Relative Concentrations of Conjugate Acids & Bases

Every weak acid has a conjugate weak base (and, of course, every weak base has a conjugate weak acid). For example, acetic acid, CH_3COOH for example, is in equilibrium with the acetate ion, CH_3COO^-, as shown by the following reaction

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

According to Le Châtelier's principle, adding a strong acid, a source of H_3O^+, shifts this equilibrium to the left, increasing the concentration of CH_3COOH, and adding a strong base, a source of OH^-, consumes H_3O^+ and shifts the equilibrium to the right, increasing the concentration of CH_3COO^-. Clearly there are pH levels that favor acetic acid and pH levels that favor the acetate ion, although the exact pH levels are not clear from this simple treatment.

The acid dissociation constant for a weak acid is a good starting point for considering how pH affects the relative amount of a weak acid and its conjugate weak base. For acetic acid the K_a expression is

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Taking the log of both sides, multiplying through by –1, and substituting in pH for –log$[H_3O^+]$ and pK_a for –logK_a gives

$$pK_a = pH - \log\frac{[CH_3COO^-]}{[CH_3COOH]}$$

Solving for the ratio of weak base-to-weak acid, we obtain

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = 10^{pH - pK_a}$$

This equation shows us that the relative amounts of CH_3COOH and of CH_3COO^- are determined by how close the solution's pH is to acetic acid's pK_a value, which is 4.74. Some actual values are shown in the following table:

pH	pH – pK_a	$\frac{[CH_3COO^-]}{[CH_3COOH]}$
1.74	–3.00	0.0010
2.74	–2.00	0.010
3.74	–1.00	0.10
4.74	0	1.0
5.74	+1.00	10
6.74	+2.00	100
7.74	+3.00	1000

We can use these results to make some general statements about the relative importance of acetic acid's conjugate weak acid and conjugate weak base forms as a function of pH. At a pH of 3.74, for example, there is one acetate ion for every 10 molecules of acetic acid; thus, for all practical purposes, at any pH < 3.74, CH_3COOH accounts for more than 90% of a mass balance on acetic acid and it is the only important form of acetic acid in solution. At a pH of 5.74, there are 10 acetate ions for every one molecule of acetic acid; thus, at any pH > 5.74, CH_3COO^- accounts for more than 90% of a mass balance on acetic acid and it is the only important form of acetic acid in solution. Between a pH of 3.74 and of 5.74 both CH_3COOH and CH_3COO^- are important forms of acetic acid in solution.

More generally, for the weak acid HA we can state 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

These general statements about the relative importance of a conjugate weak acid and its conjugate weak base are quite useful when it comes to understanding the behavior of buffers and when writing chemical reactions. Both of these topics are explored in greater detail in other essays.