Designing Buffers

The purpose of using a buffer in an experiment is to limit any significant change in pH that might occur. For example, when using an enzyme in a biochemistry experiment the solution must be carefully buffered because the enzyme will function over a narrow range of pH levels. If the pH drifts too far from the optimal range, then the enzyme ceases to function and the experiment is doomed to failure. Similar problems are found in all areas of chemistry. An aqueous synthetic reaction in inorganic chemistry, for instance, may produce acid as a byproduct. If the reaction becomes very slow under acidic conditions, then a buffer is included to prevent the pH from drifting too low. In both of these examples a suitable buffer is the difference between a useful experiment and one that is a failure.

So, how do we design a buffer for a particular experiment? There are several important considerations. What is the buffer's desired pH? Does the buffer need to be better at neutralizing acid or base? What is the desired buffer capacity? Is there a maximum concentration of dissolved ions that we can tolerate? Each of these issues is discussed in this tutorial.

Question 1: What is the Buffer's Desired pH of the Buffer?
This question is the first one to consider because it limits the possible choices for the conjugate weak acid/weak base pair. Recall that a buffer can be made for any pH within ±1 pH units of the weak acid's pK_a; that is, the pH range for a buffer is

$$\text{pH} = \text{p}K_a \pm 1$$

For example, if a buffer needs to have a pH of 7.00, then the weak acid must have a pK_a between 6.00 and 8.00. If the weak acid has a pK_a of 6.00, then a buffer can be prepared with a pH between 5.00 and 7.00. For a weak acid with a pK_a of 8.00, buffers with pH levels between 7.00 and 9.00 are possible.

Example 1. A buffer with a pH of 9.87 is needed. Which of the following conjugate weak acid/weak base pairs can be used?

$H_3PO_4/H_2PO_4^-$ $H_2PO_4^-/HPO_4^{2-}$ HPO_4^{2-}/PO_4^{3-} CH_3COOH/CH_3COO^-

H_2CO_3/HCO_3^- HCO_3^-/CO_3^{2-}

Solution. Given a target pH of 9.87, the conjugate weak acid's pK_a must be between 8.87 and 10.87. The pK_a values for the possible conjugate weak acids are:

CH_3COOH: pK_a = 4.757 H_3PO_4: pK_a = 2.15

H_2CO_3: pK_a = 6.35 $H_2PO_4^-$: pK_a = 7.20

HCO_3^-: pK_a = 10.33 HPO_4^{2-}: pK_a = 12.38

The only conjugate weak acid in this list with a suitable pK_a is HCO_3^-; thus, the buffer must use HCO_3^- and CO_3^{2-}.

Question 2: Does the buffer need to be better at neutralizing acid or base?
If only one conjugate weak acid/weak base is available, then this question is of no importance. However, in many circumstances several possible buffering agents are possible. For example, if

our target pH is 7.00, we can prepare a buffer using a weak acid with a pK_a as small as 6.00 or as large as 8.00. If the buffer is for a system where it is necessary to protect against the addition of a strong acid only, then we want the buffer to have more of its conjugate weak base than of its conjugate weak acid (because it is the conjugate weak base that reacts with the strong acid). Using the Henderson-Hasselbalch equation as a guide

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{conjugate weak base}]}{[\text{conjugate weak acid}]}$$

we see that any buffer where the concentration of conjugate weak base is greater than the conjugate weak acid will have a pH > pK_a. If we want a buffer to provide better protection against a strong acid, therefore, then the conjugate weak acid's pK_a must be less than the buffer's desired pH. This suggests the following simple guidelines:

> To protect against the addition of a strong acid, choose a buffer whose pK_a is less than desired pH.
>
> To protect against the addition of a strong base, choose a buffer whose pK_a is greater than desired pH.

Example 2. Using the same list of possible buffers from Example 1, what is the best choice if you need a buffer with a pH of 6.85 that must be able to protect against the addition of strong base?

Solution. With a target pH of 6.85, the weak acid must have a pK_a between 5.85 and 7.85; both H_2CO_3 and $H_2PO_4^{2-}$ meet this condition. To protect against the addition of strong base, we want the buffer to have more of its conjugate weak acid than its conjugate weak base. We need, therefore, to use a weak acid whose pK_a is greater than the desired pH. Of the two choices, only $H_2PO_4^-$ meets this condition. A $H_2PO_4^-/HPO_4^{2-}$ buffer is the best choice.

Question 3: What is the desired buffer capacity?

Given that a buffer's purpose is to maintain its pH against the addition of strong acid or strong base, a useful buffer must be able to neutralize whatever quantity of acid or base we might reasonably expect to enter the system. The amount of strong acid or strong base that can be neutralized is called the buffer's buffer capacity. What determines the buffer capacity is the concentration of the conjugate weak acid and conjugate weak base used to prepare the buffer. A higher concentration of these buffering reagents leads to a greater buffer capacity.

Example 3. Suppose you are carrying out an aqueous reaction in which the solution's pH must remain within the limits of 6.8 ± 0.2 pH units. The buffer of choice is made using $H_2PO_4^-$ (pK_a = 7.2) and HPO_4^{2-}. During the reaction, no more than 0.0010 mol of strong acid will be released. What are the minimum concentrations of $H_2PO_4^-$ and HPO_4^{2-} necessary to prevent the solution's pH from drifting below 6.6? Assume that the desired initial pH is 7.0 and that the buffer's volume is 100.0 mL.

Solution. Using the Henderson-Hasselbalch equation, the initial buffer must have a mole ratio of HPO_4^{2-} to $H_2PO_4^-$ equaling

$$7.0 = 7.2 + \log\frac{(\mathrm{mol\ HPO_4^{2-}})_o}{(\mathrm{mol\ H_2PO_4^-})_o}$$

$$\frac{(\text{mol HPO}_4^{2-})_\text{o}}{(\text{mol H}_2\text{PO}_4^-)_\text{o}} = 0.631$$

to obtain the desired pH of 7.0. For a pH of 6.6, which is our lower limit, the smallest allowed mole ratio is

$$6.6 = 7.2 + \log\frac{(\text{mol HPO}_4^{2-})_\text{o}}{(\text{mol H}_2\text{PO}_4^-)_\text{o}}$$

$$\frac{(\text{mol HPO}_4^{2-})_\text{o}}{(\text{mol H}_2\text{PO}_4^-)_\text{o}} = 0.251$$

Adding strong acid to the buffer changes the pH because some of the conjugate weak base, HPO_4^{2-}, is converted to the conjugate weak acid, $H_2PO_4^-$. Knowing that the maximum amount of strong acid is 0.0010 mol, means that

$$\frac{(\text{mol HPO}_4^{2-})_\text{o} - 0.001}{(\text{mol H}_2\text{PO}_4^-)_\text{o} + 0.001} = 0.251$$

From the initial mole ratio, we know that (mol HPO_4^{2-})$_\text{o}$ = 0.631×(mol $H_2PO_4^-$)$_\text{o}$. Substituting into the equation above and solving for the initial moles of $H_2PO_4^-$ gives

$$\frac{0.631\times(\text{mol H}_2\text{PO}_4^-)_\text{o} - 0.001}{(\text{mol H}_2\text{PO}_4^-)_\text{o} + 0.001} = 0.251$$

$$(\text{mol H}_2\text{PO}_4^-)_\text{o} = 0.0033$$

$$(\text{mol HPO}_4^{2-})_\text{o} = 0.0021$$

Because the buffer's volume is 100.0 mL, the minimum initial concentrations of the buffer reagents are 0.033 M $H_2PO_4^-$ and 0.021 M HPO_4^{2-}.

Question 4: Why not make the buffer capacity really large to avoid having the buffer fail?
In the previous sections we considered how to prepare a buffer by selecting a suitable conjugate weak acid and conjugate weak base and ensuring that their respective concentrations are capable of neutralizing a specified amount of strong acid or strong base. You might reasonably ask why it is necessary to design the buffer to have a specific buffer capacity. It would, after all, be easier to just prepare the buffer with high concentrations of the buffering agents, knowing that the resulting buffer capacity will be far greater than needed.

Another important consideration when designing a buffer is the total concentration of ions in solution, a property of a solution called its ionic strength. Many systems, particularly in biology and biochemistry, can tolerate only a limited range of ionic strengths. The reason for this is that large differences in ionic strength on two sides of a cell membrane causes fluids to move across the membrane in an attempt to even out the concentrations of dissolved ions (a process known as osmotic flow). The result is catastrophic for cells; thus, the effect of pouring salt on slugs (which many of you have probably seen or done).

Example 4. A $H_2PO_4^-$/HPO_4^{2-} buffer is needed with a pH of 7.0. To maintain a low ionic strength, the maximum total concentration of phosphate species is limited to 1.0 mM. What concentrations of $H_2PO_4^-$ and HPO_4^{2-} are needed?

Solution. From Example 3, we know that the buffer must have a concentration ratio of

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 0.631$$

Knowing that

$$[H_2PO_4^-] + [HPO_4^{2-}] = 1.0\ \text{mM}$$

we have

$$\frac{1.0\ \text{mM} - [HPO_4^{2-}]}{[H_2PO_4^-]} = 0.631$$

which gives the concentrations of $H_2PO_4^-$ and HPO_4^{2-} as

$$[H_2PO_4^-] = 0.61\ \text{mM}$$

$$[HPO_4^{2-}] = 1.0\ \text{mM} - 0.61\ \text{mM} = 0.39\ \text{mM}$$