BUFFERS AND pH of BUFFERS

A buffer is a solution that resists changes in pH upon the addition of a small amount of acid or base. The action of a buffer is dependent on the common ion effect.

A buffer is made with a weak acid and a soluble salt containing the conjugate base of the weak acid or a buffer may be prepared from a weak base and a soluble salt containing the conjugate acid of the weak base. Some examples of buffer material pairs are:

<p style="text-align:center">acetic acid and sodium acetate,</p>

<p style="text-align:center">phosphoric acid and potassium phosphate,</p>

<p style="text-align:center">oxalic acid and lithium oxalate.</p>

<p style="text-align:center">carbonic acid and sodium carbonate,</p>

<p style="text-align:center">or ammonium hydroxide and ammonium nitrate.</p>

The concentrations of buffers are relatively high compared to the concentrations of the acids and bases added. Addition of small amounts of acid or base will not affect the pH of the buffer very much.

A buffer is most effective in solutions of pH at or close to the pKa of the weak acid. (Or solutions of pOH at or close to the pKb of the weak base). The most buffering capacity is available when the concentration of weak acid or base is close to the concentration of the conjugate ion and when the concentration of both is greatest.

Thinking backwards, if you need a buffer at a particular pH lower than seven, choose the weak acid that has a pK_a close to that pH and a conjugate base to go with it.

Consider a weak acid, HA:

$$HA \ + \ H_2O \ \rightleftharpoons \ H_3O^{+1} \ + \ A^{-1}$$
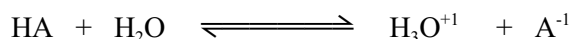
We can start again from the equilibrium expression of the ionization of a weak acid or a weak base:

$$K_a \ = \ \frac{[H_3O^+][A^-]}{[HA]}$$

Because HA is a weak acid, the presence of the conjugate anion, A^{-1} would further suppress the already slightly ionized acid HA by shifting the above equilibrium to the left, according to LeChatelier. Thus:

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

Furthermore: $[A^{-1}]_{equilibrium} \ = \ [[A^{-1}]_{initisl} \ = \ [A^{-1}]_{salt}$

In buffer solutions the concentration of hydrogen ion is **not** equal to the concentration of conjugate ion, i.e $[H_3O^{+1}] \ \neq \ [A^{-1}]$. The concentration of conjugate ion from the dissociation of the acid is negligible, so we can calculate as if all the conjugate ion comes from the salt. If the soluble salt has only one mol of conjugate ion per mol of salt, the concentration of conjugate ion is the same as the concentration of salt.

The calculation of the pH again is from the hydrogen ion concentration. Solve for the hydrogen ion concentration if you need it, the pH of the solution, the pOH, or the hydroxide ion concentration.

$$[H_3O^+] \; = \; \frac{K_a[HA]}{[A^-]}$$

which is the same as:

$$[H_3O^+] \; = (K_a) \; \frac{[acid]}{[conjugate\ base]} \qquad = \quad K_a \; \frac{[HA]_{initial}}{[A^{-1}]_{salt}}$$

This expression helps to explain how a buffer works. If a small amount of acid or base is added to a buffered solution, according to LeChatelier's principle, the reaction will occur tha minimizes the change, hence neither the acid nor the base concentrations will change that much. Thus, the pH of the buffer will not change appreciably. The key is that the concentrations of the acid nd the conjugate base must be relatively high compared to the amount of the acid or base added.

The **Henderson- Hasselbalch** (H-H) equation can be somewhat confusing, but it is nothing more than the negative log of the equation above, the equilibrium expression solved for the hydrogen ion concentration. If you know the equilibrium equation, know how to solve the equilibrium equation for the hydrogen ion concentration, and know how to convert the hydrogen ion concentration to the pH, you can thus determine the pH. If you really need the H-H equation for a test, it is best to make sure you are getting it right by deriving it from the equilibrium expression.

$$-\log [H_3O^+] \; = \; pH \qquad\qquad -\log K_a \; = \; pK_a$$

$$-\log (1/[A^-]) \; = \; +\log [A^-] \qquad -\log ([HA]) \; = \; -\log [HA]$$

Component-by-component take the negative log of the equilibrium expression and change the multiplication to addition. (They are logs now). You get:

$$pH \; = \; pK_a + \log [A^-] - \log [HA],$$

which is the same as:

$$pH = pK_a - \log \left(\frac{[HA]}{[A^-]}\right)$$

this being the usual way you see the H-H Eqn.

There are four perfectly correct ways to write the H-H equation. They are:

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

or

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

or

$$pOH = pK_b \; + \; \log \frac{[conjugate\ cation]}{[base]}$$

or

$$pOH = pK_b - \; \log \frac{[base]}{[conjugate\ cation]}$$

An *equimolar* buffer is one in which the concentration of the weak acid (or base) is the same as the concentration of the conjugate ion. This may not seem particularly significant to you, but there are several important ideas that can be easily seen from it. Start with the ionization equilibrium expression and cancel the [HA] with the [A⁻]. This shows that in an equimolar buffer K_a = [H⁺].

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

$$\text{if} \quad [HA] = [A^-]$$

$$K_a = [H^+]$$

This shows how a buffer works. As acid or base is added to a buffer solution, the buffer equilibrium will trade off [HA] with [A⁻] to come to a new equilibrium. When that happens, there will be a much smaller change in the hydrogen ion concentration than if the acid or base were added to an unbuffered solution.

Now let's do a similar trick with the H-H equation. If [HA] = [A-], the term [HA]/[A-] = 1 and log 1 = 0, so pH = pK$_a$.

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

This indicates that in an equimolar buffer the pH = pKa and that the RATIO of the [HA] to the [A⁻] will determine the pH of the solution. The further the ratio gets from one to one, the further the pH gets from the pKa. The buffer has its greatest buffering power at the pKa of the weak acid (or base). Hence, a buffer is effective in maintaining a particular pH only to the extent that the ratio [acid] / [base] is insensitive to the addition of acid or base. The [acid] / [base] ratio is most insensitive to change when [acid] = [base]. The higher the concentration of both the weak acid and its conjugate ion, the more buffering power is available.

If the ratio of [A⁻¹] / [HA] is 10 : 1, then pH = pK$_a$ + log 10/1 = pK$_a$ + 1

If the ratio of [A⁻¹] / [HA] is 1 : 10, then pH = pK$_a$ + log 1/10 = pK$_a$ - 1

Thus, a buffer works best for values of: **pH = pK$_a$ ± 1**

Hence, the acid chosen should have its pK$_a$ value ± range of desired pH.
The actual concentrations of acid and base are not important only the [acid] / [base] ratio is of importance.

Note: Dilution has no effect on the pH of the buffer, since both [A⁻¹] and [HA] are changed equally, hence the pH of the buffer is unaffected by dilution.

To Prepare a Buffer Solution

Two major requirements must be considered:
1. Buffer solutions should have the capacity to control the pH after the addition of small amounts of H^{+1} / or OH^{-1} are added.
2. The buffer should control the pH at the desired value.

To meet the buffering capacity, i.e to maintain the pH constant of a buffer:

Since $[H_3O^{+1}] = K_a \dfrac{[acid]}{[conj. Base]}$, and: $pH = pK_a + \log \dfrac{[A^-]}{[HA]}$

When [base] == [acid], then: $\qquad\qquad pH = pK_a$

Thus, to keep the pH constant, i.e. $[H_3O^{+1}]$ constant, two factors can be controlled:

1. Select the acid so that its $K_a = [H_3O^{+1}]$ or $pK_a = pH$ of the acid.
   If equimolar $[A^{-1}] / [HA]$, then select pK_a of the acid to determine the pH of the buffer.

2. Then, the exact value of the $[H_3O^{1}+]$ required is achieved by adjusting the ratio of [acid]/[conjugate base]. The actual concentrations of the acid/base are not important, only the ratio is important. This ratio controls the pH of the buffer.

This is why commercially prepared buffers are sold as concentrated solutions. To use them, you only need to take a small amount and dilute it with water to convenient volumes.

Example:
Describe how you would prepare a "phosphate" buffer with a pH of about 7.40

Solution
Work backwards:
(1) $pH = pK_a$
(2) to obtain exact pH, determine the ratio [acid]/[conjugate base]

From the value of K_a:

$$K_a (H_3PO_4) = 7.5 \times 10^{-3}$$
$$K_a (H_2PO_4^{-1}) = 6.2 \times 10^{-8}$$
$$K_a (HPO_4^{-2}) = 4.8 \times 10^{-13}$$

The most suitable acid is $H_2PO_4^{-1}$, since the $K_a (H_2PO_4^{-1}) = 6.2 \times 10^{-8}$
.: pK_a value will be ~ 7, calculating the $pK_a = 7.21$
and knowing the Henderson-Hasslebalch Equation:

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$
$$7.4 = 7.21 + \log \frac{[A^-]}{[HA]}$$
$$\therefore \frac{[A^-]}{[HA]} = \frac{1.5}{1.0}$$

See: : Assignment: Acid - Base Equilibria: Buffer Problems
There are 3 types of calculations in connection with buffers:
1. To find the pH of a buffer system
2. Effect on the pH of adding some strong acid or strong base to a buffer solution.
3. To determine which acid and its salt would make a buffer solution for a particular pH.