> *"Biological control of the pH of cells and body fluids is of central importance in all aspects of intermediary metabolism and cellular function."*
>
> *Albert L. Lehninger*

Buffers

In humans, biochemical/physiological parameters resist change (homeostasis): for example, blood pH and body temperature are balanced within a relatively narrow range of values. Human blood has a pH of about 7.4, and complex chemical systems work to maintain that pH. The most important component of those systems is the carbonic acid buffer system. The carbonic acid buffer system is also active on a much, much larger scale in balancing the pH of the oceans, which historically has been about 8.1. A buffer system occurs when a weak acid and its conjugate base are present in the same solution.

Buffer systems are an important application of acid–base equilibria. The study of acid–base equilibria is very useful because many other chemical systems can be understood through the same mathematical approach. The most common experimental method used to study acid–base systems is titration analysis, through which we can determine the pK_a of a weak acid and the pK_b of its conjugate base, the two essential components of a buffer.

The Buffer Equation *(Henderson-Hasselbach)*

Let's consider a weak acid equilibrium system and its corresponding equilibrium constant:

$$\mathrm{HA(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{A^-(aq)} \qquad K_a = \frac{[\mathrm{H^+}]\,[\mathrm{A^-}]}{[\mathrm{HA}]}$$

HA represents a weak monoprotic acid, and A^- is its conjugate base. Solving the equilibrium constant expression for hydrogen ion concentration,

$$[\mathrm{H^+}] = K_a \frac{[\mathrm{HA}]}{[\mathrm{A^-}]}$$

Taking the log of each side and multiplying by –1,

$$-\log\,[\mathrm{H^+}] = -\log\left(K_a \frac{[\mathrm{HA}]}{[\mathrm{A^-}]} \right)$$

Algebraically rearranging,

$$-\log\,[\mathrm{H^+}] = -\log K_a - \log \frac{[\mathrm{HA}]}{[\mathrm{A^-}]}$$

$$-\log [H^+] = -\log K_a + \log \frac{[A^-]}{[HA]}$$

Using the fact that pZ = –log Z, we arrive at the buffer equation:

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

Note that since this equation is derived from the equilibrium constant expression, all concentrations must be equilibrium concentrations. However, we often find it useful and accurate to make the approximation that the weak acid is only slightly dissociated. Thus the equilibrium concentration of HA is approximately equal to the initial concentration, or

$$[HA]_{\text{equilibrium}} = [HA]_{\text{initial}}$$

A similar assumption is also valid for weak bases:

$$[A^-]_{\text{equilibrium}} = [A^-]_{\text{initial}}$$

The Effectiveness of a Buffer

Consider a 100.0 mL solution containing 0.010 mol acetic acid, $HC_2H_3O_2$, and 0.010 mol sodium acetate, $NaC_2H_3O_2$. We have

$$\frac{[A^-]}{[HA]} = 1 \qquad \text{and} \qquad \log 1 = 0$$

therefore, $pH = pK_a$. Looking up pK_a for acetic acid, we find $pH = pK_a = 4.75$.

Now let's consider what will happen if we add 0.005 mol of HCl to this solution. The strong acid will react with the acetate ion.

	$H^+(aq) +$	$C_2H_3O_2^-(aq) \rightleftharpoons$	$HC_2H_3O_2(aq)$
Initial Moles	0.005	0.010	0.010
Change	– 0.005	– 0.005	+ 0.005
Final Moles	0	0.005	0.015

The buffer equation can now be applied to determine the new solution pH:

$$pH = pK_a + \log \frac{[A^-]}{[HA]} = 4.75 + \log \frac{(0.005\ \text{mol}/0.1000\ \text{L})}{(0.015\ \text{mol}/0.1000\ \text{L})} = 4.27$$

The pH of the solution changes from 4.75 to 4.27 upon addition of the acid. Let's compare this to what will happen if we add the same amount of HCl to a nonbuffered solution that begins at pH

= 4.75. A 1.8×10^{-5} M HCl solution has a pH of 4.75. The number of moles of $H^+(aq)$ in this solution is

$$0.1000\ \text{L} \times 1.8 \times 10^{-5}\ \text{mol/L} = 1.8 \times 10^{-6}\ \text{mol}$$

The amount of HCl added was 0.005 mol, so after the acid is added, the number of moles is 0.005 + 0.0000018 = 0.005 mol. The new hydrogen ion concentration is

$$\frac{0.005\ \text{mol}}{0.1000\ \text{L}} = 0.05\ \text{M}$$

and the solution pH is

$$\text{pH} = -\log[\text{H}^+] = -\log(0.05) = 1.3$$

In this unbuffered solution, the pH changes from 4.75 to 1.3, which is much a much larger change than in the buffered solution.

A consideration that must be made when preparing a buffer is to have sufficient quantities of both the weak acid and its conjugate base to completely react with any base or acid that may be added to the system. The buffer capacity of a system is defined in terms of the concentrations of the acid–base conjugate pair. Greater concentrations will withstand greater additions of base or acid while still resisting a significant pH change. If we were to add so much acid so that it reacted with all of the base in a buffer system, the buffering capacity of the system would be exceeded, and further additions of acid would result in large changes in pH.

A guideline for preparing a buffer system is to choose an acid with a pK_a within one pH unit of the desired buffer. This ensures that the ratio of base to acid will range between 1 to 10 and 10 to 1, and thus sufficient quantities of both acid and base will be present in the buffering system.