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$_2$A with $K_1 = 1.00 \times 10^{-4}$ and $K_2 = 1.00 \times 10^{-8}$. Find the pH and concentrations of H$_2$A, HA$^-$, and A$^{2-}$ in (a) 0.100 M H$_2$A; (b) 0.100 M NaHA; (c) 0.100 M Na$_2$A.

9-7. Use the method of Box 9-2 to calculate the concentrations of H$^+$, H$_2$A, 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. Box 9-1 states that marine life with CaCO₃ 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:

\[
\text{CO}_2(g) \rightleftharpoons \text{CO}_2(aq)
\]

\[
K_H = \frac{[\text{CO}_2(aq)]}{P_{\text{CO}_2}} = 10^{-1.2073} \text{ mol kg}^{-1} \text{ bar}^{-1} \text{ at } 0^\circ\text{C}
\]

\[
= 10^{-1.6048} \text{ mol kg}^{-1} \text{ bar}^{-1} \text{ at } 30^\circ\text{C}
\]
CO$_2(aq)$ + H$_2$O $\rightleftharpoons$ HCO$_3^-$ + H$^+$  \hfill (B)

\[ K_{a1} = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2(aq)]]} = 10^{-6.1004} \text{ mol kg}^{-1} \text{ at 0°C} \]
\[ = 10^{-5.8008} \text{ mol kg}^{-1} \text{ at 30°C} \]

HCO$_3^-$ $\rightleftharpoons$ CO$_3^{2-}$ + H$^+$  \hfill (C)

\[ K_{a2} = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} = 10^{-9.3762} \text{ mol kg}^{-1} \text{ at 0°C} \]
\[ = 10^{-8.8324} \text{ mol kg}^{-1} \text{ at 30°C} \]

CaCO$_3(s, \text{aragonite}) \rightleftharpoons$ Ca$^{2+}$ + CO$_3^{2-}$  \hfill (D)

\[ K_{sp}^{\text{arg}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 10^{-6.1113} \text{ mol}^2 \text{kg}^{-2} \text{ at 0°C} \]
\[ = 10^{-6.1391} \text{ mol}^2 \text{kg}^{-2} \text{ at 30°C} \]

CaCO$_3(s, \text{calcite}) \rightleftharpoons$ Ca$^{2+}$ + CO$_3^{2-}$  \hfill (E)

\[ K_{sp}^{\text{cal}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 10^{-6.3652} \text{ mol}^2 \text{kg}^{-2} \text{ at 0°C} \]
\[ = 10^{-6.3713} \text{ mol}^2 \text{kg}^{-2} \text{ at 30°C} \]

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 $P_{\text{CO}_2}$ and [H$^+$].

(b) From the result of (a), calculate [CO$_3^{2-}$] (mol kg$^{-1}$) at $P_{\text{CO}_2}$ = 800 µbar and pH = 7.8 at temperatures of 0°C (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?