14.6: Polyprotic Acids and Bases

Whereas monoprotic acids (like HCl pictured below) only have one hydrogen ion (aka proton - pictured below in white) to donate, polyprotic acids can donate multiple protons (see the H_2SO_4 molecule pictured below). Following a similar logic, polyprotic bases are bases that can accept multiple protons. With the basics of polyprotic acids and bases covered, let's dive into some of the details of how these special acids and bases work.
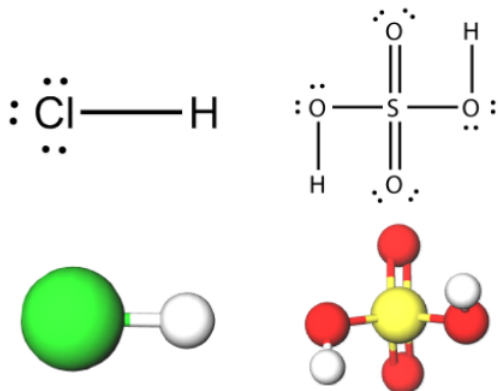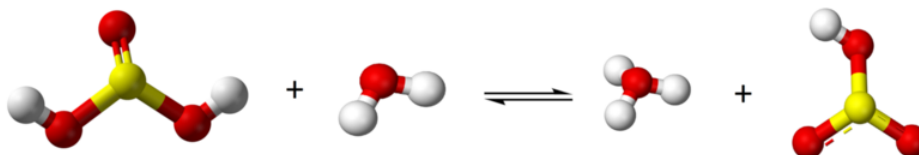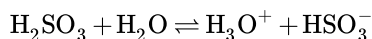

Figure 14.6.1: Lewis dot structure and ball-and-stick structure of HCl and H_2SO_4 strong acids.

In the case of polyprotic acids and bases we can write down an equilibrium constant for each proton lost or gained. These constants are subscripted 1, 2, etc., to distinguish them. For sulfurous acid, a *diprotic acid*, we can, for example, write
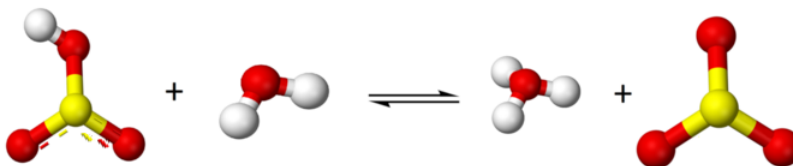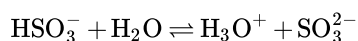
Step 1

$$H_2SO_3 + H_2O \rightleftharpoons H_3O^+ + HSO_3^-$$

with appropriate acid constant

$$K_{a1} = \frac{[\,H_3O^+\,]\,[\,HSO_3^-\,]}{[\,H_2SO_3\,]} = 1.7 \times 10^{-2} \text{ mol L}^{-1} \tag{14.6.1}$$

and

Step 2

$$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{2-}$$

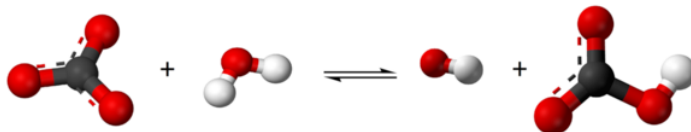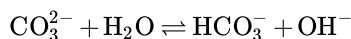
with appropriate acid constant

$$K_{a2} = \frac{[\,H_3O^+\,]\,[\,SO_3^{2-}\,]}{[\,HSO_3\,]} = 5.6 \times 10^{-8} \text{ mol L}^{-1} \tag{14.6.2}$$

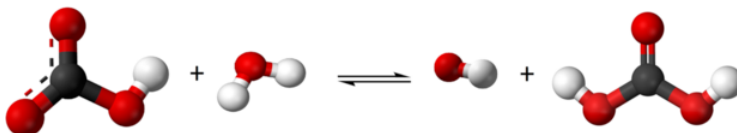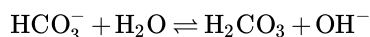The carbonate ion, CO_3^{2-}, is an example of a *diprotic* base.

Step 1

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

with appropriate base constant

$$K_{b1} = \frac{[\,HCO_3^-\,]\,[\,OH^-\,]}{[\,CO_3^{2-}\,]} = 2.1 \times 10^{-4} \text{ mol L}^{-1} \tag{14.6.3}$$

Step 2

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

with appropriate base constant

$$K_{b2} = \frac{[\,H_2CO_3\,]\,[\,OH^-\,]}{[\,CO_3^-\,]} = 2.4 \times 10^{-8} \text{ mol L}^{-1} \tag{14.6.4}$$

A general treatment of the pH of solutions of polyprotic species is beyond our intended scope, but it is worth noting that in many cases we can treat polyprotic species as monoprotic. In the case of \ce{H2SO3}\), for example, $K_{a1} \gg K_{a2}$ indicating that H_2SO_3 is a very much stronger acid than HSO_3^-. This means that when H_2SO_3 is dissolved in water, we can treat it as a monoprotic acid and ignore the possible loss of a second proton. Solutions of salts containing the carbonate ion, such as Na_2CO_3 or K_2CO_3 can be treated similarly.

✔ **Example 14.6.1: pH Calculation**

Find the pH of a 0.100-*M* solution of sodium carbonate, Na_2CO_3. Use the base constant $K_{b1} = 2.10 \times 10^{-4}\, mol\, L^{-1}$ (Equation 14.6.3).

Solution

We ignore the acceptance of a second proton and treat the carbonate ion as a monoprotic base. We then have

$$[\,OH^-\,] = \sqrt{K_b c_b} = \sqrt{2.10 \times 10^{-4} \text{ mol L}^{-1} \times 0.100 \text{ mol L}^{-1}} \tag{14.6.5}$$
$$= 4.58 \times 10^{-3} \text{ mol L}^{-1} \tag{14.6.6}$$

Checking, we find that

$$\frac{[\,OH^-\,]}{c_b} = \frac{40.58 \times 10^{-3}}{0.1} \approx 4.6 \text{ percent}$$

so that our approximation is only just valid.

We now find

$$pOH = -\log\left(4.58 \times 10^{-3}\right) = 2.34$$

while

$$\text{pH} = 14 - \text{pOH} = 14 - 2.34 = 11.6$$

Since the carbonate ion is a somewhat stronger base than NH_3, we expect a 0.1-M solution to be somewhat more basic, as actually found.

A glance at the K_a and and K_b tables (Tables E1 and E2) reveals that most acid and base constants involve numbers having negative powers of 10. As in the case of $[H_3O^+]$ and $[OH^-]$, then, it is convenient to define

$$pK_a = -\log\frac{K_a}{\text{mol L}^{-1}}$$

$$pK_b = -\log\frac{K_b}{\text{mol L}^{-1}}$$

Using these definitions, the larger K_a or K_b is (i.e., the stronger an acid or base, respectively), the smaller pK_a or pK_b will be. For a strong acid like HNO_3, $K_a = 20$ mol L^{-1} and

$$pK_a = -\log 20 = -(1.30) = -1.30$$

Thus for very strong acids or bases pK values can even be negative.

This page titled 14.6: Polyprotic Acids and Bases is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Ed Vitz, John W. Moore, Justin Shorb, Xavier Prat-Resina, Tim Wendorff, & Adam Hahn.