

Ladder Diagrams

In an earlier essay we concluded that CH_3COOH is the only significant form of acetic acid in solutions when the pH is less than 3.74 and that CH_3COO^- is the only important species when the pH is greater than 5.74. In between these two pH levels a solution of acetic acid contains relatively similar concentrations of CH_3COOH and of CH_3COO^- with the ratio

$$\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

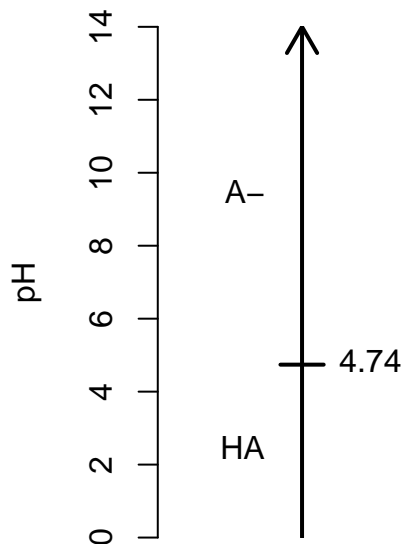
equal to 0.1 at a pH of 3.74 and 10 at a pH of 5.74. More generally, for any weak acid, HA, we noted that

- when $\text{pH} < \text{p}K_{\text{a,HA}} - 1$, HA is the only important species in solution
- when $\text{pH} > \text{p}K_{\text{a,HA}} + 1$, A^- is the only important species in solution
- when $\text{p}K_{\text{a,HA}} - 1 < \text{pH} < \text{p}K_{\text{a,HA}} + 1$, both HA and A^- are important species in solution

Sometimes it is helpful to think about equilibrium chemistry more qualitatively. In such cases a ladder diagram is a useful tool.

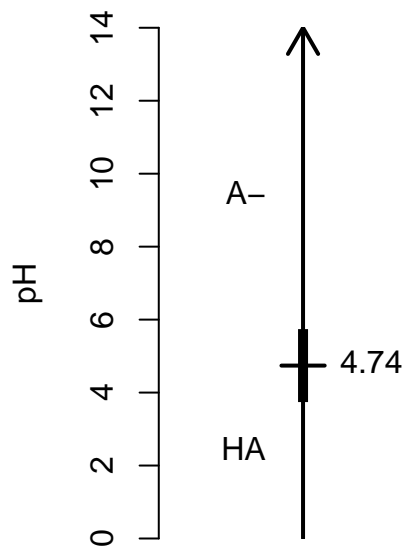
Drawing a Ladder Diagram

Let's begin by drawing a ladder diagram for acetic acid, the $\text{p}K_{\text{a}}$ of which is 4.74. We begin by drawing a vertical arrow that represents pH. As shown below, the top of the arrow represents solutions that are more basic and the bottom of the arrow represents solutions that are more acidic. A horizontal line—which we call a step on the ladder—is added at a pH that is equal to acetic acid's $\text{p}K_{\text{a}}$.



We know that when $\text{pH} = \text{p}K_{\text{a}}$, the concentrations of CH_3COOH and of CH_3COO^- are equal. We also know that when $\text{pH} < \text{p}K_{\text{a}}$, there is more acetic acid, which we label here as HA, and that when $\text{pH} > \text{p}K_{\text{a}}$, there is more acetate ion, which we label here as A^- .

Finally, we add a rectangular box along the pH axis that extends from a pH value of $\text{p}K_{\text{a}} + 1$, or 5.74, to a pH value of $\text{p}K_{\text{a}} - 1$, or 3.74. This box spans pH levels for which the $[\text{CH}_3\text{COOH}]$ and the $[\text{CH}_3\text{COO}^-]$ are relatively similar (that is, the concentrations are within a factor of 10 of each other).



To summarize, the ladder diagram for acetic acid shows that above a pH of 5.74 the only important form of acetic acid is CH_3COO^- and that below a pH of 3.74 the only important form of acetic acid is CH_3COOH . For a pH between 5.74 and 4.74 both CH_3COOH and CH_3COO^- are present, but there is more CH_3COO^- . For a pH between 4.74 and 3.74 both CH_3COOH and CH_3COO^- are present, but there is more CH_3COOH .