Unless conditions require the use of the exact solution, approximate equations are preferable because they are easier to apply and provide greater physical insight. If a calculation (ignoring water autoionization) of the ionization of a weak acid gives a concentration of H_3O^+ smaller than 10^{-6} M or if a calculation of base ionization gives a concentration of OH^- smaller than 10^{-6} M, then we have to use the more exact treatment. For buffer solutions, a pH near 7 does not necessarily mean that water ionization is important, unless the acid or base concentration becomes very small.

EXAMPLE 15.14

Calculate the pH of a 1.00×10^{-5} M solution of HCN(aq). The K_a of HCN(aq) is 6.17×10^{-10}.

SOLUTION

Suppose the autoionization of water is ignored and the method of Examples 15.3 and 15.4 is used. This gives $[H_3O^+] = 7.9 \times 10^{-8}$ M, which of course makes no sense, because it is *lower* than the concentration of hydronium ion in pure water. HCN is a very weak acid, but it is nonetheless an acid, not a base.

So, we have to use the exact cubic equation for $[H_3O^+]$, inserting into it the proper coefficients and taking $c_a = 1.00 \times 10^{-5}$ and $c_b = 0$. This gives

$$[H_3O^+]^3 + 6.17 \times 10^{-10}[H_3O^+]^2 - \\ 1.617 \times 10^{-14}[H_3O^+] - 6.17 \times 10^{-24} = 0$$
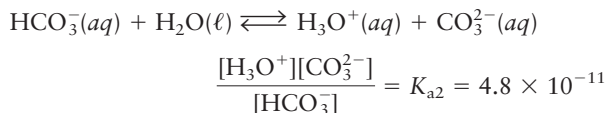
Unfortunately, there is no method as simple as the quadratic formula to solve a cubic equation. The easiest way to solve this equation is to try a series of values for $[H_3O^+]$ on the left side, varying them to obtain a result as close as possible to 0 (see Appendix C). It is safe to assume that the final answer will be slightly larger than 1×10^{-7}, so the initial guesses should be of that magnitude. Carrying out the procedure gives

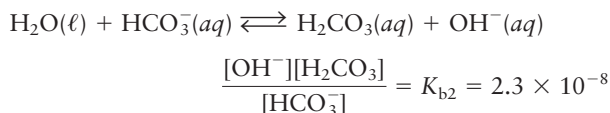$$[H_3O^+] = 1.27 \times 10^{-7} \text{ M} \qquad \text{pH} = 6.90$$

Related Problems: 69, 70

Amphoteric Equilibria

A second situation in which an exact analysis of acid–base equilibrium is useful occurs when an amphoteric species is dissolved in water. The hydrogen carbonate ion (HCO_3^-) is amphoteric because it can act as an acid in the equilibrium

$$HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

$$\frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = K_{a2} = 4.8 \times 10^{-11}$$

or as a base in the equilibrium

$$H_2O(\ell) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

$$\frac{[OH^-][H_2CO_3]}{[HCO_3^-]} = K_{b2} = 2.3 \times 10^{-8}$$

If sodium hydrogen carbonate ($NaHCO_3$) is dissolved in water, there is a competition between the tendency of HCO_3^- to accept hydrogen ions and to donate them. Because $K_{b2} > K_{a2}$, there should be more production of OH^- than of H_3O^+, so the solution should be basic.

In an exact treatment of this equilibrium, there are six unknown concentrations—those of Na^+, H_2CO_3, HCO_3^-, CO_3^{2-}, OH^-, and H_3O^+. Two equilibrium equations were already presented, and a third relates $[OH^-]$ and $[H_3O^+]$ to K_w. If $[HCO_3^-]_0$ is the original concentration of $NaHCO_3$, then from stoichiometry

$$[HCO_3^-]_0 = [HCO_3^-] + [H_2CO_3] + [CO_3^{2-}]$$

because the total amount of carbonate material is conserved. Any reduction in $[HCO_3^-]$ must be compensated by a corresponding increase in either $[H_2CO_3]$ or $[CO_3^{2-}]$. Next we use the principle of conservation of charge. The positively charged species present are Na^+ and H_3O^+, and the negatively charged species are HCO_3^-, CO_3^{2-}, and OH^-. Because there is overall charge neutrality,

$$[Na^+] + [H_3O^+] = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-]$$

where the coefficient 2 for $[CO_3^{2-}]$ arises because each carbonate ion is doubly charged. In addition, the Na^+ concentration is unchanged, so

$$[Na^+] = [HCO_3^-]_0$$

In principle, these six equations can be solved simultaneously to calculate the exact $[H_3O^+]$ for an arbitrary initial concentration of HCO_3^-. The result is complex and gives little physical insight. Instead, we give only a simpler, approximate solution, which is sufficient in the cases considered here. Subtracting the carbonate balance equation from the charge balance equation gives

$$[H_3O^+] = [CO_3^{2-}] - [H_2CO_3] + [OH^-]$$

The three equilibrium expressions are used to rewrite this as

$$[H_3O^+] = K_{a2}\frac{[HCO_3^-]}{[H_3O^+]} - \frac{[H_3O^+][HCO_3^-]}{K_{a1}} + \frac{K_w}{[H_3O^+]}$$

where $[CO_3^{2-}]$ and $[H_2CO_3]$ have been eliminated in favor of $[HCO_3^-]$.

Multiplying by $K_{a1}[H_3O^+]$ gives

$$K_{a1}[H_3O^+]^2 + [HCO_3^-][H_3O^+]^2 = K_{a1}K_{a2}[HCO_3^-] + K_{a1}K_w$$

$$[H_3O^+]^2 = \frac{K_{a1}K_{a2}[HCO_3^-] + K_{a1}K_w}{K_{a1} + [HCO_3^-]}$$

This equation still contains two unknown quantities, $[H_3O^+]$ and $[HCO_3^-]$. Because both K_{a2} and K_{b2} are small, $[HCO_3^-]$ should be close to its original value, $[HCO_3^-]_0$. If $[HCO_3^-]$ is set equal to $[HCO_3^-]_0$, this becomes

$$[H_3O^+]^2 \approx \frac{K_{a1}K_{a2}[HCO_3^-]_0 + K_{a1}K_w}{K_{a1} + [HCO_3^-]_0}$$

which can be solved for $[H_3O^+]$. In many cases of interest, $[HCO_3^-]_0 \gg K_{a1}$, and $K_{a2}\,[HCO_3^-]_0 \gg K_w$. When this is so, the expression simplifies to

$$[H_3O^+]^2 \approx K_{a1}K_{a2}$$

$$[H_3O^+] \approx \sqrt{K_{a1}K_{a2}}$$

$$\text{pH} \approx \frac{1}{2}\,(pK_{a1} + pK_{a2})$$

so the pH of such a solution is the average of the pK_a values for the two ionizations.

EXAMPLE 15.15

What is the pH of a solution that is 0.100 M in $NaHCO_3$?

SOLUTION

First, the two assumptions are checked:

$$[HCO_3^-]_0 = 0.100 \gg 4.3 \times 10^{-7} = K_{a1}$$

$$[HCO_3^-]_0 K_{a2} = 4.8 \times 10^{-12} \gg 1.0 \times 10^{-14} = K_w$$

so both are satisfied. Therefore,

$$[H_3O^+] = \sqrt{K_{a1}K_{a2}} = 4.5 \times 10^{-9}\,\text{M}$$

$$pH = 8.34$$

and the solution is basic, as expected.

Titration of a Polyprotic Acid

A polyprotic acid has more than one equivalence point. The first equivalence point occurs when the volume V_{e1} of base added is sufficient to remove one hydrogen ion from each acid molecule, V_{e2} is the volume sufficient to remove two hydrogen ions from each, and so forth. A diprotic acid shows two equivalence points, and a triprotic acid, three. The equivalent volumes are related to each other by

$$V_{e1} = \frac{1}{2} V_{e2} = \frac{1}{3} V_{e3}$$

Figure 15.17 shows a titration curve for triprotic phosphoric acid. The three equivalence points are at 100.0 mL, 200.0 mL, and 300.0 mL. Calculating the pH as a function of the volume of added base presents no new complications beyond those already considered. The initial pH is given by a calculation analogous to that of Example 15.12, and the pH in the flat regions between equivalence points is obtained by a buffer calculation like that for a diprotic acid. For example, the pH after addition of 50.0 mL of base is that of an equimolar $H_3PO_4/H_2PO_4^-$ buffer (subsequent ionization of $H_2PO_4^-$ can be ignored). Finally, the pH at the first equivalence point is that for a solution of NaH_2PO_4 and uses the amphoteric equilibria equations presented earlier in this section (PO_4^{3-} can be ignored in this case). The pH at the second equivalence point is an amphoteric equilibrium in which HPO_4^{2-} is in equilibrium with $H_2PO_4^-$ and with PO_4^{3-}.
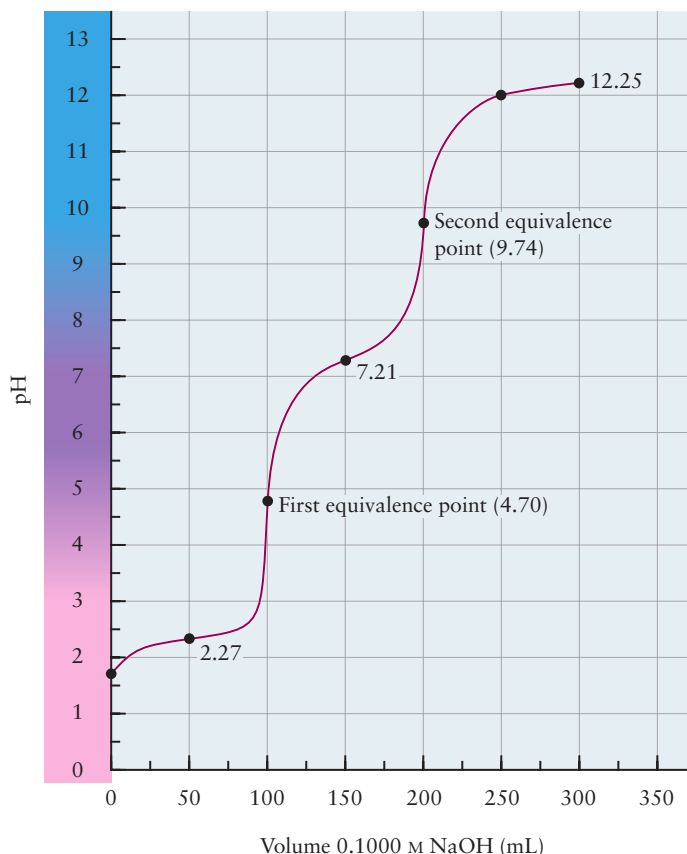

FIGURE 15.17 A titration curve for the titration of a polyprotic acid (phosphoric acid) by a strong base. The curve shown is for 100.0 mL of 0.1000 M H_3PO_4 titrated with 0.1000 M NaOH. No clear third equivalence point is seen at 300 mL because K_a for HPO_4^{2-} is not much greater than K_a for H_2O in aqueous solution.

15.9 Organic Acids and Bases: Structure and Reactivity

One of the goals of organic chemistry is to understand the relationship between *structure* and *function*. How does the molecular structure of an organic compound (including its attached functional groups) affect its chemical reactivity? As an example of the exploration of structure–function relationships we consider here the trends in acid strength in organic compounds. This extends the earlier discussion of acid strength in inorganic acids (see Section 15.3) and illustrates the usefulness of chemical concepts such as electronegativity and resonance in predicting reactivity. This section depends on the thermodynamic description in Section 14.3.

Table 15.2 lists a number of organic acids with pK_a values in aqueous solution between 0 (strong acid) and 14 (weak acid). Almost all of them are carboxylic acids with the characteristic —COOH functional group. Acid ionization constants