

2.3.3

Buffers

Because it is essential for many chemical reactions that pH is maintained within a narrow range, biological systems employ various **buffer systems**. Buffers are chemicals that tend to *resist* changes in pH. Note that buffers do not *prevent* changes; they *resist* changes. Let's see if we can figure out how this works.

The determination as to whether something will be weak or strong (acid/base) is dependent upon a value called the **K_a** or **disassociation constant**. A K_a value is calculated from the ratio of the products to the reactants at equilibrium ($K_a = \frac{[\text{products}]}{[\text{reactants}]}$). For example, the K_a of acetic acid is 1.73×10^{-5} . In fact, the K_a values for all weak acids are all very small so we employ the same logic as that of pH and use the negative log which means we use the letter p. Thus, the **pK_a** for acetic acid is 4.73. Also, like the pH system, strong acids will have very low pK_a values while weak acids will have higher pK_a values.

A typical buffer system is composed of a weak acid and the conjugate base of that acid. Remember, weak acids are those that do not dissociate completely but reach an equilibrium between the reactants and the products of the reaction. An important buffer system is the bicarbonate buffer system. The components of this system are shown below.



Carbonic Acid Hydrogen Ion Bicarbonate Ion

In this case, the carbonic acid is the weak acid, and the bicarbonate ion is its conjugate base. The entire reaction is in equilibrium. If the equilibrium is disrupted by the addition of more hydrogen ions, the reaction will proceed to the left until equilibrium is restored. When it proceeds to the left, some of the excess hydrogen ions will combine with bicarbonate forming carbonic acid, hence removing some of the excess hydrogen ions from the solution. Essentially, the buffer has "soaked up" some of the extra hydrogen ions, thus preventing a large change in pH.

Another way of thinking of this system is to assume it behaves like a teeter-totter. If we have equal weights on each side, the teeter-totter is balanced (in equilibrium). If we add excess weight to one side (excess hydrogen ions), it will be out of balance. The only way to restore balance (equilibrium) is to move some of the excess weight to the opposite side until the teeter-totter is balanced again (equilibrium restored). Obviously, in this simple example, we realize that we cannot move all of the added weight to the opposite side because it would again be out of balance, but if *some* of the excess weight is moved to the other side, balance can be restored. Like the teeter-totter, when extra hydrogen ions are added, not all can be combined with bicarbonate, so there will still be a few more hydrogen ions than at the beginning (this is why buffers *resist* pH changes instead of *prevent* changes in pH). The pH will decrease, but not nearly as much as it would have if all added hydrogen ions were allowed to remain without being buffered. We could use the same analogy to see what happens when hydrogen ions are removed from the solution by the addition of a base. Since the

equation is again out of equilibrium, the reaction will proceed to the right (dissociation of carbonic acid) until some of the hydrogen ions have been replaced. Again, there will be a slight increase in pH, but not nearly as great as would happen in the absence of the buffer.

An important buffer rule is that buffer systems work best at a pH that is near the pKa for the system.

In 1908 two researchers developed an equation that predicts the resultant pH of a given buffer system, the equation is named after them and is called the Henderson-Hasselbalch equation.

(Henderson-Hasselbalch equation)

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

In this equation A^- is the concentration of conjugate base and HA is the amount of weak acid. If we know the pKa of the buffer, we can then calculate the resultant pH of the solution. Alternatively, if we know the amount of HA, A^- and the pH (and remember our math log rules!) we can calculate the pKa of the weak acid.



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