pH: Buffers.

A. Introduction

This handout follows Weak Acids. It is the final topic handout. Frequent reference is made to the previous handouts of the pH series: Water (W), Strong Acids (SA) and Weak Acids (WA).

As with WA, the emphasis here is on qualitative ideas. Quantitative material is presented to show you that our qualitative conclusions have a quantitative basis. Further, some of you may want to follow the quantitative issues more carefully. The equations are not particularly difficult, but they can get tedious. As a practical matter, most lab work involving buffers requires primarily a qualitative understanding.

B. Overview

A buffer is a solution that resists changes in pH. If you add some acid or base to a buffer, the pH changes less than "expected".

> [More precisely, we might refer to such a solution as an acid-base buffer. We can have solutions that buffer other things. For example, we might use a calcium ion buffer, to control [Ca^{2+}]. But acid-base (or hydrogen ion) buffers are most common, and we often call them simply buffers, for convenience. If you do need to deal with buffers for other things, the logic is similar.]

Buffers work because of the behavior of weak acids; you got some hints of the basis of buffer action in WA. You know that a given concentration of a weak acid gives off less H^+ than the same concentration of a strong acid -- because the weak acid is only partly ionized. And you saw that adding more of the acid causes a bigger change in a strong acid solution than in a weak acid solution (WA problems 5 & 6). What we didn't look at in WA is what happens if you add some strong acid to a solution of a partially ionized weak acid; we will do that here.

We also briefly introduced the idea that acetate ion is itself a weak base, the conjugate base of acetic acid (end of Sect J-WA).

C. Reversing reversible reactions

Most of the ideas that we need for discussing buffers have been introduced in the previous pH handouts. I want to start here by reviewing those ideas, but in the context of buffer action.

In W and WA we presented chemical equations for reactions that proceeded only partially. Look at Eq 1-W, for the ionization of water, and Eq 1-WA & 4-WA, for the ionization of weak acids (and Eq 7-WA for a weak base). Not only do these reactions occur only "to a small extent", they are also reversible; we used double arrows $\rightleftarrows$ in these equations to indicate that they are reversible.

Each of these chemical equations is accompanied by an equation for a K value, an equilibrium constant. The equations for K all have the general form: concentrations of products divided by concentrations of reactants (concentrations of things on the right side of the equation divided by concentrations of things on the left).

> (However, $[H_2O]$ is omitted in the K expressions. That is a technicality of K expressions that does not affect our general points here.)

Contrast this with the reactions for ionization of strong acids (or bases) (Eq 1-SA, 2-SA, 3-SA). These reactions proceed completely; strong acids are completely ionized. Single arrows $\rightarrow$ are used to show that the reactions proceed only to the right (towards ionization), and are not reversible. No K was calculated for these reactions.

> [Later, in Sect F-WA, we noted that strong acids can be thought of as the extreme case of a continuum, that strong acids have very high K. Nevertheless, it still holds that these acids are -- as a practical matter -- fully ionized, regardless of conditions.]

To understand buffers we need to focus on the behavior of reversible reactions, specifically, the reversible reactions of ionization of water and weak acids.

Example C-1. Adding H^+ to water.

Consider the water ionization. If we have some pure water, $[H^+] = [OH^-] = 10^{-7}$ M. Now we add a strong acid, say, 0.1 M HCl. The HCl ionizes completely, producing 0.1 M H^+. However, the K expression is no longer satisfied. What happens? H^+ reacts with OH^-, to produce water; the water ionization is "driven" backwards by the high amount of H^+. How far does this reverse reaction proceed? Until the K expression is restored. Can we predict the result? Yes, and we use chemical logic to make the prediction.

After adding the acid, and before equilibrium is restored, $[H^+] = 0.1$ M and $[OH^-] = 10^{-7}$ M. The amount of OH^- limits how far the reverse reaction can proceed; there is plenty of H^+. And if all the OH^- reacted (the extreme possibility), it would consume 10^{-7} M H^+. As a result, we can predict what $[H^+]$ will be when equilibrium is reestablished. It will be 0.1 M. Well, maybe 0.1-10^{-7} M, but for all practical purposes, $[H^+]$ = 0.1 M. That is, nearly all of the added H^+ appears as increased $[H^+]$, and is directly reflected in a change in the pH.

If $[H^+]$ = 0.1 M, then we can calculate $[OH^-]$, using Eq 3-W, the equilibrium expression for the ionization of water; $[OH\text{-}]=10^{-13}$ M.

Summarizing… We start with pure water, satisfying the water ionization equilibrium. We add a large amount of H^+; some of it reacts with the OH^-, driving the water ionization reaction backwards to restore the water ionization equilibrium. The amount of H^+ left is essentially what we add with the acid, since H^+ is in large excess. We then calculate $[OH^-]$ from the K_w expression.

With luck, there is little that is fundamentally new in this example. You have calculated the $[H^+]$ and $[OH^-]$ of strong acid solutions before. What is new here is the perspective, the level of detail of what happens when the acid is added to water. We focus here on restoring an equilibrium, on "driving" a reaction in one direction by adding one of the chemicals in the equation. In this case, we decided that the consumption of the added H^+ in the reverse reaction would be negligible; in Sect C of SA, we didn't even look at this possibility. Although such H^+ consumption was negligible here, we will soon see examples where it is not.

> [Some of you may recall Le Chatelier's principle (LCP). LCP states that if you perturb a chemical equilibrium, the reaction adjusts to reduce the perturbation and restore the equilibrium. The preceding discussion illustrates LCP.]

Example C-2. Adding H^+ to a solution of a weak acid and its conjugate base.

Let's now look at another case, and apply similar logic.

Consider the acetic acid ionization reaction (Eq 1-WA), along with its equilibrium expression (Eq 2-WA). Let's start with a 1.0 M solution of sodium acetate, at pH = 7.0. (This choice of specific conditions is rather arbitrary.) Since pH = 7.0, we know that $[H^+] = [OH^-] = 10^{-7}$ M. We also know that $[CH_3COO^-] \sim 1.0$ M, with $[CH_3COOH] \sim 0.0056$ M; these are from Eq 2-WA, but don't worry about whether you can calculate them yourself at this point. Thus we have a solution with lots of acetate ions. And the solution has two reversible reactions at equilibrium: water and acetic acid ionizations.

Now we add 0.1 M HCl, just as we did before. What happens? Specifically, what is the new pH? When we added 0.1 M HCl to water at pH = 7, $[H^+]$ became 0.1 M. We shall see that adding this same 0.1 M HCl to the acetate solution at pH = 7 results in $[H^+] = 2\text{x}10^{-6}$ M (pH 5.7). The presence of the acetate ions causes the change in $[H^+]$ to be much less than we might have expected. Let's look at why, in the same kind of detail as we did before.

We add 0.1 M HCl. It ionizes completely, to produce 0.1 M H^+. So far, this is just as above. But now two equilibria are disturbed, the water equilibrium and the acetic acid equilibrium.

The high $[H^+]$ will tend to drive the water equilibrium backwards, as before. But there is very little $[OH^-]$, and so this has little effect on the $[H^+]$.

The high $[H^+]$ also drives the acetic acid equilibrium backwards. In this case, there is plenty of room to drive it. There is lots of acetate ion present; in fact, there is much more acetate ion (1 M) than hydrogen ion (0.1 M). How far backwards does the acetate reaction go? The extreme case would be that it runs out of the limiting reactant, in this case the H^+. If all the H^+ reacted, the reaction would consume 0.1 M acetate ions and produce 0.1 M acetic acid. In this case, $[CH_3COO^-]$ is now 0.9 M (original 1.0 M less 0.1 M reacted), and $[CH_3COOH] = 0.1$ M (the original 0.0056 M plus the 0.1 M produced). And we can now calculate $[H^+]$ from the acetic acid K_a expression; it is 2.0×10^{-6} M (pH 5.7).

The pH change in this case is quite small (compared to Example C-1) because the acetate ions "consumed" most of the H^+. We say that the acetate ions "buffered" (reduced) the pH change upon adding acid.

Acetate ions can't buffer pH changes due to OH^-. However, acetic acid molecules can. The argument is essentially the same as above. (More precisely, added OH^- ions are consumed by H^+ ions in the solution; this drives the acetic acid equilibrium toward acetate, thus liberating more H^+ ions.) Mixtures of acetic acid and acetate ions can buffer against either H^+ or OH^-. And thus we have an acid-base buffer: a mixture of a weak acid and its conjugate base, which can consume either H^+ or OH^-, thus reducing the pH change when these ions are added.

D. The acetic acid equilibrium: quantitative re-examination

The purpose of this section is to extend the development of the idea of how buffers work. We focus on quantitative issues here. Going through these equations, and doing a few calculations yourself, will help you appreciate how buffers work, and what their limitations are.

In WA, we focused on the acetic acid equilibrium. We then generalized to any weak acid of the form HA. Eq 1-WA & 2-WA for acetic acid are just specific cases of the more general Eq 4-WA & 5-WA. Similarly, here we will focus on acetic acid for most of the discussion. However, everything we say for acetic acid is true for HA -- with different specific numbers, because different HA have different K_a values.

In the problems in WA, the only chemical in the solution was the acid, such as acetic acid. Of course, that need not be so. We can have solutions that contain acetic acid plus other things -- other things such as HCl or sodium acetate, which are other sources of H^+ and CH_3COO^- ions. We need to -- and can -- take these into account when doing calculations of equilibria, such as with Eq 2-WA.

Example D-1. What are $[CH_3COO^-]$ & $[CH_3COOH]$ after adjusting the pH?

In Example C-2 we talked about a solution of 1.0 M sodium acetate, which had been adjusted so that pH = 7.0. We then presented values for $[CH_3COO^-]$ & $[CH_3COOH]$, claiming that they came from Eq 2-WA. How did we get those values?

Eq 2-WA contains four terms, K_a and three concentrations. We know K_a ($1.8\text{x}10^{-5}$) for acetic acid). And we have the measured value of $[H^+]$ (10^{-7} M, from the pH). Thus we know two of the four terms. That may seem like it's not enough, but it is useful.

Eq 2-WA can be rearranged to

$$(1) \qquad \frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{K_a}{[H^+]}$$

The left side of Eq 1 shows the ratio of acetate concentration to acetic acid concentration. We know the two terms on the right, so we can calculate that $[CH_3COO^-]/[CH_3COOH] = 1.8\text{x}10^{-5}/10^{-7} = 180$. That is, the ratio of acetate to acetic acid is very high. We thus conclude that $[CH_3COO^-]$ must very nearly equal the original 1.0 M, and $[CH_3COOH]$ must be 1/180 of that, or about 0.0056 M. These are the numbers that were presented above. We got them from calculating a ratio of acetate to acetic acid, using Eq 1 (a form of Eq 2-WA), then realizing the implications of that ratio for our solution.

To do: As a check, put the three concentrations calculated here into Eq 2-WA, and see that you get the known value of K_a for acetic acid.

> There is a more rigorous way of looking at why Eq 1 is useful even though it still leaves us with two unknowns (when we specify K_a and $[H^+]$). There is a second relationship between the remaining variables, $[CH_3COO^-]$ & $[CH_3COOH]$: their sum must equal the original added concentration of acetate. That is: $[CH_3COO^-] + [CH_3COOH] = 1.0$ (in this case, with 1.0 M sodium acetate); we sometimes refer to this as a conservation equation. That is, we really have two equations, with two unknowns; thus, the equations can be completely solved. Although we did not formally use the conservation equation in the discussion above, our logic implied it.

Example D-2. What is the pH of a given mixture of acetic acid and acetate ions?

In the Example of Sect C-WA, we calculated the pH of 0.10 M acetic acid. As noted, nothing else was in that solution. Now, let's calculate the pH if we add 0.10 M acetic acid to a solution which already contains 0.20 M acetate ions.

> (For example, we might have first dissolved 0.20 M sodium acetate. But emphasize: the order of adding the chemicals is not important. It is convenient

> for our discussion in some cases to state an order of addition, but the final result depends only on what is added.)

Our solution to this problem follows the solution in Sect C-WA very closely. I suggest that you re-read that along with this.

We want $[H^+]$. Let's call it x.

If ionization of the added acetic acid produces x of the H^+, it must also produce x of the acetate ion. This is as before. But now, we already have some acetate ion (0.20 M, to be specific). Thus $[CH_3COO^-]$ will be 0.20+x -- the amount we already had <u>plus</u> the additional amount from the ionization of the acetic acid.

What is $[CH_3COOH]$? As before, it is 0.10-x.

Now substitute the concentrations that we have figured out into Eq 2-WA (just as we did before in Eq 3-WA):

$$(2) \quad 1.8\text{x}10^{-5} = \frac{x * (0.20+x)}{0.10-x}$$

In the previous example, we argued that x<<0.1. It will be even less here, since we already started with some acetate ions. (Think of the added acetate ions as driving Eq 1-WA backwards.) If x<<0.1, in the denominator, then x<<0.2, in the numerator. Thus we neglect both of the x that are in additive terms.

With these approximations (which we can verify after we get x), Eq 2 becomes $1.8\text{x}10^{-5} = 0.20x/0.10$. That's easy to solve; it's not even a quadratic equation anymore. $x = 9.0\text{x}10^{-6}$; this is $[H^+]$, in M. The pH is 5.05. (Check… x<<0.1 and x<<0.2, as we approximated.)

As already suggested, x (= $[H^+]$) is lower in this case (or the pH is higher) than in the acetate-free problem of Sect C-WA. We would expect that; the extra acetate serves to drive Eq 1-WA backwards, thus reducing $[H^+]$.

<u>Problems</u>

1. Calculate the pH if 0.10 M acetic acid is added to a solution that already contains 0.05 M acetate ions (e.g., 0.05 M sodium acetate).
2. Calculate the pH if 0.10 M formic acid is added to a solution containing 0.20 M formate ions.
* 3. Calculate the pH if 0.10 M acetic acid is added to a solution containing 10^{-6} M acetate ions. (Careful!)
* 4. Calculate the pH if 0.10 M acetic acid is added to a solution containing 0.10 M sodium chloride.

Examples D-1 & D-2 illustrate some ways that the equilibrium equation Eq 2-WA (or its more general form Eq 5-WA) can be used when there is more than just acetic acid (or HA) in the solution.

Let's now rearrange Eq 2-WA to another form, one which is particularly useful in discussing buffers.

$$(3) \quad [H^+] = K_a * \frac{[CH_3COOH]}{[CH_3COO^-]}$$

This equation expresses $[H^+]$ in terms of the concentrations of acetic acid and acetate, specifically in terms of the ratio of those two concentrations.

If you take the log of both sides, multiply by -1, and substitute the appropriate "p" expressions (Sect F of W), Eq 3 can be stated as

$$(4) \quad pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

To do: Verify that Eq 4 follows from Eq 3. (It's a good test of your ability to handle logs!)

Eq 3 & 4 are fully equivalent, and we will use them interchangeably. You could calculate $[H^+]$ from Eq 3 and convert it to pH, or just calculate pH from Eq 4.

E. Generalizing… The Henderson-Hasselbalch equation

Of course, Eq 3 & 4 can be generalized for any weak acid, HA. For example, Eq 4 in the general form becomes

$$(5) \quad pH = pK_a + \log \frac{[A^-]}{[HA]}$$

Eq 5 is often called the Henderson-Hasselbalch equation, and is a useful tool for discussing buffers.

These equations (3, 4, 5 -- they are all equivalent) have some interesting properties.

First, the pH depends only on the ratio of $[A^-]$ to [HA] (for a given HA, with a specific value of K_a).

If $[HA] = [A^-]$ (that is, if the ratio is 1), then $pH = pK_a$. This is an important statement in dealing with buffers. If we want a buffer to be a good general buffer, against both acids and bases, then we need to have both HA and A^- present. One good way to have both HA and A^- present is to have them at equal concentrations; in this case, $pH = pK_a$.

The preceding discussion leads to the common statement that buffers are most useful "near" the pK_a. For acetic acid, $pK_a = 4.74$. Acetic acid is a good buffer near pH 4.74, near its pK_a.

Recall Example D-1, with sodium acetate at pH = 7. There was very little acetic acid present at that pH. This would not be a good general buffer; the $[CH_3COOH]$ is so low that it would not be able to consume much base.

> There is a second reason why buffers are most effective near the pK_a. If one looks at the magnitude of the pH change for a given amount of H^+ added, it is smallest at the pK_a. By moving somewhat above the pK_a, the buffer could consume more acid (but less base). However, the slope of the response curve, pH vs added acid (or base), is most favorable at the pK_a. If you want to explore this, you should calculate some numerical examples, or graph Eq 5, or calculate the derivative (slope) of Eq 5 when expressed as pH vs added H^+.
>
> A corollary of this discussion is that under some circumstances one might prefer a buffer somewhat away from the pK_a. If your main concern is consuming a large amount of acid (but not base), and you can't increase the buffer concentration, then starting above the pK_a of the buffer system would be appropriate.

The limits of "near" will be discussed in Sect F.

What if $[CH_3COOH]/[CH_3COO^-] = 10$? According to Eq 3, then $[H^+] = 10*K_a = 1.8x10^{-4}$ M. That is pH 3.74. One could get that pH directly by using Eq 4.

<u>Problems</u>. (I encourage you to use both Eq 3 & 4 in solving these problems.)

5. Calculate pH when $[CH_3COOH]/[CH_3COO^-] = 0.1$.
6. Calculate pH when $[CH_3COOH]/[CH_3COO^-] = 100$.
7. Calculate pH when $[CH_3COOH]/[CH_3COO^-] = 0.01$.
8. Calculate pH when $[CH_3COO^-]/[CH_3COOH] = 100$.
9. Calculate pH when $[CH_3COOH] = 0.04$ M and $[CH_3COO^-] = 0.08$ M.
10. Calculate pH when $[CH_3COOH] = 0.39$ M and $[CH_3COO^-] = 0.78$ M.
11. Calculate pH when $[CH_3COOH] = 0.08$ M and $[CH_3COO^-] = 0.04$ M.

To do: Make a table showing pH vs $[CH_3COOH]/[CH_3COO^-]$, using the data from the problems and examples above. Put the table in order.

The example and problems provide an interesting pattern. Each factor of 10 change in the ratio $[CH_3COOH]/[CH_3COO^-]$ causes a 1 unit change in pH. In fact, this is general for buffer systems: a factor of 10 change in the ratio $[HA]/[A^-]$ causes a 1 unit pH change. This follows from the form of Eq 5, and the simple fact that log 10 = 1. (And remember, when that ratio is 1, pH = pK_a.)

Problems

12. Qualitatively… if [CH_3COOH] > [CH_3COO^-], is the pH > pK_a, or < pK_a?
13. Consider formic acid, $pK_a = 3.75$. Calculate the pH for various ratios of [formic acid]/[formate], just as you did with the acetic acid-acetate buffer system above. (If you are clever, you won't even need your calculator.) Include the results in your table.
14. If the total acetic acid added is 0.10 M, what are [CH_3COOH] and [CH_3COO^-] when the ratio is 1:1?
* 15. Continuing… We now add H^+ until the ratio is 9:1 (high acid). What are [CH_3COOH] and [CH_3COO^-]?

[If you use a spreadsheet or equation-solving program, you might try exploring some of these equations on your computer.]

F. Choosing a buffer

In the previous sections we have discussed how buffers work: they "consume" added H^+ or OH^- ions so that they (these added ions) do not change the pH (very much). And we have looked at the quantitative basis of these effects. As a result, we can begin to formulate some guidelines for choosing a buffer.

Step 1. The ideal buffer would be one with a pK_a very near the pH of our solution. When pH = pK_a, [HA] = [A^-]. This allows the buffer to consume both acid and base (and, as noted briefly, minimizes the pH change for a particular addition).

Problems

A table of common buffers used in biology is attached (Section J, last page).

Try to answer each question on the basis of the guidelines presented so far. (In the real world, buffer choices are more complex than we have discussed; we will discuss some of the additional complexities later.)

16. Choose a buffer that would be very effective at pH 3.8.
17. How would you make the buffer system, at, say 0.1 M? [What chemical(s) would you use? How much (in M)?]
18. You want to buffer a solution at pH 9.2. Your choice of buffer?

Of course, having the pK_a "very near" the pH may well be unachievable. This leads to…

Step 2. A rule of thumb is that buffers are useful within about +/- 1 pH unit of the pK_a. I should stress that this is somewhat arbitrary. Buffers lose their effectiveness gradually as the pH moves away from pK_a; there is no cut-off. However, the basis of the rule of thumb is the set of calculations in Sect E showing that when pH is 1 unit from pK_a, the ratio of buffer components is now 10:1 (rather than 1:1 at the pK_a).

Problems

19. Would Tris buffer be suitable for use at pH = 7.0?
20. The buffers listed in capital letters are a special group of buffers that are particularly intended for use in biological systems. They were developed by a biologist named Good, and are commonly known as Good buffers. Choose a Good buffer (listed in all CAPS) for use at pH 7.0.
* 21. One of the important buffers in your blood is based on phosphoric acid. Blood pH is about 7.4. Which step of the phosphoric acid ionization is most relevant in this situation? Write the chemical equation for this ionization.

Steps 3… Other issues may well be involved in your choice of buffer.

The buffer must be chemically compatible with your experiment. For example, if you are trying to buffer growth media for bacteria or fungi, you may well find that the organisms will eat common organic acid buffers.

The pK_a of buffers changes with temperature -- dramatically for some buffers, such as Tris. You may need to consider this. If nothing else, it may be important to measure buffer pH at the temperature of intended use.

Some buffers bind things other than H^+. In particular, some bind metal ions (and are therefore known as chelators). Some data on metal binding is in some lists of buffers.

These are just examples of additional considerations, beyond those of the pK_a, that may affect your choice of buffer. As noted, reading suppliers' literature about their buffers may be helpful.

G. Some misconceptions

Sometimes we make simple statements about buffers, either from laziness or misunderstanding, that seem to endow the buffers with rather remarkable properties. Looking at a couple of these mis-simplifications may help to increase your understanding of what a buffer really does.

Misstatement #1: Buffers prevent pH changes. No, they merely reduce pH changes. Buffers work by driving a reversible reaction. Some of the added H^+ is consumed by the weak base, thus less H^+ is left free to lower the pH. Of course, sometimes the remaining pH change may be so small that it is immeasurable or "negligible". But it is still finite.

Misstatement #2: A good buffer system will resist any amount of acid that is added. No, buffers have capacity. Each A^- ion can consume one H^+ ion. Thus the maximum amount of acid a buffer can consume is given by the initial $[A^-]$. But the pH will decrease constantly as that amount is consumed. How much pH change is acceptable to you? That's an issue of your work. But it places a further limit on how much acid you will allow the buffer to consume.

H. What does "buffer capacity" mean?

The term buffer capacity is often used. It is clear that the term refers to how much acid or base the buffer can consume. And it seems natural to suspect there is a formal quantitative definition of the term, which seems to be quantitative. Interestingly, there is not. Or perhaps it would be better to say that there are multiple definitions. One might define buffer capacity in terms of how much acid or base can be consumed within a specified amount of pH change. That may have practical value. One might also define buffer capacity in terms of the slope of the Henderson-Hasselbalch equation (Section E) -- an approach with mathematical appeal, but probably not of much practical use in the lab.

The main point for now is that the term does not have a generally accepted quantitative meaning. If someone wants to use the term, be sure to establish the meaning being used.

Happy buffering!

I. Answers

Sect D

1. 4.44 2. 4.05

3. The numerator will be x * (10^{-6} + x). Is x << 10^{-6}? No. We know from the Example in Sect C-WA that [CH_3COO^-] is about 10^{-3} M. In this problem, the added 10^{-6} M acetate is negligible compared to the x that will come from the CH_3COOH. The amount of acetate added here is so low that it has no significant effect. Thus we neglect the 10^{-6} in the numerator, and the x in the denominator. The problem reduces to the same as that in Sect C-WA, with pH 2.87. The message: be careful about doing these problems by rote. Each step involves chemical logic. Be sure you remember why a step is done, and whether the assumptions made are relevant. When done, check the approximations.

4. Sodium chloride gives Na^+ and Cl^- ions. Neither of these ions is relevant to acetic acid ionization, Eq 1-WA & 2-WA. In particular, Cl^- does not consume H^+. (How do you know? Cl^- is the conjugate base of HCl, a strong acid. Therefore, Cl^- is a <u>very</u> weak base.) Thus the problem is no different than the example of Sect C-WA. pH = 2.87.

Sect E

5. 5.74 6. 2.74 7. 6.74 8. 6.74

9. 5.04 10. 5.04 (Only the ratio matters.) 11. 4.44

12. pH < pK_a. Look at the form of Eq 5, or the results in your table. Or think… the solution has more of the <u>acid</u> form, thus the pH must be <u>acidic</u>. It's useful to recognize this qualitative point; it may rescue you from silly errors with Eq 5.

13. At 1:1, pH = pK_a = 3.75. At 10:1 (high acid), the pH will be one unit lower (more acidic); at 1:10 (high formate), the pH will be one unit higher (more basic). Etc.
14. 0.05 M each
15. 0.09 M acid, 0.01 M acetate. (The 9:1 number given here is very close to the 10:1 in the earlier problems. Each is the easier number to use in the particular type of calculation.) Note that when the ratio changes from 1:1 to 9 or 10:1, no individual concentration changes by 9 or 10 fold. We added H^+; $[CH_3COOH]$ goes up, $[CH_3COO^-]$ goes down. The ratio changes faster than either individual value.

Sect F

16. Formic acid. Its pK_a is very near the desired pH.
17. The first important point is to distinguish the buffer based on formic acid from a solution of formic acid. As you know from WA, 0.1 M formic acid has a pH = 2.4. The buffer at its pK_a is an equal mix of formic acid (HA) and formate ions (A^-). You could make it by adding 0.05 M each of formic acid and a formate salt (such as sodium formate). Or you could take 0.1 M formic acid, and add a strong base (such as NaOH) until the pH = 3.8. These approaches are equivalent.
18. Boric acid/borate.

19. The pK_a for Tris is 8.3. The requested use is somewhat more than 1 pH unit from the pK_a. Not recommended. This answer deserves elaboration. If we use Tris at pH 7, we have a high ratio of $[HA]/[A^-]$. There is <u>very</u> <u>little</u> A^- left, and thus very little ability to buffer against further additions of H^+. On the other hand, there is plenty of HA, and thus a good ability to consume base. Tris at pH 7 might be suitable if you knew that your main need was to buffer against base additions. Biochemists often use Tris, and often use it near pH = 7. This is based somewhat on tradition and on ignorance, and somewhat on the longtime lack of suitable buffers with pK_a near 7. As noted, the +/- 1 pH unit rule is a guideline, and not a sharp cutoff. Sometimes, Tris works ok at pH 7. But it's not to be generally recommended.
20. None of the Good buffers are listed <u>at</u> pK_a = 7.0. But one is only 0.1 pH unit away (ACES). Three others are 0.2 units away; these include the relatively common PIPES and MOPS.
21. 2nd step. The buffers table shows pK_{a2} for phosphoric acid at 7.21. The second ionization is $H_2PO_4^- \rightarrow H^+ + HPO_4^{2-}$.

J. Table of buffers

The table of buffers, at right, is from a brochure called “Buffers: A Guide for the preparation and use of buffers in biological systems”, published by Calbiochem. The table shown is from the 1992 printing.

Calbiochem is a major supplier of biochemicals, including buffers. (Suppliers of research chemicals and equipment often provide extensive educational and reference material in their catalogs and supplementary publications.)

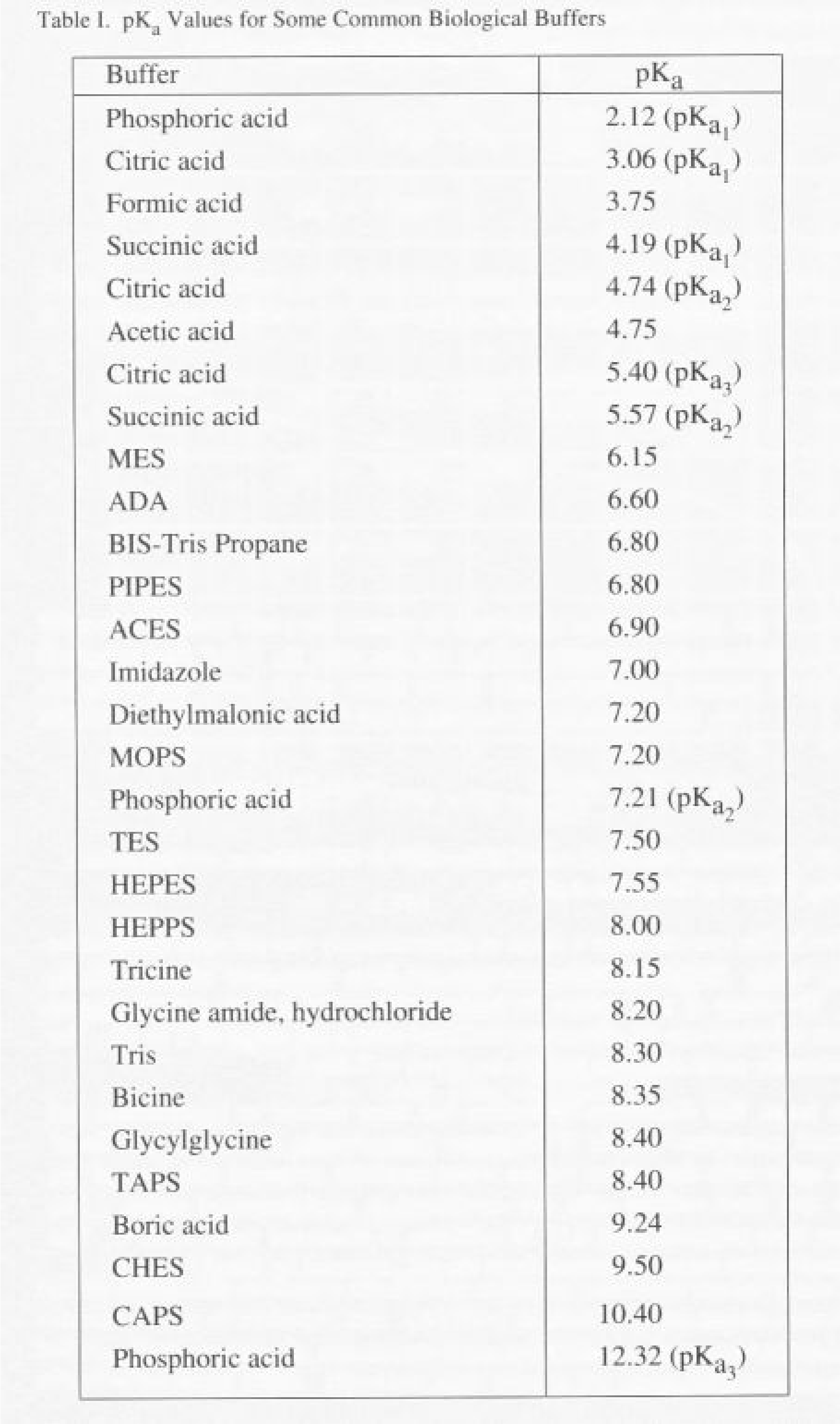

Table I. pK_a Values for Some Common Biological Buffers

Buffer	pK_a
Phosphoric acid	2.12 (pK_{a_1})
Citric acid	3.06 (pK_{a_1})
Formic acid	3.75
Succinic acid	4.19 (pK_{a_1})
Citric acid	4.74 (pK_{a_2})
Acetic acid	4.75
Citric acid	5.40 (pK_{a_3})
Succinic acid	5.57 (pK_{a_2})
MES	6.15
ADA	6.60
BIS-Tris Propane	6.80
PIPES	6.80
ACES	6.90
Imidazole	7.00
Diethylmalonic acid	7.20
MOPS	7.20
Phosphoric acid	7.21 (pK_{a_2})
TES	7.50
HEPES	7.55
HEPPS	8.00
Tricine	8.15
Glycine amide, hydrochloride	8.20
Tris	8.30
Bicine	8.35
Glycylglycine	8.40
TAPS	8.40
Boric acid	9.24
CHES	9.50
CAPS	10.40
Phosphoric acid	12.32 (pK_{a_3})

The booklet is available, free, as a pdf file, from their web site: http://www.emdbiosciences.com/html/CBC/booklets.htm; choose the Buffers item. A link to this site is on my page of Internet resources for Intro Chem.