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# The Geochemistry of Natural Waters

*SECOND EDITION*

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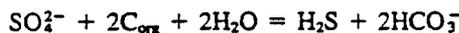
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or, from (4-19),

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

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

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

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

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

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

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

(4-25)

the controlling vari-  
centration and pH  
mple, photosynthe-  
on. Respiration and  
decrease saturation.  
represented in a sim-

y will increase sat-  
decay.

equilibrium with calcite

(4-26)

(4-27)

(4-28)

(4-29)

(4-30)

(4-31)

(4-32)

(4-33)

and  $2m_{\text{CO}_3^{2-}}$  will be  
on (small quantities  
quantities; they may  
33) then simplifies

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

or

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

or

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

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

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

which rearranges to

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

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  $P_{\text{CO}_2}$ , 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

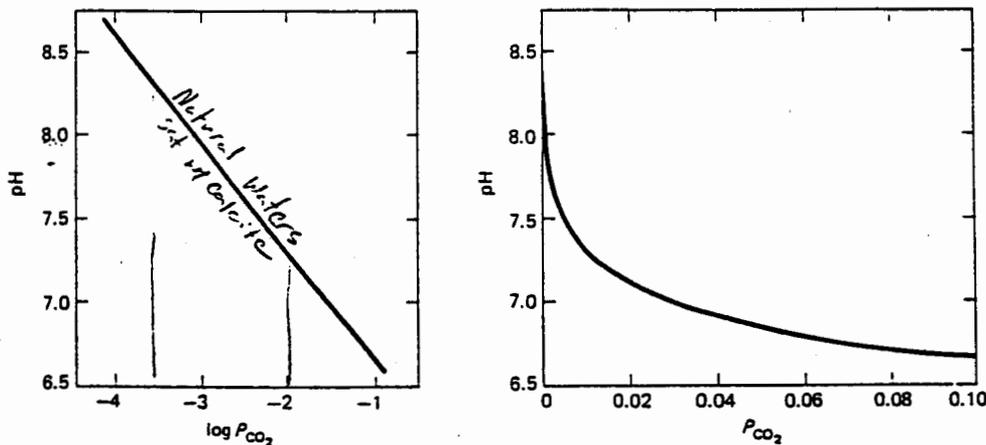


Figure 4-4 Relationship between pH and  $P_{\text{CO}_2}$  for pure water in equilibrium with calcite at 25°C and 1 atm total pressure. Note the difference of form when  $P_{\text{CO}_2}$  is plotted as a logarithm.

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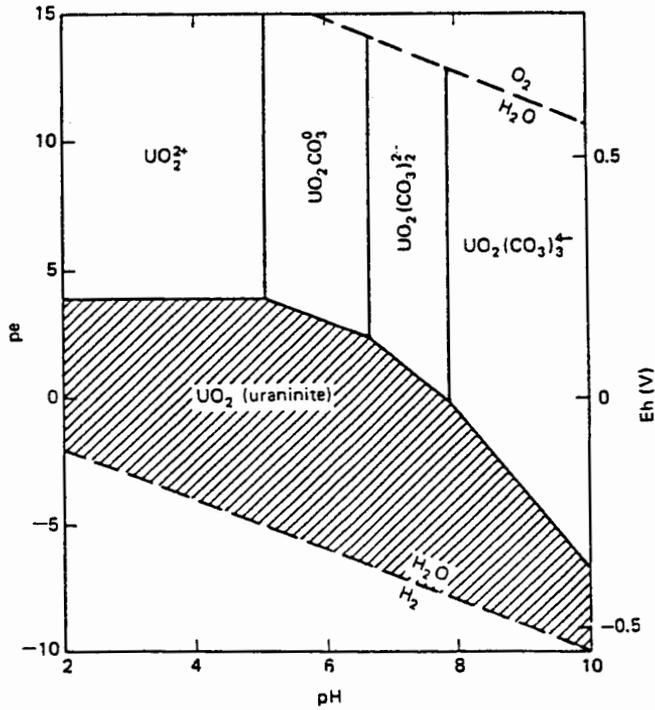


Figure 15-8 Simplified pe-pH diagram for the system U-O-H<sub>2</sub>O-CO<sub>2</sub> at 25°C and P<sub>CO<sub>2</sub></sub> = 10<sup>-2</sup> atm, showing the stability fields of ideal solid uraninite and dissolved species. Solubility boundaries are drawn at 10<sup>-6</sup> m dissolved uranium species (modified from Langmuir, 1978).

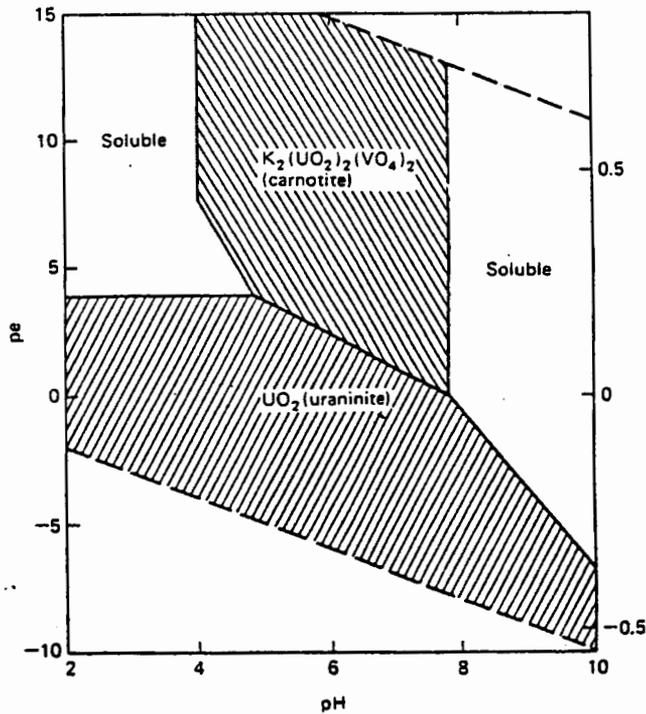


Figure 15-9 Simplified pe-pH diagram for the system U-O-H<sub>2</sub>O-CO<sub>2</sub>-V-K at 25°C and P<sub>CO<sub>2</sub></sub> = 10<sup>-2</sup> atm, K<sup>+</sup> = 10<sup>-3</sup> m, V = 10<sup>-6</sup>. Solubility boundaries are drawn at 10<sup>-6</sup> m dissolved uranium species (modified from Langmuir, 1978).