The Geochemistry of Natural Waters

SECOND EDITION

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or, from (4–19),

$$\frac{a_{Ca^{2+}}a_{HCO_3^-}^2}{P_{CO_2}} = \frac{K_{cal}K_1K_{CO_2}}{K_2} \qquad (4\text{–}25)$$

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 $m_{HCO_3^-}$. 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

$$SO_4^{2-} + 2C_{org} + 2H_2O = H_2S + 2HCO_3^-$$
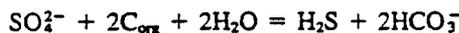
Where C_{org} represents carbon in organic matter. Thus anaerobic decay will increase saturation with respect to carbonate minerals, the opposite of aerobic decay.

Example 2

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

$$a_{H_2CO_3} = K_{CO_2}P_{CO_2} \qquad (4\text{–}26)$$

$$K_1 = \frac{a_{H^+}a_{HCO_3^-}}{a_{H_2CO_3}} \qquad (4\text{–}27)$$

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

$$a_{HCO_3^-} = \frac{K_1 K_{CO_2}P_{CO_2}}{a_{H^+}} \qquad (4\text{–}28)$$

$$K_2 = \frac{a_{H^+}a_{CO_3^{2-}}}{a_{HCO_3^-}} \qquad (4\text{–}29)$$

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

$$a_{CO_3^{2-}} = \frac{K_1 K_2 K_{CO_2}P_{CO_2}}{a_{H^+}^2} \qquad (4\text{–}30)$$

$$K_{cal} = a_{Ca^{2+}}a_{CO_3^{2-}} \qquad (4\text{–}31)$$

Substituting (4–30) in (4–31) gives

$$K_{cal} = \frac{a_{Ca^{2+}}K_1 K_2 K_{CO_2}P_{CO_2}}{a_{H^+}^2} \qquad (4\text{–}32)$$

The charge balance equation is

$$m_{H^+} + 2m_{Ca^{2+}} = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{OH^-} \qquad (4\text{–}33)$$

If we restrict our attention to the pH region below 9, m_{H^+}, m_{OH^-}, and $2m_{CO_3^{2-}}$ will be small compared to $2m_{Ca^{2+}}$ and $m_{HCO_3^-}$ 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

$$2m_{Ca^{2+}} = m_{HCO_3} \tag{4-34}$$

or

$$\frac{2a_{Ca^{2+}}}{\gamma_{Ca^{2+}}} = \frac{a_{HCO_3}}{\gamma_{HCO_3}}$$

or

$$a_{Ca^{2+}} = \tfrac{1}{2} a_{HCO_3} \frac{\gamma_{Ca^{2+}}}{\gamma_{HCO_3}} \tag{4-35}$$

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

$$K_{cal} = \frac{\tfrac{1}{2} K_1 K_{CO_2} P_{CO_2}}{a_{H^+}} \frac{K_1 K_2 K_{CO_2} P_{CO_2}}{a_{H^+}^2} \frac{\gamma_{Ca^{2+}}}{\gamma_{HCO_3}}$$

which rearranges to

$$a_{H^+}^3 = P_{CO_2}^2 \frac{K_1^2 K_2 K_{CO_2}^2 \gamma_{Ca^{2+}}}{2K_{cal} \gamma_{HCO_3}} \tag{4-36}$$

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_{CO_2}, a preliminary calculation is made assuming that $\gamma_{Ca^{2+}} = \gamma_{HCO_3}$; the concentrations of all species are calculated on this assumption, and these concentrations are used to calculate $\gamma_{Ca^{2+}}$ and γ_{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
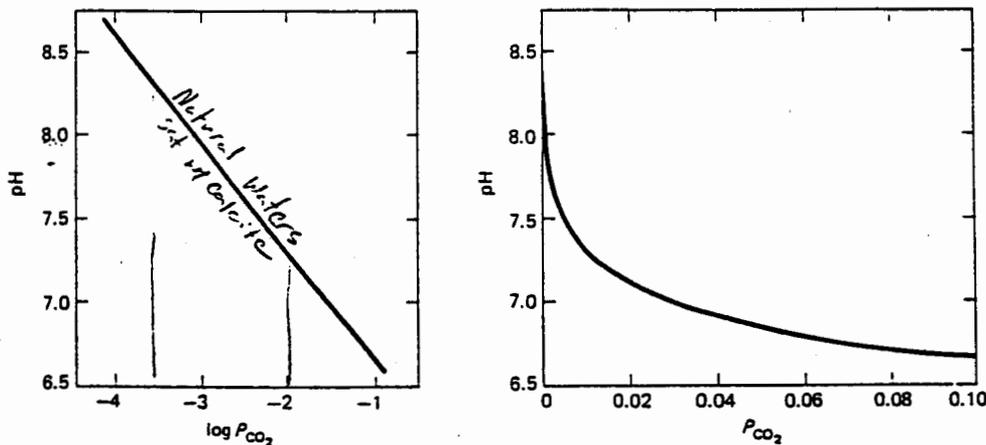

Figure 4-4 Relationship between pH and P_{CO_2} for pure water in equilibrium with calcite at 25°C and 1 atm total pressure. Note the difference of form when P_{CO_2} is plotted as a logarithm.

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Figure 15-8 Simplified pe–pH diagram for the system U–O–H$_2$O–CO$_2$ at 25°C and $P_{CO_2} = 10^{-2}$ atm, showing the stability fields of ideal solid uraninite and dissolved species. Solubility boundaries are drawn at 10^{-6} m dissolved uranium species (modified from Langmuir, 1978).

Figure 15-9 Simplified pe–pH diagram for the system U–O–H$_2$O–CO$_2$–V–K at 25°C and $P_{CO_2} = 10^{-2}$ atm, $K^+ = 10^{-3}$ m, V $= 10^{-6}$. Solubility boundaries are drawn at 10^{-6} m dissolved uranium species (modified from Langmuir, 1978).

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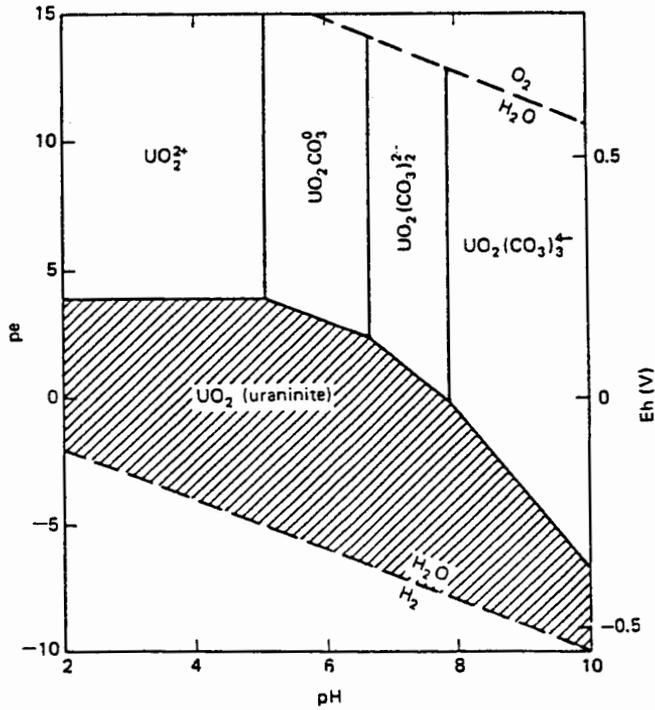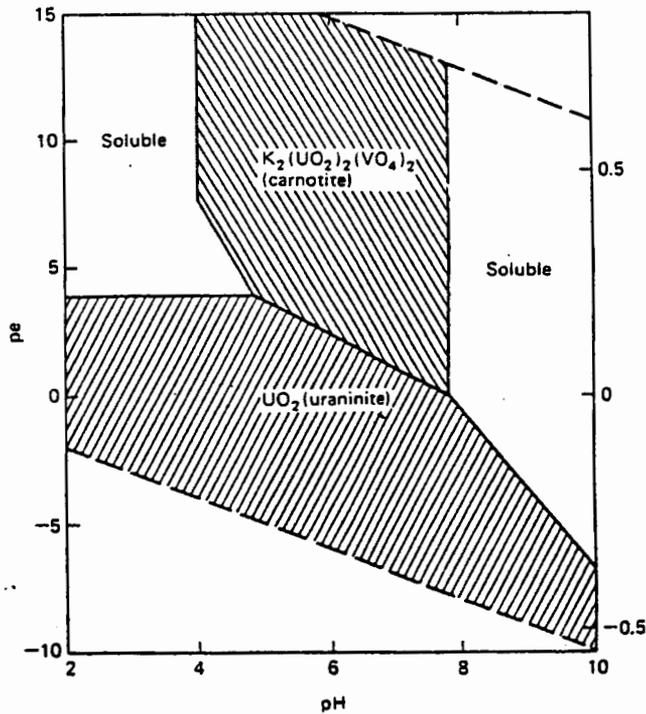In na
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