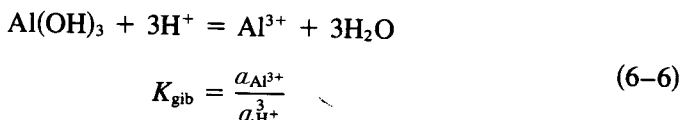


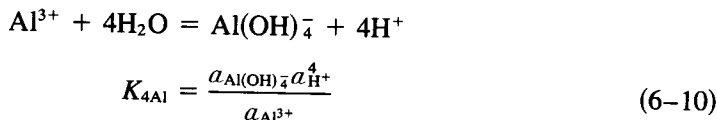
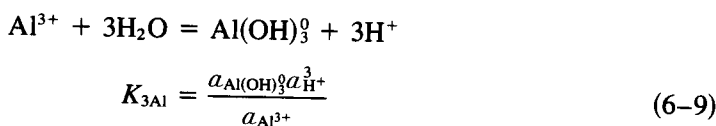
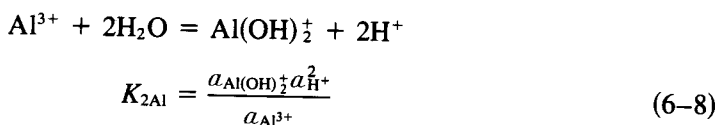
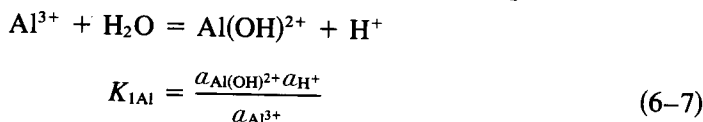
rounding the solution field cannot represent chemical equilibrium, since the water is supersaturated with respect to one or more solid phases. Note also that sepiolite must always be metastable in contact with water at 25°C, because solutions in equilibrium with sepiolite are always supersaturated with respect to one of the other solid phases.

### Solubility of Gibbsite

The solubility of gibbsite  $[\text{Al}(\text{OH})_3]$  is complicated by the fact that dissolved aluminum can exist in several forms in solution. In the absence of other ligands, the most important are  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_3^0$ , and  $\text{Al}(\text{OH})_4^-$ . The activity of  $\text{Al}^{3+}$  in equilibrium with gibbsite is given by



At low pH,  $\text{Al}^{3+}$  is the dominant species in solution, and the solubility of gibbsite decreases rapidly as pH increases. As pH increases, however, the relative importance of the hydroxy complexes increases, and their behavior controls the solubility of gibbsite. Formation of the complexes can be described by the equations

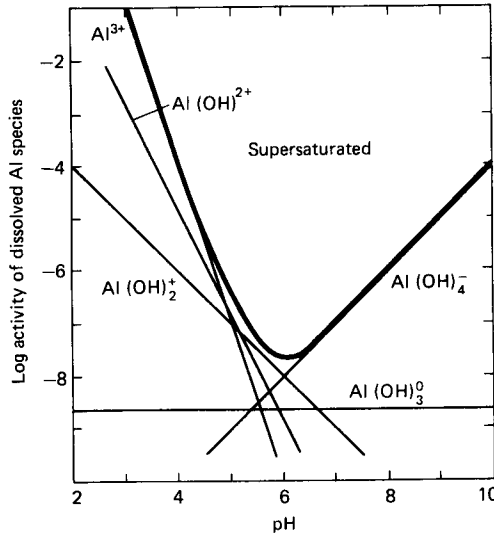


The total dissolved aluminum concentration is the sum of the concentrations of the individual species

$$m_{\text{Al}(\text{total})} = m_{\text{Al}^{3+}} + m_{\text{Al}(\text{OH})^{2+}} + m_{\text{Al}(\text{OH})_2^+} + m_{\text{Al}(\text{OH})_3^0} + m_{\text{Al}(\text{OH})_4^-}$$

Substituting Equations (6-6) through (6-10) and neglecting activity coefficients gives

$$m_{\text{Al}(\text{total})} = \bar{m}_{\text{Al}^{3+}} \left[ 1 + \frac{K_{1\text{Al}}}{a_{\text{H}^+}} + \frac{K_{2\text{Al}}}{a_{\text{H}^+}^2} + \frac{K_{3\text{Al}}}{a_{\text{H}^+}^3} + \frac{K_{4\text{Al}}}{a_{\text{H}^+}^4} \right] \quad (6-11)$$



**Figure 6-3** Activities of dissolved aluminum species in equilibrium with gibbsite  $[\text{Al}(\text{OH})_3]$  at  $25^\circ\text{C}$ . Heavy line is sum of individual activities. Data from Nordstrom et al., 1984.

Combining Eqs. (6-11) and (6-6) gives the total concentration of dissolved aluminum in equilibrium with gibbsite:

$$m_{\text{Al}(\text{total})} = K_{\text{gib}} \left[ a_{\text{H}^+}^3 + K_{1\text{Al}} a_{\text{H}^+}^2 + K_{2\text{Al}} a_{\text{H}^+} + K_{3\text{Al}} + \frac{K_{4\text{Al}}}{a_{\text{H}^+}} \right] \quad (6-12)$$

The activities of each of the species for a solution in equilibrium with gibbsite are shown in Fig. 6-3. Note the following:

1. The solubility of gibbsite is very low except at very low and high pH.
2. As the pH increases, the complexes containing progressively more hydroxide groups become progressively more important.
3. When cationic species dominate, the solubility of gibbsite decreases with increasing pH. When anionic species dominate, the solubility increases with increasing pH. This observation can be generalized to the solubilities of all oxides and hydroxides and of many other solids.

### Solubility of Aluminosilicates

The behavior of aluminum makes it impossible to present the solubility of aluminum silicates in as simple a way as was done for magnesium silicates. In principle, a three-dimensional diagram is needed with aluminum concentration, silica activity, and pH as axes. Three-dimensional diagrams can be represented by contours on a two-dimensional diagram. The solubilities of gibbsite, kaolinite  $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$ , and pyrophyllite  $[\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2]$  at four different silica activities are shown in Fig. 6-4. The aluminum concentration in equilibrium with gibbsite is independent of sil-

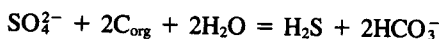
### HW3-2

For this problem you need to set up a mass balance between the available cation exchange capacities in the soil. Then compare this with the rate  $[H^+]$  in the rain and determine the time.

or, from (4-19),

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

Equation (4-25) is useful in understanding natural waters, since the controlling variables in many natural systems are  $\text{CO}_2$  and  $\text{HCO}_3^-$ . Carbonate concentration and pH can often be thought of as consequences of  $P_{\text{CO}_2}$  and  $m_{\text{HCO}_3^-}$ . For example, photosynthesis decreases dissolved  $\text{CO}_2$ , which will increase the state of saturation. Respiration and aerobic decay, on the other hand, increase dissolved  $\text{CO}_2$  and decrease saturation. Anaerobic decay with sulfate reduction (see Chapter 14) may be represented in a simplified way by the equation



Where  $\text{C}_{\text{org}}$  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  $P_{\text{CO}_2}$ ?

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

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

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,  $m_{\text{H}^+}$ ,  $m_{\text{OH}^-}$ , 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

$$2m_{\text{Ca}^{2+}} = m_{\text{HCO}_3^-} \tag{4-34}$$

or

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

or

$$a_{\text{Ca}^{2+}} = \frac{1}{2} a_{\text{HCO}_3^-} \frac{\gamma_{\text{Ca}^{2+}}}{\gamma_{\text{HCO}_3^-}} \tag{4-35}$$

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

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

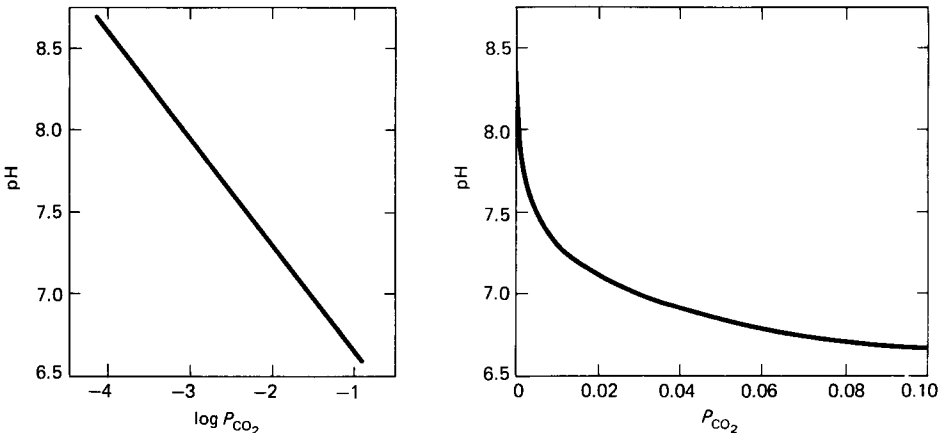
which rearranges to

$$a_{\text{H}^+}^3 = P_{\text{CO}_2}^2 \frac{K_1^2 K_2 K_{\text{CO}_2}^2 \gamma_{\text{Ca}^{2+}}}{2K_{\text{cal}} \gamma_{\text{HCO}_3^-}} \tag{4-36}$$

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  $P_{\text{CO}_2}$ , 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  $\gamma$  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  $P_{\text{CO}_2}$  lies between  $10^{-2}$  atm and the atmospheric value of  $10^{-3.5}$  atm. Waters with  $P_{\text{CO}_2}$  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  $P_{\text{CO}_2}$  for pure water in equilibrium with calcite at 25°C and 1 atm total pressure. Note the difference of form when  $P_{\text{CO}_2}$  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  $P_{\text{CO}_2}$ , we can manipulate the same set of equations. Dividing Eq. (4-27) by (4-29) gives

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

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

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

From (4-34)

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

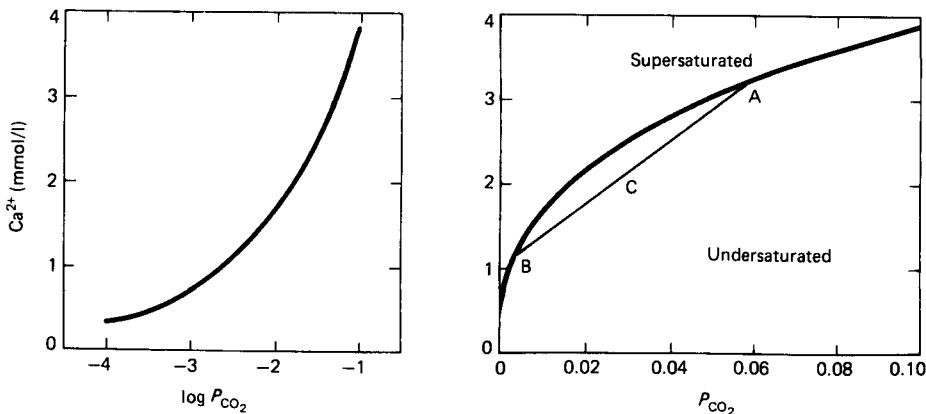
Substituting this in (4-37) and substituting  $a_{\text{Ca}^{2+}} = m_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}}$  gives

$$\frac{K_1}{K_2} = \frac{4m_{\text{Ca}^{2+}}^3 \gamma_{\text{Ca}^{2+}} \gamma_{\text{HCO}_3^-}^2}{K_{\text{cal}} K_{\text{CO}_2} P_{\text{CO}_2}}$$

or

$$m_{\text{Ca}^{2+}}^3 = P_{\text{CO}_2} \frac{K_1 K_{\text{cal}} K_{\text{CO}_2}}{4 K_2 \gamma_{\text{Ca}^{2+}} \gamma_{\text{HCO}_3^-}^2} \quad (4-38)$$

This relationship is plotted in Fig. 4-5. It is interesting to note that the relationship between  $m_{\text{Ca}^{2+}}$  and  $P_{\text{CO}_2}$  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  $P_{\text{CO}_2}$  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  $\text{CO}_2$  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)

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

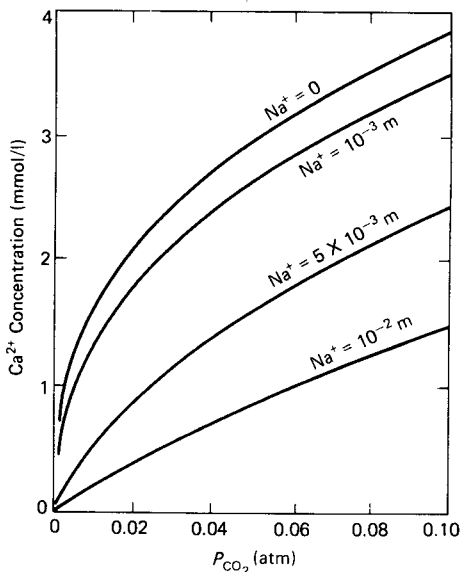
Substituting this equation for Eq. (4-34) in Example 2 and following the same derivation, Eq. (4-38) becomes

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

This relationship is shown graphically in Fig. 4-6. The presence of excess  $\text{NaHCO}_3$  decreases the concentration of  $\text{Ca}^{2+}$  in equilibrium with calcite. This is the familiar common-ion effect in solution chemistry. In alkaline brines where the  $\text{Na}^+$  concentration is very high, the dissolved  $\text{Ca}^{2+}$  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  $\text{CO}_2$  pressures?



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