8-26. Describe how to prepare 100 mL of 0.200 M acetate buffer, pH 5.00, starting with pure liquid acetic acid and solutions containing ~3 M HCl and ~3 M NaOH.

9-4. Consider the diprotic acid H_2A with $K_1 = 1.00 \times 10^{-4}$ and $K_2 = 1.00 \times 10^{-8}$. Find the pH and concentrations of H_2A, HA^-, and A^{2-} in **(a)** 0.100 M H_2A; **(b)** 0.100 M NaHA; **(c)** 0.100 M Na_2A.

9-7. Use the method of Box 9-2 to calculate the concentrations of H^+, H_2A, HA^-, and A^{2-} in 0.001 00 M monosodium oxalate, NaHA.

9-12. *Effect of temperature on carbonic acid acidity and the solubility of CaCO₃.*[9] Box 9-1 states that marine life with $CaCO_3$ shells and skeletons will be threatened with extinction in cold polar waters before that will happen in warm tropical waters. The following equilibrium constants apply to seawater at 0° and 30°C, when concentrations are measured in moles per kilogram of seawater and pressure is in bars:

$$CO_2(g) \rightleftharpoons CO_2(aq) \tag{A}$$

$$K_H = \frac{[CO_2(aq)]}{P_{CO_2}} = 10^{-1.2073} \text{ mol kg}^{-1} \text{ bar}^{-1} \text{ at } 0°C$$

$$= 10^{-1.6048} \text{ mol kg}^{-1} \text{ bar}^{-1} \text{ at } 30°C$$

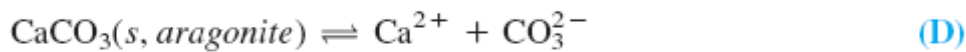$$CO_2(aq) + H_2O \rightleftharpoons HCO_3^- + H^+ \qquad \text{(B)}$$
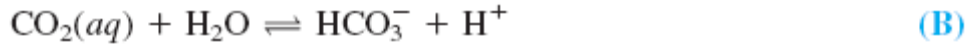
$$K_{a1} = \frac{[HCO_3^-][H^+]}{[CO_2(aq)]} = 10^{-6.1004} \text{ mol kg}^{-1} \text{ at } 0°C$$
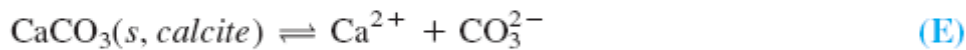
$$= 10^{-5.8008} \text{ mol kg}^{-1} \text{ at } 30°C$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \qquad \text{(C)}$$

$$K_{a2} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = 10^{-9.3762} \text{ mol kg}^{-1} \text{ at } 0°C$$

$$= 10^{-8.8324} \text{ mol kg}^{-1} \text{ at } 30°C$$

$$CaCO_3(s, \textit{aragonite}) \rightleftharpoons Ca^{2+} + CO_3^{2-} \qquad \text{(D)}$$

$$K_{sp}^{arg} = [Ca^{2+}][CO_3^{2-}] = 10^{-6.1113} \text{ mol}^2 \text{ kg}^{-2} \text{ at } 0°C$$

$$= 10^{-6.1391} \text{ mol}^2 \text{ kg}^{-2} \text{ at } 30°C$$

$$CaCO_3(s, \textit{calcite}) \rightleftharpoons Ca^{2+} + CO_3^{2-} \qquad \text{(E)}$$

$$K_{sp}^{cal} = [Ca^{2+}][CO_3^{2-}] = 10^{-6.3652} \text{ mol}^2 \text{ kg}^{-2} \text{ at } 0°C$$

$$= 10^{-6.3713} \text{ mol}^2 \text{ kg}^{-2} \text{ at } 30°C$$

The first equilibrium constant is called K_H for Henry's law (Problem 9-11). Units are given to remind you what units you must use.

(a) Combine the expressions for K_H, K_{a1}, and K_{a2} to find an expression for $[CO_3^{2-}]$ in terms of P_{CO_2} and $[H^+]$.

(b) From the result of (a), calculate $[CO_3^{2-}]$ (mol kg^{-1}) at P_{CO_2} = 800 μbar and pH = 7.8 at temperatures of 0° (polar ocean) and 30°C (tropical ocean). These are conditions that could be reached around the year 2100 if we continue to release CO_2 at the present rate.

(c) The concentration of Ca^{2+} in the ocean is 0.010 M. Predict whether aragonite and calcite will dissolve under the conditions in (b).

9-24. The acid HA has $pK_a = 7.00$.

(a) Which is the principal species, HA or A^-, at pH 6.00?

(b) Which is the principal species at pH 8.00?

(c) What is the quotient $[A^-]/[HA]$ at pH 7.00? at pH 6.00?

9-25. The diprotic acid H_2A has $pK_1 = 4.00$ and $pK_2 = 8.00$.

(a) At what pH is $[H_2A] = [HA^-]$?

(b) At what pH is $[HA^-] = [A^{2-}]$?

(c) Which is the principal species at pH 2.00: H_2A, HA^-, or A^{2-}?

(d) Which is the principal species at pH 6.00?

(e) Which is the principal species at pH 10.00?

9-26. The base B has $pK_b = 5.00$.

(a) What is the value of pK_a for the acid BH^+?

(b) At what pH is $[BH^+] = [B]$?

(c) Which is the principal species at pH 7.00: B or BH^+?

(d) What is the quotient $[B]/[BH^+]$ at pH 12.00?

9-28. The acid HA has $pK_a = 4.00$. Use Equations 9-17 and 9-18 to find the fraction in the form HA and the fraction in the form A^- at pH $= 5.00$. Does your answer agree with what you expect for the quotient $[A^-]/[HA]$ at pH 5.00?