meq/kg of free acidity, how many millimeters per century would be dissolved?
10. A river water has the following chemical analysis:

Na^+	11.4 ppm	SO_4^{2-}	58 ppm
K^+	1.56 ppm	Alkalinity	1.30 meq/kg
Ca^{2+}	24.0 ppm	pH	8.10
Mg^{2+}	10.0 ppm	Temp.	$10^\circ C$
Cl^-	1.9 ppm		

With what P_{CO_2} would the water be in equilibrium? By how much is it supersaturated or undersaturated with respect to calcite? (Calculate activity coefficients by the Debye-Hückel equation, Chapter 2.)

SUGGESTED READING

- BERGER, W. H. 1976. Biogenous deep sea sediments: production, preservation, and interpretation. *Chemical Oceanography*, 2nd ed., Vol. 5, J. P. Riley and R. Chester, eds. Academic Press, New York, pp. 265-387.
- BUTLER, J. N. 1982. *Carbon Dioxide Equilibria and Their Applications*. Addison-Wesley, Reading, MA, 255 p.
- GARRELS, R. M., and C. L. CHRIST. 1965. *Solutions, Minerals, and Equilibria*. Harper & Row, New York, Chap. 3. Several clear examples of calculations involving dissolution and precipitation of calcite.
- GIESKES, J. M. 1974. The alkalinity-total carbon dioxide system in sea water. *The Sea, Ideas and Observations*, Vol. 5: *Marine Chemistry*, E. D. Goldberg, ed. Wiley-Interscience, New York, pp. 123-151.
- HOLLAND, H. D., ET AL. 1964. On some aspects of the chemical evolution of cave waters. *J. Geol.*, 72, pp. 36-67. Example of the application of simple calculations to a natural system.
- LANGMUIR, D. 1971. The geochemistry of some carbonate ground waters in central Pennsylvania. *Geochim. Cosmochim. Acta*, 35, pp. 1023-1045.
- MORSE, J. W. 1983. The kinetics of calcium carbonate dissolution and precipitation. *Reviews in Mineralogy*, Vol. 11, pp. 227-264.
- PLUMMER, L. N. 1977. Defining reactions and mass transfer in part of the Floridan Aquifer. *Water Resour. Res.*, 13, pp. 801-812.
- STUMM, W., and J. J. MORGAN. 1981. *Aquatic Chemistry*, 2nd ed. Wiley-Interscience, New York, Chaps. 3 and 4. Detailed systematics of acid-base reactions, the carbonate system, and alkalinity titrations.