Source: http://chimge.unil.ch

Buffer Solutions

The pH of human blood must stay in a relatively narrow range around pH = 7.4 (7.35-7.45) in order to ensure cellular survival. It can be maintained within these limits thanks to buffer systems utilizing plasmatic carbonates, phosphates or proteins for example. The buffer ability of blood, in addition to its role in the metabolism, can also minimize the consequences of an accidental ingestion of acid (or base).

A buffer solution is a solution able to absorb a certain quantity of acid or base without undergoing a strong variation in pH.

A buffer solution is a mixture of a weak acid HA and its conjugate base A⁻ (usually added under the form of the sodium or potassium salt, NaA or KA). Alternatively a mixture of a weak base B and of its conjugate acid BH⁺ is also a buffer solution. Note that a solution of a weak acid or a weak base is by itself a buffer solution, but its capacity is quite limited, so that the addition of the conjugate particle is necessary to the preparation of a practical buffer solution.

Examples:
Weak acids and their conjugate base

\[
\text{CH}_3\text{CO}_2\text{H} / \text{CH}_3\text{CO}_2^- \\
H_2\text{CO}_3 / \text{HCO}_3^- \\
\text{Weak bases and their conjugate acid} \\
\text{NH}_3 / \text{NH}_4^+ \\
H_2\text{PO}_4^2-/ \text{H}_3\text{PO}_4
\]

A buffer solution is in fact a solution containing two acid-base couples.

\[
\text{HA} + \text{H}_2\text{O} \rightleftharpoons K_a A^- + \text{H}_3\text{O}^+ \\
\text{weak acid 1} \quad \text{base 2} \quad \text{conjugate base 1} \quad \text{conjugate acid 2}
\]

When either a strong base or a strong acid is added to the buffer solution, the resulting pH can
be calculated provided the following conditions are valid:

* $pK_a > 2$ (sufficiently weak acid)

* $0.1 \leq \frac{[A^-]}{[HA]} \leq 10$ (buffer ability)

then:

$$[HA] \approx [HA]_0 \quad \text{therefore} \quad \text{pH} = pK_a + \log \frac{[A^-]_0}{[HA]_0}$$

Example: Acetic buffer CH$_3$CO$_2$H / CH$_3$CO$_2$\(^-\) ($pK_a = 4.76$)

Calculate the pH of a mixture containing 100 ml of acetic acid (CH$_3$CO$_2$H) 0.15 M and 200 ml of sodium acetate (NaCH$_3$CO$_2$) 0.25 M?

Calculate the pH of a mixture containing 200 ml of acetic acid 0.25 M and 100 ml of sodium acetate 0.15 M?

Special case: One mixes equivalent volumes of the acid and of its conjugate base; for instance, 200 ml of acetic acid 0.25 M and 200 ml of sodium acetate 0.15 M.

The $pK_a$ of the weak acid must not differ more than one unit from the targeted pH value. Then simply use the Henderson-Hasselbalch equation.

Example: Preparation of a buffer solution with pH = 5.2.

$pK_a$ (CH$_3$CO$_2$H / CH$_3$CO$_2$\(^-\)) = 4.76, so that this mixture acetic acid (CH$_3$CO$_2$H)/sodium acetate (CH$_3$CO$_2$\(^-\)) can be used.

According to the Henderson-Hasselbalch relationship, pH = $pK_a + \log ([A^-]/[AH])$

$$5.2 = 4.76 + \log([A^-]/[AH])$$

$$0.44 = \log([A^-]/[AH])$$

$$[A^-]/[AH] = 10^{-0.44} = 2.75$$

pH = 4.76 + log (16.7 · 10^{-2} / 5 · 10^{-2}) = 5.28

To prepare one liter of this buffer solution: mix 2.75 moles of acetate and 1 mole of acetic and complete to 1 liter with distilled water.
The capacity of the buffer can be adjusted increasing or decreasing the acid (or base) concentration (keeping $[A^-]/[AH] = 2.75$).

Indeed, when most of the weak acid (or of it conjugate base) is transformed into its conjugate base (weak acid) base, the buffer solution becomes ineffective.