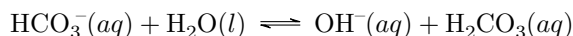
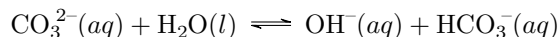
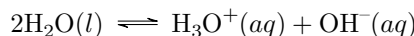


Polyprotic Acids and Bases

Polyprotic acids and bases present an additional complication because they have more than one dissociation reaction that determines the solution's pH. Consider, for example, a solution of 0.10 M Na_2CO_3 for which we wish to calculate the pH. Because the carbonate ion, CO_3^{2-} has two basic sites, we must consider the following two equilibrium reactions



along with the dissociation of water



These three equilibrium reactions include five species with concentrations that are unknown to us: OH^- , H_3O^+ , H_2CO_3 , HCO_3^- , and CO_3^{2-} .

To calculate the solution's pH we need five equations; these include the three equilibrium constant expressions

$$K_{b1} = \frac{[\text{OH}^-][\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = 2.1 \times 10^{-4}$$

$$K_{b2} = \frac{[\text{OH}^-][\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = 2.2 \times 10^{-8}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

a mass balance equation for carbonate

$$0.10 \text{ M} = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3]$$

and a charge balance equation

$$[\text{Na}^+] + [\text{H}_3\text{O}^+] = 2 \times [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-]$$

Note that the concentration of CO_3^{2-} in the charge balance equation is multiplied by 2 as this equation balances the concentration of charge not the concentration of ions.¹

Five equations and five unknowns is a mess! Given that the rigorous treatment of a monoprotic weak acid leads to a third-order polynomial equation, we reasonably can expect that the solution to this problem is a fourth-order polynomial equation. To simplify the problem we make some assumptions. Our first assumption starts by noting that $K_{b2} \ll K_{b1}$, which suggests that the concentration of H_2CO_3 probably is very small; thus we assume that $[\text{H}_2\text{CO}_3] \approx 0$, which reduces the mass balance equation to

$$0.10 \text{ M} = [\text{CO}_3^{2-}] + [\text{HCO}_3^-]$$

¹Here, as we did in an earlier essay, we use a rigorous approach to solving equilibrium problems to help understand the general conclusion stated at the end of this essay. You do not need to know how to do the sort of rigorous calculations outlined here. This is covered in greater detail in Chem 352.

Solving for the equilibrium concentration of carbonate gives

$$[\text{CO}_3^{2-}] = 0.10 - [\text{HCO}_3^-]$$

which we substitute into the charge balance equation

$$[\text{Na}^+] + [\text{H}_3\text{O}^+] = 2 \times (0.10 - [\text{HCO}_3^-]) + [\text{HCO}_3^-] + [\text{OH}^-]$$

Next, we note that the $[\text{Na}^+] = 0.20 \text{ M}$ and, because the solution is basic, make the reasonable assumption that $[\text{H}_3\text{O}^+]$ is negligible; thus

$$0.20 = 0.20 - 2 \times [\text{HCO}_3^-] + [\text{HCO}_3^-] + [\text{OH}^-]$$

$$0 = -[\text{HCO}_3^-] + [\text{OH}^-]$$

$$[\text{HCO}_3^-] = [\text{OH}^-]$$

Now, we substitute the equilibrium concentrations for OH^- and for CO_3^{2-} into K_{b1}

$$K_{b1} = \frac{[\text{OH}^-][\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = \frac{[\text{HCO}_3^-][\text{HCO}_3^-]}{0.10 - [\text{HCO}_3^-]} = \frac{X^2}{0.10 - X} = 2.1 \times 10^{-4}$$

Note that we have reduced this problem to one equivalent to finding the pH of a monoprotic weak base. To solve we assume that $0.10 - X \approx 0.10$ and find that $X = 4.58 \times 10^{-3}$. To check the assumption we calculate the percent error, finding that

$$\% \text{ error} = \frac{0.10 - (0.10 - 0.00458)}{0.10} \times 100 = +4.6\%$$

This error is within reason. We now know some of the equilibrium concentrations; these are

$$[\text{HCO}_3^-] = X = 4.6 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = [\text{HCO}_3^-] = 4.6 \times 10^{-3} \text{ M}$$

$$[\text{CO}_3^{2-}] = 0.10 - [\text{HCO}_3^-] = 0.095 \text{ M}$$

There is, of course, one last assumption to check: that the concentration of H_2CO_3 is essentially zero. The calculated equilibrium concentration for H_2CO_3 is

$$[\text{H}_2\text{CO}_3] = \frac{K_{b2}[\text{HCO}_3^-]}{[\text{OH}^-]} = K_{b2} = 2.2 \times 10^{-8} \text{ M}$$

which is close enough to zero to suggest that our first assumption is reasonable. You don't want or need to go through this lengthy process when you work with polyprotic weak acids and bases. Instead, use the general "rule-of-thumb" that this approach works if $\frac{K_{a1}}{K_{a2}} \geq 500$ or if $\frac{K_{b1}}{K_{b2}} \geq 500$. Under these conditions, you can safely treat a polyprotic weak acid or weak base as if it is a monoprotic weak acid or weak base.