

Chapter 57

BUFFERS

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So far, we have covered much of what happens when a single acid, base or salt compound is dissolved into water. The compound may dissociate partly or completely, it may be acidic or basic, or it may have no pH effect. We now move into buffers, which involve both members of a conjugate pair dissolved in the same solution.

57.1 Buffer fundamentals

The word buffer is used in the normal dictionary sense as something which reduces the impact of an event. In chemistry, buffers are used to reduce the impact on some property when a change occurs in the system. Among the various types of buffers which are involved in chemical applications, acid-base buffers are among the most important. An acid-base buffer reduces the change in pH when an amount of an acidic or basic component is increased or decreased within a system. The increase or decrease can result from physically adding acid or base to a solution or it can result from some reaction which produces an acid or base. When studying chemical reactions in aqueous solution, it is often important to keep the pH steady (or nearly so), and a buffer can do that. The applications of buffers far exceed their role in chemical studies, however, and they are hugely important in biological systems, including you. Single cells and entire bodies are heavily dependent on buffers because a large number of biochemical reactions involve acids and bases, and even a small swing in pH can kill.

An acid-base buffer is typically prepared by dissolving both partners of a weak conjugate pair in the same solution. Their concentrations in the solution must be sufficient to dominate the pH of the system. Let's say we have a buffer solution and we add a strong acid. Without a buffer, this could increase $[H^+]$ and decrease pH drastically but, in a buffer, the conjugate base reacts with the added acid, thus reducing the impact. Conversely, let's say we have a buffer solution and we add a strong base. Without a buffer, this could increase OH^- and increase pH drastically, but now the conjugate acid in a buffer reacts with the added base, thus reducing the impact. In all cases, there is still a change in pH, but the change is much smaller than it would be without a buffer.

Let's do a comparison with numbers. Consider 1.00 L of pure water and 1.00 L of a buffer solution. Pure water has pH 7.00. For this comparison, the buffer solution contains 0.10 mol KH_2PO_4 and 0.06 mol K_2HPO_4 , and this solution will have pH 7.0. Now add strong acid or base to separate containers of each.

Strong acid: Add 0.010 mol HCl.

The addition of 0.010 mol HCl to 1.00 L pure water causes the pH to plummet to 2.00. (You can calculate this.)

The addition of 0.010 mol of HCl to 1.00 L of the buffer solution causes the pH to decrease very slightly, only to 6.9. (You can calculate this later.)

Strong base: Add 0.010 mol NaOH.

The addition of 0.010 mol NaOH to 1.00 L pure water causes the pH to jump to 12.00. (You can calculate this.)

The addition of 0.010 mol of NaOH to 1.00 L of the (original) buffer solution causes the pH to increase very slightly, only to 7.1. (You can calculate this later.)

In both cases, the buffer dramatically reduced the impact on the pH of adding the strong acid or base. That's the buffer's job. The illustrations here involve the addition of a strong acid or base, but a buffer will also work (even better) when adding a weak acid or base.

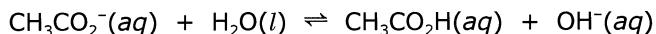
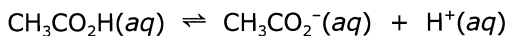
This is a general illustration. Now we get into more details.

Example 1. Consider a buffer solution which is composed of 0.100 mol CH_3CO_2H and 0.100 mol $NaCH_3CO_2$ in 1.00 L solution volume. CH_3CO_2H and $CH_3CO_2^-$ are the conjugate pair; the Na^+ ion is of no pH effect and is irrelevant. For this Example, there are three Parts.

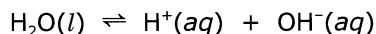
- What is the pH of the original buffer solution?
- What is the pH of the solution after adding 0.010 mol HCl?
- What is the pH after adding 0.010 mol NaOH to a separate solution of the original buffer (from Part A)?

► Part A

The solution contains equal amounts of conjugate acid and base. Each is doing its own thing



along with autoionization.



Some of the 0.100 mol of $\text{CH}_3\text{CO}_2\text{H}$ deprotonates, and some of the 0.100 mol of CH_3CO_2^- protonates. Some H^+ is formed, some OH^- is formed, and some of these are neutralized by each other. The changes which occur for $\text{CH}_3\text{CO}_2\text{H}$ and CH_3CO_2^- upon going to equilibrium tend to offset each other, so those amounts do not change significantly. Thus, the final amounts at equilibrium are 0.100 mol of $\text{CH}_3\text{CO}_2\text{H}$ and 0.100 mol of CH_3CO_2^- . Since we are in 1.00 L of solution, then these mole numbers are also molar numbers which means these are also the numbers for the activities. We can calculate $[\text{H}^+]$ at equilibrium using K_a .

$$K_a = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} = 1.8 \times 10^{-5}$$

$$[\text{H}^+] = K_a \times \frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{CH}_3\text{CO}_2^-]} = 1.8 \times 10^{-5} \times \frac{0.100}{0.100} = 1.8 \times 10^{-5}$$

Since $[\text{H}^+] = 1.8 \times 10^{-5} \text{ M}$, then $\text{pH} = 4.74$. That's for the original buffer solution.

OK, there's a key point in there to note, and that's the part about "tend to offset each other". This is important because it changes the calculation in a big way. We can now plug in the given amounts of the conjugate pair directly without doing a table of changes and the $\pm x$ routine. The reason for this is that we are starting with appreciable amounts of both partners of the conjugate pair present. When you start a solution with appreciable amounts of both members of a conjugate pair present, then the shift to equilibrium will often be so small that the amounts will not change within the allowed sigfigs. I said often, not always. Exceptions to this will occur as K_a or K_b gets bigger ($> 10^{-3}$ or so), and/or concentrations get very dilute ($< 0.01 \text{ M}$ or so), and/or the conjugate ratio itself becomes very large or very small. So, yes, complications can happen. There are more complex equations which are more general but we will not do those. For our purposes, we will follow the "often" outcome. I shall summarize this outcome as the No-Change Guideline.

No-Change Guideline

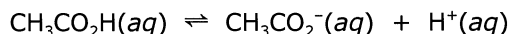
For a solution which begins with appreciable amounts of both members of a conjugate pair, then the shift to equilibrium will often be small. Assume there are no significant changes to the amounts of the conjugate acid and base which are present.

Subject to the caveats as duly noted, we will use this No-Change Guideline for buffers in the present Chapter and later for titrations in the next Chapter. Note that the Guideline is for the amounts of the conjugate pair; you still need to calculate $[\text{H}^+]$ as was shown above.

This ends Part A.

► Part B

Now we add 0.010 mol of strong acid, HCl, to the original buffer. The Cl^- has no pH effect and is ignored. We focus on the H^+ part. H^+ is involved in the conjugate pair equilibrium.



The increase in H^+ from the added HCl shifts the equilibrium to the left. Some CH_3CO_2^- is protonated and this forms more $\text{CH}_3\text{CO}_2\text{H}$. How much reaction occurs? A strong will react with a weak opposite. When adding a strong acid to a weak base, the strong acid will protonate the weak base (which is the same as saying the weak base will deprotonate the strong acid). You treat this much as a stoichiometry problem. Here are the stoichiometry aspects which are involved in this Part.

The original buffer starts with: 0.100 mol CH_3CO_2^- 0.100 mol $\text{CH}_3\text{CO}_2\text{H}$

0.010 mol HCl is then added and this reacts with the conjugate base. For the amounts given, HCl is limiting and acetate is in excess. The 0.010 mol HCl reacts with 0.010 mol of the original CH_3CO_2^- to form 0.010 mol of additional $\text{CH}_3\text{CO}_2\text{H}$.

Amount reacted/formed due to the HCl:	-0.010 mol CH_3CO_2^-	+0.010 mol $\text{CH}_3\text{CO}_2\text{H}$
The solution now contains:	0.090 mol CH_3CO_2^-	0.110 mol $\text{CH}_3\text{CO}_2\text{H}$

OK, so far, these are just simple stoichiometric relationships. Although an equilibrium shift can technically occur from this point, the shift will not be significant and we invoke the No-Change Guideline. Thus, the amounts of the conjugate pair remain 0.090 mol CH_3CO_2^- and 0.110 mol $\text{CH}_3\text{CO}_2\text{H}$ at the end. We use these numbers to find $[\text{H}^+]$, following the same calculation as in Part A. Again, since the solution volume is 1.00 L, then the numbers for moles and the numbers for molarities are the same.

$$[\text{H}^+] = K_a \times \frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{CH}_3\text{CO}_2^-]} = 1.8 \times 10^{-5} \times \frac{0.110}{0.090} = 2.2 \times 10^{-5}$$

From $[\text{H}^+] = 2.2 \times 10^{-5} \text{ M}$, we get $\text{pH} = 4.66$.

Summary point: the strong acid reacted with the weak base of the buffer to produce more weak acid. This changed the relative amounts of the conjugate pair and this changed the pH. The equilibrium amount of $[\text{H}^+]$ increased from $1.8 \times 10^{-5} \text{ M}$ to $2.2 \times 10^{-5} \text{ M}$. The pH went down, from 4.74 to 4.66. This is a very small change compared to adding the same number of moles of HCl to 1.00 L of pure water: that would send the pH down to 2.00 as in the illustration earlier in the Chapter.

By the way, although the solution volume is 1.00 L in this example, don't always count on that. If the volume is not 1.00 L, then you need to be careful with moles versus molarities. K_a 's and K_b 's use activities based on molarities. On the other hand, we will see a simplification in a mere moment below.

► Part C

We return to a solution of the original buffer from Part A and we add NaOH. The Na^+ has no effect. The OH^- deprotonates some $\text{CH}_3\text{CO}_2\text{H}$ and forms more CH_3CO_2^- . How much reaction occurs? Again, a strong will react with a weak opposite, and now the strong base will deprotonate the weak acid. Again, you first treat this as a stoichiometry problem.

The original buffer starts with:	0.100 mol CH_3CO_2^-	0.100 mol $\text{CH}_3\text{CO}_2\text{H}$
0.010 mol NaOH is added and this reacts with the conjugate acid. For the amounts given, NaOH is limiting and acetic acid is in excess. The 0.010 mol NaOH reacts with 0.010 mol of the original $\text{CH}_3\text{CO}_2\text{H}$ to form 0.010 mol of additional CH_3CO_2^- .		
Amount reacted/formed due to the NaOH:	+0.010 mol CH_3CO_2^-	-0.010 mol $\text{CH}_3\text{CO}_2\text{H}$
The solution now contains:	0.110 mol CH_3CO_2^-	0.090 mol $\text{CH}_3\text{CO}_2\text{H}$

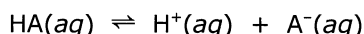
We again invoke the No-Change Guideline and assume there is no significant equilibrium shift. The amounts of the conjugate pair stay the same at 0.110 mol CH_3CO_2^- and 0.090 mol $\text{CH}_3\text{CO}_2\text{H}$, and these go into finding $[\text{H}^+]$.

$$[\text{H}^+] = K_a \times \frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{CH}_3\text{CO}_2^-]} = 1.8 \times 10^{-5} \times \frac{0.090}{0.110} = 1.5 \times 10^{-5}$$

Now, $[\text{H}^+] = 1.5 \times 10^{-5} \text{ M}$ and $\text{pH} = 4.82$.

Summary point: the strong base reacted with the weak acid of the buffer to produce more weak base. This changed the relative amounts of the conjugate pair and this changed the pH. The equilibrium amount of $[\text{H}^+]$ decreased from $1.8 \times 10^{-5} \text{ M}$ to $1.5 \times 10^{-5} \text{ M}$. The pH went up, from 4.74 to 4.82. This is a very small change compared to adding the same number of moles of NaOH to 1.00 L of pure water: that would send the pH to 12.00 as in the illustration earlier in the Chapter.

These Parts A - C illustrate the types of calculation involved for buffers. Notice in these calculations that $[\text{H}^+]$ was calculated from the ratio of the conjugate pair and from K_a . This leads to a very useful relationship, derived as follows. I'll switch back to generic for this derivation.



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

Re-arrangement of K_a gives the form used in all three Parts upstairs.

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

Now take the negative log of both sides.

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

We'll p-function the first two entries but keep the log of the conjugate pair ratio.

$$\text{pH} = \text{p}K_a - \log \frac{[HA]}{[A^-]}$$

Invert the conjugate ratio; this will negate the log term.

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

We will now convert this to the final form below,

$$\text{pH} = \text{p}K_a + \log \frac{\text{base}}{\text{acid}}$$

and this form is general for use with any weak acid (HA) and its conjugate base (A^-), as well as for a weak base (B) and its conjugate acid (BH^+).

The above equation is a very useful relationship which provides a pH directly from a K_a and a conjugate ratio, base/acid. Its use is general and not limited to buffer calculations. This equation has historically been called the Henderson-Hasselbalch equation, which we'll just call HH. Note that, for a specific conjugate pair (which has their own specific $\text{p}K_a$), the pH is a function of the conjugate ratio and not the actual amounts individually. Furthermore, since HH is a re-arranged K expression, the base/acid ratio involves unitless activities but we continue with the molar connection. You can also use moles directly for this application, and that's because the V terms drop. Check it out.

$$\frac{[\text{base}]}{[\text{acid}]} = \frac{\text{mol base/V}}{\text{mol acid/V}} = \frac{\text{mol base}}{\text{mol acid}}$$

Thus, it doesn't matter in the end which way you do it. What does matter, however, is that you remember it's base over acid. If you get the two upside down, you're wrong (unless the ratio is one).

We could have used HH in our prior calculations for Parts A - C. Here it is for Part B, for illustration purposes. $\text{CH}_3\text{CO}_2\text{H}$ has $K_a = 1.8 \times 10^{-5}$, so $\text{p}K_a = 4.74$.

$$\text{pH} = \text{p}K_a + \log \frac{\text{base}}{\text{acid}} = 4.74 + \log \frac{0.090}{0.110} = 4.74 + \log(0.82) = 4.74 - 0.086 = 4.65$$

Upstairs we obtained a pH of 4.66. Notice that the two calculation methods give a slight difference. It is not unusual to be off by ± 0.01 for these methods due to our ways of handling the sigfigs involved. Both numbers are correct in such a case.

Technically, the amounts for the base/acid ratio in HH are the amounts at equilibrium. Our use of HH will follow the No-Change Guideline. Because of this, HH gets the same caveats as noted previously for that Guideline.

By the way, buffer calculations are inherently more prone to nonideal behavior than simple pH calculations for just an acid or a base. That's because buffer solutions tend to involve high concentrations of ionic solutes, and many are at even higher concentrations than are illustrated here. The high concentrations of ionics will cause deviations from ideal behavior. The calculations here illustrate the concepts involved in the operation of a buffer and they illustrate the effect on pH. In reality, the pH may well differ from what is calculated, but that's OK. In actual practice when you set up a buffer, you can do the calculations as shown here and make the solution accordingly, but then you check the real pH and make further adjustments as necessary.

57.2 Capacity

Some buffers may do their job well and some may not. When you set up a buffer for a particular application, you need to take into account the desired buffer capacity and the target pH range. Buffer capacity refers to the level of protection which is available against a change in pH upon the addition of an acid or a base. A higher buffer capacity will give more protection, which can be viewed in two ways:

The change in pH will be smaller for some specific amount of acid or base to be added; or, more acid or base can be added and still keep the pH within a narrow range.

There are two important factors for buffer capacity. One is the concentrations of the conjugate pair. For any buffer to work well, the concentrations of the buffer components must dominate the system. Those concentrations should be in generous excess to the expected amounts of acid or base to be added. In Parts B and C of Example 1 with the $\text{CH}_3\text{CO}_2\text{H}/\text{CH}_3\text{CO}_2^-$ buffer, the conjugate concentrations were ten-fold to the added strong acid or strong base. As seen by those calculations, the change in pH was small. For a comparison, let's redo those calculations using lower concentrations of buffer components. We will set this up at 1/5 of the prior concentrations, which means the buffer components will only be two-fold of added acid and base.

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Example 2. Consider a buffer solution which is composed of 0.020 mol $\text{CH}_3\text{CO}_2\text{H}$ and 0.020 mol NaCH_3CO_2 in 1.00 L solution volume. There are again three Parts.

- What is the pH of the original buffer solution?
 - What is the pH of the solution after adding 0.010 mol HCl?
 - What is the pH of the solution after adding 0.010 mol NaOH to a separate solution of the original buffer (from Part A)?
-

We'll just use HH in this go-round.

► Part A

You have 0.020 mol $\text{CH}_3\text{CO}_2\text{H}$ and 0.020 mol CH_3CO_2^- in 1.00 L. Mole and molar numbers are the same again, but you can use either anyway.

$$\text{pH} = \text{p}K_a + \log \frac{\text{base}}{\text{acid}} = 4.74 + \log \frac{0.020}{0.020} = 4.74 + \log(1.0) = 4.74 - 0.00 = 4.74$$

This solution has pH = 4.74, which is the same as for original Example 1A. Example 1A had higher concentrations of the conjugate pair but their ratio was the same. Again, it's the ratio that matters to the pH and not the individual amounts.

► Part B

The strong acid HCl reacts with the weak base CH_3CO_2^- and makes more $\text{CH}_3\text{CO}_2\text{H}$ acid.

The original buffer starts with: 0.020 mol CH_3CO_2^- 0.020 mol $\text{CH}_3\text{CO}_2\text{H}$

0.010 mol HCl is added. This reacts with 0.010 mol of the original CH_3CO_2^- to produce 0.010 mol of additional $\text{CH}_3\text{CO}_2\text{H}$.

Amount reacted/formed due to the HCl: -0.010 mol CH_3CO_2^- +0.010 mol $\text{CH}_3\text{CO}_2\text{H}$

The solution now contains: 0.010 mol CH_3CO_2^- 0.030 mol $\text{CH}_3\text{CO}_2\text{H}$

As before, the No-Change Guideline assumes no shift from here. Put these numbers into HH.

$$\text{pH} = \text{p}K_a + \log \frac{\text{base}}{\text{acid}} = 4.74 + \log \frac{0.010}{0.030} = 4.74 + \log(0.33) = 4.74 - 0.48 = 4.26$$

The pH falls to 4.26. This is a much larger drop than in Example 1B when the pH only went to 4.66. The solution here has a much smaller buffer capacity than the solution in Example 1B due to the lower concentration of buffer components.

► Part C

The strong base NaOH reacts with the weak acid $\text{CH}_3\text{CO}_2\text{H}$ and makes more conjugate base CH_3CO_2^- .

The original buffer starts with:	0.020 mol CH_3CO_2^-	0.020 mol $\text{CH}_3\text{CO}_2\text{H}$
0.010 mol NaOH is added. This reacts with 0.010 mol of the original $\text{CH}_3\text{CO}_2\text{H}$ to produce 0.010 mol of additional CH_3CO_2^- .		
Amount reacted/formed due to the NaOH:	+0.010 mol CH_3CO_2^-	-0.010 mol $\text{CH}_3\text{CO}_2\text{H}$
The solution now contains:	0.030 mol CH_3CO_2^-	0.010 mol $\text{CH}_3\text{CO}_2\text{H}$

These numbers go into HH.

$$\text{pH} = \text{p}K_a + \log \frac{\text{base}}{\text{acid}} = 4.74 + \log \frac{0.030}{0.010} = 4.74 + \log(3.0) = 4.74 + 0.48 = 5.22$$

The pH rises to 5.22. This is a much larger increase than in Example 1C when the pH only rose to 4.82. Again, the solution here has a smaller buffer capacity than the solution in Example 1C due to the lower concentration of buffer components.

Let's compare and conclude. We have calculations for our buffers from Examples 1 and 2, and we have the illustration from the beginning of the Chapter for pure water. Here're the pH results.

Parts:	Buffer, Example 1 (0.100 M each)	Buffer, Example 2 (0.020 M each)	Pure water
A. Original 1.00 L	4.74	4.74	7.00
B. Original + 0.010 mol HCl	4.66	4.26	2.00
C. Original + 0.010 mol NaOH	4.82	5.22	12.00

Here're the conclusions.

The original buffers of Examples 1A and 2A have the same pH. This is because they have the same conjugate ratio even though they have different amounts of each individual component.

The buffer of Example 1 has a greater capacity than the buffer of Example 2. It withstands the strong acid and base better, giving a much smaller change in pH.

Although the buffer of Example 2 has a lower buffer capacity, it is still doing the job. The change in pH is much smaller than for pure water.

Remember: higher concentrations of the conjugates give higher buffer capacity. This ends the first factor for buffer capacity. Now for the second factor.

The conjugate ratio itself also has an effect on buffer capacity. There is no exact cutoff here, but a useful guide is to keep the conjugate amounts within a range of ten-fold or so of each other. This means the ratio itself can vary from 10/1 to 1/10. This will limit which conjugate pair you can use for a particular application. To see this connection, consider HH.

$$\text{pH} = \text{p}K_a + \log \frac{\text{base}}{\text{acid}}$$

By letting the conjugate ratio vary within a range of 10^{+1} to 10^{-1} , the log will vary within a range of +1.0 to -1.0. Thus, for best buffer capacity,

$$\text{pH} = \text{p}K_a \pm 1.0$$

which means that the target pH range should be within ± 1.0 of the $\text{p}K_a$ of the conjugate pair. For example, you can use $\text{CH}_3\text{CO}_2\text{H}/\text{CH}_3\text{CO}_2^-$ with a $\text{p}K_a = 4.74$ as an effective buffer in a pH range of 3.7 - 5.7 but you would not want to use it at pH = 8.00. Instead, you would use another conjugate pair which had a $\text{p}K_a$ in the range of 7.0 - 9.0.

When actually choosing a conjugate pair for a particular application, there are three general ways to set this up as long as it fulfills the $\text{pH} = \text{p}K_a \pm 1.0$ requirement.

- First way: You can use a monoprotic weak acid and its conjugate base anion, HA and A^- .
- Second way: You can use a weak base and its conjugate cation, B and BH^+

For this second way, keep in mind that HH uses $\text{p}K_a$ and not $\text{p}K_b$. Thus, for example, if you use NH_3 and NH_4^+ , then you must use the $\text{p}K_a$ for NH_4^+ . You can derive the K_a from the K_b as was done in Section 56.2

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

and then negate its log to get $pK_a = 9.25$. There is another route which also starts from

$$K_a \times K_b = K_w = 1.0 \times 10^{-14}$$

for which the p function gives

$$pK_a + pK_b = pK_w = 14.00$$

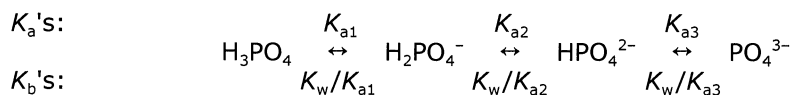
and this equation is also very handy. Thus, ammonia's $K_b = 1.8 \times 10^{-5}$ gets you $pK_b = 4.74$ and this gets you ammonium's pK_a .

$$pK_a = pK_w - pK_b = 14.00 - 4.74 = 9.26$$

Notice the two routes can differ by one in the last digit for pK_a but that's OK again within our handling of sigfigs. As long as you do the math right, either value is fine.

- Third way: You can use two ions of a polyprotic series.

If you use two members of a polyprotic series, then you must use the pK_a for that step which has that particular conjugate pair. Remember to be careful with the polyprotic series. Let's illustrate this using $H_2PO_4^-$ and HPO_4^{2-} as the conjugate pair. Here's the whole kit and caboodle again for H_3PO_4 from the last Chapter.



Note that $H_2PO_4^-$ and HPO_4^{2-} are connected by K_{a2} and that means pK_{a2} would set the target pH range and it would be used in HH. By the way, you can now do the calculations for the buffer which was described in the very beginning of the Chapter.

Besides the target pH range, there is one more restriction on the choice of conjugate pair for a buffer. This is a very practical one: the conjugate pair should not chemically react with whatever is present in the solution. For illustration, consider the $HClO/CIO^-$ conjugate pair. The pK_a for $HClO$ is 7.52 which puts it into the 6.5 - 8.5 range for buffering. $HClO$ and CIO^- are good oxidizing agents, however, and they are quite reactive. (Chlorine bleach, used in laundry, is a basic solution of $NaClO$.) Thus, this pair could not be used in a buffer with solutes which are subject to oxidation. Biological applications often use buffers and, if you were trying to grow bacteria near neutral conditions, you would kill them off with this conjugate pair. So, overall, be aware that chemical reactivity can also affect the choice of which buffer components to use, although this aspect may not be so obvious.

Speaking of biological applications, are you feeling well buffered today?

Life's chemistry involves a myriad of acids and bases, mostly weak but with an occasional strong thrown in. CO_2 is a major acid player, with net release by animals but net consumption by plants. Other acids are also metabolic products. While these represent net outputs, individual biochemical reactions may be acidic or basic. All of these things are going on among many biological components which are themselves acids and bases. Proteins are widely abundant and these have weak acid and weak base components within them. Enzymes are likewise, and their catalytic mechanisms often require an H^+ or OH^- being at the right place at the right time. Much of biology and much of your health are critically dependent on being at the right pH. Thus, while some biochemical reactions are producing or using some acid or base, the system must be buffered against a change in pH.

The wide abundance of proteins and their weak acid/base components provide a lot of buffering capacity throughout your body, but other components also contribute. Intracellular fluids are buffered near neutral by the $H_2PO_4^-/HPO_4^{2-}$ conjugate pair (pK_a 7.20). The buffering of blood is primarily by proteins but assisted by the CO_2/HCO_3^- conjugate pair. Blood is an interesting example, since one of its jobs is to transport CO_2/HCO_3^- for exhalation. Blood pH is under very tight regulation and it typically runs 7.40 ± 0.05 in humans. This is somewhat borderline for much buffer assistance by CO_2/HCO_3^- (pK_a 6.35), but it does help. The buffer capacity can be breached by some physical activities or medical conditions, in which case small departures of blood pH from 7.40 can cause serious harm. Acidosis is the condition of blood pH less than 7.35, while alkalosis involves a pH greater than 7.45, either of which can be a problem. Breathing too much CO_2 or not exhaling it fast enough can quickly lead to acidosis. Exhaling CO_2 too fast can lead to alkalosis. As always, you must be in balance. Excessive deviations from pH 7.40 are life threatening: blood pH less than 7.0 or greater than 7.7 is fatal in hours or even minutes.

0.017 mol KOH is added. This reacts with 0.017 mol of the original $C_5H_5NH^+$ to produce 0.017 mol of additional C_5H_5N .

Amount reacted/formed due to the KOH:	+0.017 mol C_5H_5N	-0.017 mol $C_5H_5NH^+$
The solution now contains:	0.213 mol C_5H_5N	0.097 mol $C_5H_5NH^+$

$$pH = pK_a + \log \frac{\text{base}}{\text{acid}} = 5.23 + \log \frac{0.213}{0.097} = 5.23 + \log(2.2) = 5.23 + 0.34 = 5.57$$

The pH rises to 5.57 from the starting buffer's pH of 5.47. This ends Example 4.

Your turn.

Example 5. A buffer solution is prepared from 0.0468 mol sodium sulfite and 0.0561 mol sodium bisulfite in 400. mL solution volume.

- What is the pH of the original buffer solution?
- What is the pH of the solution after adding 0.0053 mol HCl?
- What is the pH of the solution after adding 0.0071 mol NaOH to a separate solution of the original buffer (from Part A)?

► Part A

The buffer involves SO_3^{2-} and HSO_3^- . You'll be using HH and you'll need a pK_a . The conjugate pair is part of the polyprotic series for SO_2 so you need to determine if you want pK_{a1} or pK_{a2} of that series. You can spell out a conjugate line diagram in the space below to help decide that. Just be sure to get the right K .

$$pK_a = -\log K_a = -\log(\text{_____}) = \text{_____}$$

Put that into HH along with the conjugate ratio; the ratio comes directly from the given moles.

$$pH = pK_a + \log \frac{\text{base}}{\text{acid}} = \text{_____} + \log \frac{\text{_____}}{\text{_____}} = \text{_____}$$

That's the pH for your starting buffer.

► Part B

The original buffer starts with:	0.0468 mol SO_3^{2-}	0.0561 mol HSO_3^-
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0.0053 mol HCl is added. This reacts with 0.0053 mol of the original SO_3^{2-} to produce 0.0053 mol of additional HSO_3^- .

Amount reacted/formed due to the HCl:	-0.0053 mol SO_3^{2-}	+0.0053 mol HSO_3^-
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The solution now contains:	_____ mol SO_3^{2-}	_____ mol HSO_3^-
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$$pH = pK_a + \log \frac{\text{base}}{\text{acid}} = \text{_____} + \log \frac{\text{_____}}{\text{_____}} = \text{_____}$$

Your answer is 7.00.

► Part C

The original buffer starts with:	0.0468 mol SO_3^{2-}	0.0561 mol HSO_3^-
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Amount reacted/formed due to the NaOH:	_____ mol SO_3^{2-}	_____ mol HSO_3^-
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The solution now contains:	_____ mol SO_3^{2-}	_____ mol HSO_3^-
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$$pH = pK_a + \log \frac{\text{base}}{\text{acid}} = \text{_____} + \log \frac{\text{_____}}{\text{_____}} = \text{_____}$$

Your answer is 7.21. Done.

The Examples here illustrate the calculations involved for buffers but they also reinforce the underlying notion of how the buffer operates. Again, a buffer buffers by having one of its conjugate partners react with an added acid or base. This changes the conjugate ratio and that changes the pH. Although the pH does change, the change is much smaller relative to what would happen if the solution was not buffered.

Problems

- True or false.
 - A higher concentration of buffer components gives a better buffer capacity.
 - The $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ buffer is common in living systems.
 - For a buffer solution, when the conjugate ratio is one, then $\text{pH} = \text{p}K_a$.
 - Increasing the ratio of the conjugate pair (base/acid) will decrease the pH of a buffer solution.
 - The conjugate pair, NH_3 and NH_4^+ , is suitable for use as a buffer at pH 4.50.
- A solution contains 0.014 mol HF and 0.0063 mol KF in 700.0 mL volume. What is the pH of the solution?
- A solution contains 0.0406 mol methylamine (CH_3NH_2) and 0.0307 mol methylammonium chloride ($\text{CH}_3\text{NH}_3\text{Cl}$) in a solution volume of 1.40 L. What is the pH?
- A solution is prepared from 1.24 g potassium carbonate and 2.69 g potassium bicarbonate in a solution volume of 2.10 L. What is the pH of the buffer?
- You need to make a buffer solution of pH 5.00. Consider the following acids along with their corresponding conjugate bases. Which is best suitable for this pH?
 HIO_3 HNO_2 HClO_2 HClO $\text{C}_6\text{H}_5\text{CO}_2\text{H}$
- A buffer solution is prepared from 0.0240 mol $\text{CH}_3\text{CO}_2\text{H}$ and 0.0336 mol NaCH_3CO_2 in 1.00 L total volume.
 - What is the pH of the original solution?
 - What is the pH after adding 1.6 mmol HNO_3 ?
 - What is the pH after adding 3.3 mmol NaOH to the original buffer?
- A buffer solution is prepared from 0.00424 mol NaH_2PO_4 and 0.00198 mol Na_2HPO_4 in a total volume of 300. mL.
 - What is the pH of the original solution?
 - What is the pH after adding 6.60 mL of 0.143 M HBr ?
 - What is the pH after adding 22.0 mL of 0.0533 M KOH to the original buffer?