Discussion of pH and pK_a Values

The Henderson-Hasselback equation is shown below.

$$pH = pKa + \log\frac{[A^-]}{[HA]}$$ Where $[A^-]$ is conjugate base and [HA] is conjugate acid

This equation is often used to determine the proportion of conjugate base $[A^-]$ and of conjugate acid [HA] one must use to attain a particular pH value of a buffer. You must know the pK_a value for the conjugate acid you will be using. However, the above equation has additional information that you should understand.

Most chemistry students have seen the Henderson-Hasselbach equation and probably used it to some extent. In addition, most students probably feel comfortable calculating the pH and the pK_a values using the defined equations shown below:

$$pH = -\log[H^+] \text{ and } pK_a = -\log[K_a]$$

While the definition of pK_a is given above, the functional definition of pK_a is often not understood. What the chemist or biochemist needs to remember is that when the pH is equal to the pK_a of an acid, the concentration of the conjugate base and of the conjugate acid are equal, meaning that there is a 50% proportion of conjugate base, and a 50% proportion of conjugate acid. By simply entering the concentrations of conjugate base and conjugate acid into the Henderson-Hasselbach equation, (no matter what the concentration is) are equal, their ratio is 1:1, meaning that the log of this ratio is zero (0).

No matter which acid (represented as a proton [H+] donor) you are looking at the above relationship holds. For example, since acetic acid has a pKa value of about 4.7, when the pH is equal to that pKa, the proportion of acetate to acetic acid would be 1:1. For another acid, such as HF, which has a pKa value of about 4.0, when the pH is equal to 4.0, the proportion of the fluoride ion to the hydrofluoric acid would be 1:1.

Ask yourself the following question, and hopefully you will come up with the correct answer. If you add base (e.g., NaOH) to one of the conjugate acid and conjugate base combinations above, would the proportion of conjugate base increase or decrease? Obviously (and this is the correct answer), the proportion of the conjugate base would increase, because in the presence of base, the conjugate acid reacts (in a neutralization reaction) to produce more of the conjugate base. Please also remember that the conjugate base, in the presence of base stays conjugate base. Only the conjugate acid will react.

$HF + NaOH \rightarrow NaF + HOH$

The above equation shows that the conjugate acid (HF) is converted into the conjugate base (F^-) in the present of NaOH. This means that the amount of fluoride ion (F-) increases and the amount of HF decreases, giving a ratio greater than 1:1. What this means, functionally, is that as you increase the pH of a solution above the pKa value of an acid, the proportion of conjugate base increases and the proportion of the conjugate acid decreases. For each pH unit increased, the proportion of conjugate base increases by a factor of ten. All you need to do is to plug these values into the Henderson-Hasselbach equation. Therefore, if you increase the base composition by the values shown below, you will see that the pH is going to rise.

Ratio of [A-]/[HA]	**log[A-]/[HA]**	**Increase in pH**
10^1:1	1.0	1.0
10^2:1	2.0	2.0
10^3:1	3.0	3.0
10^6:1	6.0	6.0

If the pH is at least 2.0 pH units above the pKa value, then the proportion of conjugate base is at least 99% of the solution. This means that whenever the pH increases more than 2.0 pH units, then the major chemical in the solution would be the conjugate base. Remember that when the pH is equal to the pKa value, the proportion of the conjugate base and conjugate acid are equal to each other. As the pH increases, the proportion of conjugate base increases and predominates. Conversely, for the same reason, as the pH decreases (solution becomes more acidic), the proportion of the conjugate acid goes up, and predominates. To take two extremes, consider the following. At pH=12, both acetic acid and hydrofluoric acid would exist as their conjugate bases (greater than 99.999999% conjugate base). Alternatively, as the pH goes down to pH=1, then their conjugate acids predominate, with a proportion of at least 99.99%. Therefore, if you know the pH of a solution, and the pKa value of an acid, you can quickly determine whether the conjugate base or conjugate acid predominates. If you are at least 2.0 pH units above the pKa, then the conjugate base is at least 99% of the total. If the pH is at least 2.0 pH units below the pKa, then the conjugate acid is at least 99% of the total.

Inherent to the explanation given above, you must know the pH of the solution containing an acid-base conjugate pair, and the pKa of that conjugate pair.