# Handout on Buffer Solutions

1) Introduction

To understand buffer solutions, you need to understand a number of concepts and then tie these together into a coherent whole. None of the concepts are particularly difficult, but it will likely take some time for you to put it all together.

This handout starts with a qualitative discussion of the reactions occurring in a buffer solution, and then performs some explicit calculations relating to these systems.

If you have suggestions for how to improve this write-up, please send me email at yaron@chem.cmu.edu.

2) Reactions occurring in a solution containing an acid (HA) and its conjugate base (A$^-$).
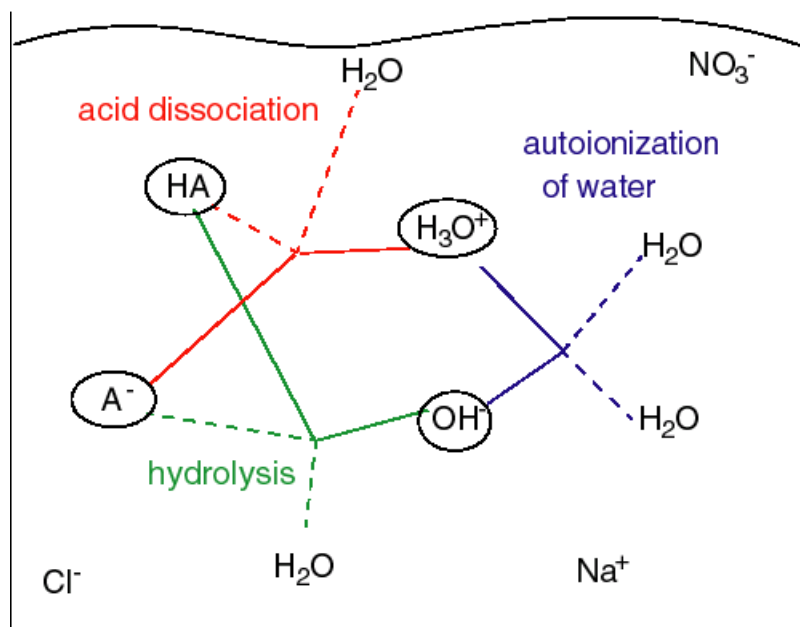
Auto ionization of water
$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$K_w = [H_3O^+][OH^-]$$

Acid Dissociation
$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
$$K_a = [H_3O^+][A^-]/[HA]$$

Hydrolysis
$$A^- + H_2O \rightleftharpoons HA + OH^-$$
$$K_b = [OH^-][HA]/[A^-]$$

Since $K_w = K_a K_b$, there are really only two 'independant' equilibrium expressions.

In making a buffer, you mix an acid (HA) with its conjugate base (NaA). The Na$^+$ floats off into solution and acts as a spectator ion. The interesting species in the solution are then HA, A$^-$, H$_3$O$^+$, and OH$^-$. There is also plenty of H$_2$O to go around. These species are all willing to exchange protons with one another. The various proton exchange reactions are:
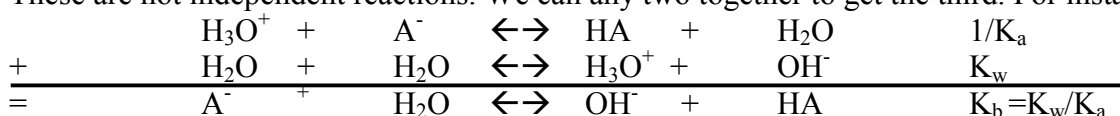
Auto-ionization of water:

$\qquad$ H$_2$O $\quad$ + $\quad$ H$_2$O $\qquad \longleftrightarrow \quad$ H$_3$O$^+$ + $\qquad$ OH$^-$ $\qquad\qquad$ K_w
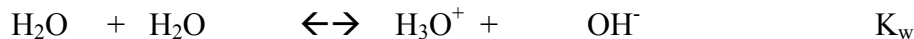
Dissociation of a weak acid:

$\qquad$ HA $\quad$ + $\quad$ H$_2$O $\qquad \longleftrightarrow \quad$ H$_3$O$^+$ + $\quad$ A$^-$ $\qquad\qquad$ K_a

Hydrolysis:

$\qquad$ A$^-$ $\quad$ $^+$ $\quad$ H$_2$O $\qquad \longleftrightarrow \quad$ OH$^-$ + $\quad$ HA $\qquad\qquad$ K_b

These are not independent reactions. We can any two together to get the third. For instance,

	H_3O^+	+	A^-	$\leftrightarrow$	HA	+	H_2O	$1/K_a$
+	H_2O	+	H_2O	$\leftrightarrow$	H_3O^+	+	OH^-	K_w
=	A^-	+	H_2O	$\leftrightarrow$	OH^-	+	HA	$K_b = K_w/K_a$

So there are really only two independent reactions occurring in the solution. You can work with any two you like. You will usually want to keep the $H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$ reaction, which is equivalent to $pOH + pH = 14$. The real choice is therefore between the weak-acid dissociation and the hydrolysis reactions.

Weak-acid dissociation:

H_2O	+	H_2O	$\leftrightarrow$	H_3O^+	+	OH^-	K_w
HA	+	H_2O	$\leftrightarrow$	H_3O^+	+	A^-	K_a

Hydrolysis:

H_2O	+	H_2O	$\leftrightarrow$	H_3O^+	+	OH^-	K_w
A^-	+	H_2O	$\leftrightarrow$	OH^-	+	HA	K_b
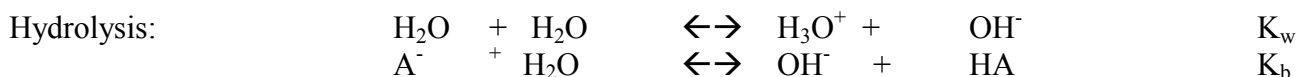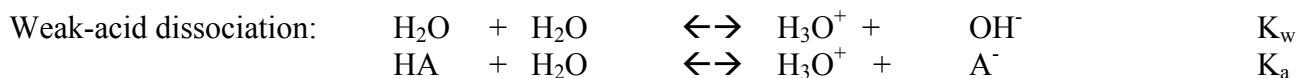
Your choice here is based on your initial conditions for the equilibrium calculation. When it is more convenient to think in term of H_3O^+, choose the weak-acid dissociation reaction. When it is more convenient to think in terms of OH^-, choose the hydrolysis reaction. For instance, when we add acid to a buffer, we are adding H_3O^+, so it is more convenient to use the weak-acid dissociation reaction. When we add base to a buffer, we are adding OH^-, so it is more convenient to use the hydrolysis reaction. We'll come back to this later when we do explicit calculations.
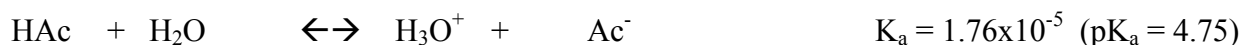
3) Magnitudes of K_a and K_b.

For weak acids, K_a is much less than 1. This means the reaction:

$$HA + H_2O \leftrightarrow H_3O^+ + A^- \qquad K_a \ll 1$$

Lies far to the left ($\leftarrow$). Another way to phrase this is that HA does not like to give its proton to water.

We will use acetic acid (vinegar) as our example,

$$HAc + H_2O \leftrightarrow H_3O^+ + Ac^- \qquad K_a = 1.76 \times 10^{-5} \; (pK_a = 4.75)$$

The hydrolysis reaction is:

$$Ac^- + H_2O \leftrightarrow OH^- + HAc \qquad K_b = K_w/K_a = 5.68 \times 10^{-10}.$$

Note that both K_a and K_b are much less than 1. This may seem a bit odd, but it is true for all useful weak acids. For K_b to be greater than 1, we would need K_a to be less than 10^{-14}, which is an incredibly small K_a. With that small of a K_a, the "acid" basically never gives up its proton and so we probably wouldn't even call it an acid.

So, for weak acids, both the acid-dissociation reaction and the hydrolysis reaction have $K \ll 1$.
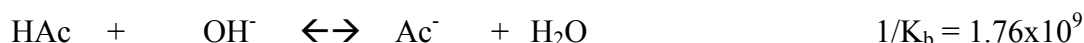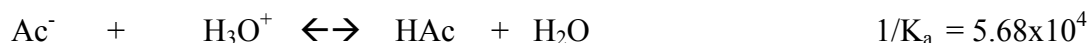
4) How buffers work

Many chemical systems are sensitive to pH. For instance, many proteins will function only when the pH is very near that of its native biological environment. Also, many chemical reactions require a specific pH to occur properly. When you need a specific pH, you can construct it by preparing a buffer solution. The proteins and other chemicals you put in your solution may exchange protons with their surroundings (i.e. they may effectively add acid or base to the surroundings). But the buffer solution will absorb any acid or base given off by the proteins etc., and the pH will remain fixed.

A buffer solution contains a roughly equal mixture of A^- and HA. To understand why this is a buffer, you need to understand two things.

A^- consumes added acid, and HA consumes added base.

If we reverse the reactions in the previous section, we get

$$Ac^- \quad + \quad H_3O^+ \quad \longleftrightarrow \quad HAc \quad + \quad H_2O \qquad\qquad 1/K_a = 5.68 \times 10^4$$

$$HAc \quad + \quad OH^- \quad \longleftrightarrow \quad Ac^- \quad + \quad H_2O \qquad\qquad 1/K_b = 1.76 \times 10^9$$

(Remember that if you reverse a reaction with equilibrium constant $K_{forward}$, the equilibrium constant for the reverse reaction is given by $K_{reverse}=1/K_{forward}$.) Note that for both of these reactions, K>>1. A buffer solution contains a mixture of Ac^- and HAc. If you add acid (H_3O^+) to this solution, it is consumed by Ac^-, according to the first reaction. Since K >>1, this reaction goes nearly to completion and the acid is consumed. If you add base (OH^-), it is consumed by HAc. Since K for this reaction is also >>1, the reaction goes nearly to completion, and the base is completely consumed.

The pH is not very sensitive to the ratio of A^-/HA

The Henderson-Hasselbalch equation relates the pH to the pK_a and the ratio of $[A^-]/[HA]$. It can be derived as follows:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad \Rightarrow \qquad \log(K_a) = \log\left(\frac{[H_3O^+][A^-]}{[HA]}\right) = \log([H_3O^+]) + \log\left(\frac{[A^-]}{[HA]}\right)$$

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

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

The pH is not a very sensitive function of the ratio of $[A^-]/[HA]$. The following table is for acetic acid, which has a $pK_a=4.75$.

[Ac⁻]/[HAc]	PH
0.1	3.75
0.5	4.45
1	4.75
2	5.05
10	5.75

Note that the log (1/10)=-1 and log(10)=1, so as [A⁻]/[HA] changes from 0.1 to 10, the pH goes from one unit below pK_a (3.75) to one unit above pK_a (5.75).

Putting it all together

Now, we can combine the above two points to see how buffers do their thing. We will start with a solution with [Ac⁻]=[HAc]=1.0M. Since log(1)=0, the Henderson-Hasselbalch equation tells us that pH=pKa = 4.75.

If we add acid to this solution, it will be absorbed by the reaction,

$$Ac^- \quad + \quad H_3O^+ \quad \longleftrightarrow \quad HAc \quad + \quad H_2O \qquad\qquad 1/K_a = 5.68 \times 10^4$$
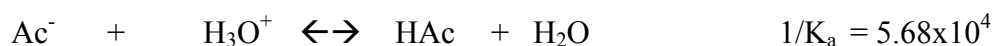
This reaction will go almost all the way to completion. So if we add acid, it will be almost totally consumed by Ac⁻. This will convert Ac⁻ into HAc and therefore change the ratio of [Ac⁻]/[HAc]. But as long we don't change the ratio by too much, the pH will remain close to pK_a.

If we add base to this solution, it will be absorbed by the reaction,

$$HAc \quad + \quad OH^- \quad \longleftrightarrow \quad Ac^- \quad + \quad H_2O \qquad\qquad 1/K_b = 1.76 \times 10^9$$

This reaction will go almost all the way to completion, so almost all of the base will be absorbed. This time, we convert HAc into Ac⁻ and therefore change the ratio of [Ac⁻]/[HAc]. Once again, as long as we don't change the ratio by too much, the pH will remain close to pK_a.

5) *Designing a buffer (qualitative considerations)*

If you add base to a buffer solution, HA absorbs the OH⁻. If you add an acid, A⁻ absorbs the H_3O^+. So if you want your buffer to be able to handle both, you should have enough HA around to absorb all the base that might be added to the buffer and enough A⁻ around to absorb all of the acid. Ideally, you would have [A⁻]=[HA], but if you have 3 or 4 times more of one than the other, that is still a useful buffer.

According to the Henderson-Hasselbalch equation, when [A⁻]=[HA], the pH is equal to the pK_a. So in creating a buffer with a desired pH, you should pick an HA/A⁻ pair that has a pK_a near your target pH. For instance, acetic acid has a pKa = 4.75. If you wanted to build a buffer with a pH of 5, acetic acid/ sodium acetate would be a decent choice since the ratio [Ac⁻]/[HAc]= 1.8 would give a pH of 5. In a solution with [Ac⁻]/[HAc]=1.8, you have plenty of both HAc and Ac⁻. If, on the other hand, you wanted to create a buffer with a pH of 3.0, then acetic acid/ sodium acetate would not be a good choice. To get a pH of 3, you would need a ratio of [Ac⁻]/[HAc]= 0.0178. In such a solution, there is very little Ac⁻, so the buffer could not absorb much acid.
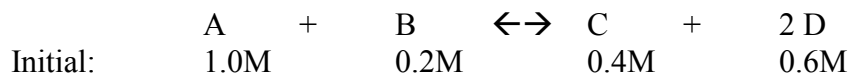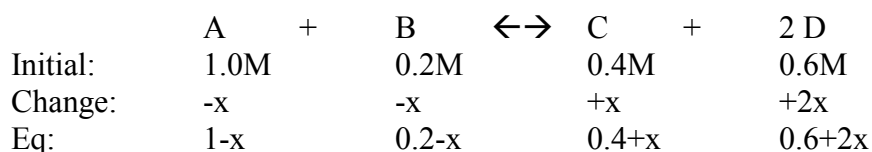
6) *Explicit Calculations*

Making approximations

Consider the reaction:

$$A \quad + \quad B \quad \longleftrightarrow \quad C \quad + \quad 2\,D \qquad K=[C][D]^2/[A][B]$$

Suppose we start with some initial amounts of the reactants and products:

	A	+	B	$\longleftrightarrow$	C	+	2 D
Initial:	1.0M		0.2M		0.4M		0.6M

It is mathematically correct to do the following:

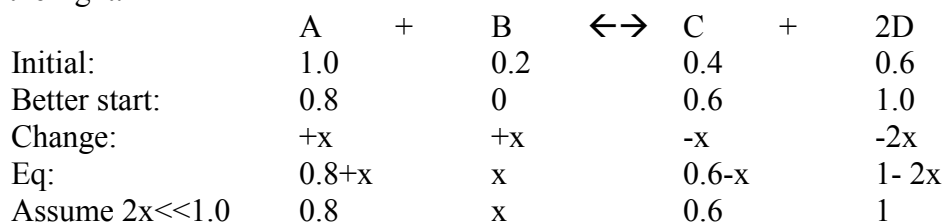|	A	+	B	$\longleftrightarrow$	C	+	2 D
Initial:	1.0M		0.2M		0.4M		0.6M
Change:	-x		-x		+x		+2x
Eq:	1-x		0.2-x		0.4+x		0.6+2x

You can then plug the "Eq:" line into the equilibrium expression,

$$K = \frac{(0.4+x)(0.6+2x)^2}{(1-x)(0.2-x)}$$

and solve for x. The problem is that this will lead to a cubic equation that will take a long time to solve.

If K>>1 or K<<1, then you are better off doing a limiting reagent problem, followed by an equilibrium calculation. For the rest of this handout, we will label the result of the limiting reagent problem as "better start".

If K>>1, then the reaction lies all the way to the right (➜) and we should begin by pushing the reaction all the way to the right.

	A	+	B	$\longleftrightarrow$	C	+	2D
Initial:	1.0		0.2		0.4		0.6
Better start:	0.8		0		0.6		1.0
Change:	+x		+x		-x		-2x
Eq:	0.8+x		x		0.6-x		1- 2x
Assume 2x<<1.0	0.8		x		0.6		1

If K is large enough, the assumption that 2x<<1.0 (or x<<0.5) will hold. We first solve the problem assuming x<<0.5, and then check to make sure the x we obtain is actually small compared to 0.5. To do this, we plug the "assume" line into the equilibrium expression,

$$K = \frac{(1)(0.6)^2}{(0.8)(x)}$$

and solve for x. If x<<0.5, to 5% or better, we are done and we've saved ourselves a lot of work. If K = 100, then the above expression would give 4.5×10^{-3}. To test x<<0.5, we calculate the ratio $4.5 \times 10^{-3}/0.5 = 9.0 \times 10^{-3} = 0.9\%$. This is within our 5% tolerance and the approximation is therefore valid.

If K<<1, then the reaction lies all the way to the left (⬅) and we should begin by pushing the reaction all the way to the left.

	A	+	B	⬅➜	C	+	2D
Initial:	1.0		0.2		0.4		0.6
Better start:	1.3		0.5		0.1		0
Change:	-x		-x		+x		+2x
Eq:	1.3-x		0.5-x		0.1+x		2x
Assume x<<0.1	1.3		0.5		0.1		2x

If K is small enough, the assumption that x<<0.1 will hold. To see, we plug the "assume" line into the equilibrium expression,

$$K = \frac{(0.1)(2x)^2}{(1.3)(0.5)}$$

We now solve this for x, and check to see if x<<0.1. If this is true to 5% of better, we are done and we've saved ourselves a lot of work.

pH of a buffer solution

Suppose we build a buffer by mixing 50ml of 1M NaAc with 50ml of 1M HAc. What is the final pH?

First we do the dilution, to figure out the concentrations of the ingredients after they are mixed:

$\qquad$ [NaAc] = 1M (50ml/100ml) = 0.5M $\qquad\qquad$ [HAc] = 1M (50ml/100ml) = 0.5M

Now, we need to choose a reaction (acid dissociation or hydrolysis). HAc and Ac⁻ appear in both reactions, so either choice is fine. Just for kicks, we'll do it both ways. We will start with the acid dissociation reaction:

	HAc	+	H_2O	⬅➜	H_3O^+	+	Ac⁻		$K_a = 1.76 \times 10^{-5}$
Initial:	0.5				0		0.5		

In order to make approximations, we should start with a limiting reagent problem. Since K<<1, we would push the reaction all the way to the left (⬅). Since the reaction is already all the way to the left, the intial line shown above is a good starting point.

|	HAc	+	H_2O	⬅➜	H_3O^+	+	Ac⁻		$K_a = 1.76 \times 10^{-5}$
Initial:	0.5				0		0.5		
Good start:	0.5				0		0.5		
Change:	-x				+x		+x		
Eq:	0.5-x				x		0.5+x		
Assume x<<0.5	0.5				x		0.5		

If we plug the assume line into the equilibrium expression and solve for x, we get x=[H_3O^+]=1.76x10⁻⁵. This result for x is << 0.5 so our assumption is fine. The pH is therefore 4.75. The fact that this approximation worked is no surprise. If you are designing a buffer, you want to use fairly large amounts of NaAc and HAc. The variable x in the "eq:" line is the amount of [H_3O^+] at equilibrium, which for typical pH's will be small compared to the amounts of NaAc and HAc you use to build a buffer.

Aside: You may be wondering how this all relates to the Henderson-Hasselbalch equation. (To save space, I will call this the H-H equation.) For instance, you may ask your self:

> "Self, why don't I just plug the concentration of NaA and HA into the H-H equation and solve for pH? Why do all this work?"

Although the H-H equation is always valid, the $[A^-]$ and $[HA]$ in the H-H equation are the **equilibrium** concentrations. Once you know $[A^-]$ and $[HA]$ at equilibrium, you can plug them into the H-H equation and get the pH. But when you mix a certain amount of NaA and HA together, you are not guaranteed that the equilibrium concentration of $[A^-]$ will be equal to the concentration of NaA you started with. This is because the reaction shown above allows $[A^-]$ to turn into $[HA]$ and vice versa. Only if this reaction does not proceed to a significant extent (i.e. only if x is small), will the equilibrium concentrations of $[A^-]$ equal the amount you started with. Similarly, you are not guaranteed that the equilibrium concentration of $[HA]$ will be the amount you started with. As seen above, x will typically be small and so the equilibrium $[HA]$ and $[A^-]$ in the H-H equation will typically be the same as the amounts of HA and NaA you mix together to make the buffer.

As promised, we will now solve the problem using the hydrolysis equation:

	Ac^-	$+$ H_2O	$\longleftrightarrow$	OH^-	$+$	HAc	$K_b = K_w/K_a = 5.68 \times 10^{-10}$.
Initial:	0.5			0		0.5	
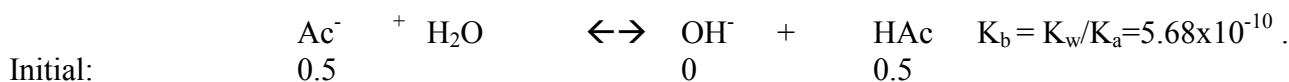
Since $K \ll 1$, we should begin by pushing the reaction all the way to the left ($\longleftarrow$). It is already all the way to the left, so the above initial condition above is a good starting point:

Good start:	0.5	0	0.5
Change:	-x	+x	+x
Eq:	0.5-x	x	0.5+x
Assume x<<0.5	0.5	x	0.5

If we plug the assume line into the equilibrium expression and solve for x, we get $x=5.68 \times 10^{-10}$. This value of x is $\ll 0.5$, so the assumption is fine. This gives $[OH^-] = 5.68 \times 10^{-10}$, or pOH= 9.25. The pH is then 4.75. This is the same as we obtained above using the acid dissociation equation.

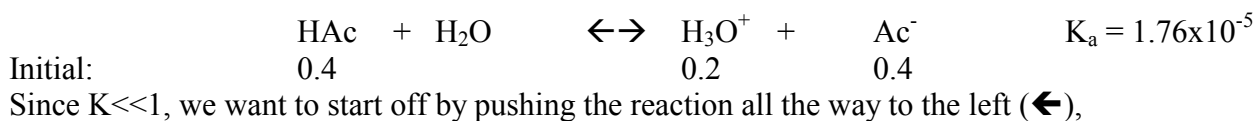**Adding an acid to a buffer**

Above, we made 100ml of a buffer with $[HAc]=[Ac^-] = 0.5M$. Suppose we add 25 ml of 1M HCl to this solution.

First, we need to take the dilution into account:

$$[HAc]=[Ac^-] = 0.5M \ (100/125) = 0.4M \qquad\qquad [HCl] = 1 \ (25/125)=0.2M$$

The above are the initial conditions for the problem. HCl is a strong acid and so it produces 0.2M $[H_3O^+]$. Since the initial conditions involve HA, A^- and H_3O^+, and not OH^-, we will choose the reaction that involves these species, the acid dissociation reaction,

	HAc	+	H_2O	←→	H_3O^+	+	Ac^-	$K_a = 1.76 \times 10^{-5}$
Initial:	0.4				0.2		0.4	

Since K<<1, we want to start off by pushing the reaction all the way to the left (←),

Good start:	0.6		0		0.2
Change:	-x		+x		+x
Eq:	0.6-x		x		0.2+x
Assume x<<0.2:	0.6		x		0.2

If we plug the assume line into the equilibrium expression and solve for x, we get $x=5.28 \times 10^{-5}$. This value for x is <<0.2, so our assumption is valid. $[H_3O^+]=5.28 \times 10^{-5}$ means the pH = 4.27.

Aside: The above result can be understood within the context of the H-H equation. After taking dilution into account, we added 0.2M of acid to a buffer containing $[HAc]=[Ac^-] = 0.4$M. The Ac^- absorbed the 0.2M of acid and got converted to HAc. This changed the concentrations to $[HAc]=0.6$M, $[Ac^-] = 0.2$M. If you plug this into the H-H equation, you would find a pH of 4.27. Note, however, that this "shortcut" approach implicitly assumes that x in the above solution method is <<0.2. Such assumptions will be valid if we haven't broken the buffer, i.e. if there are still substantial amounts of both HA and A^- present in the solution.
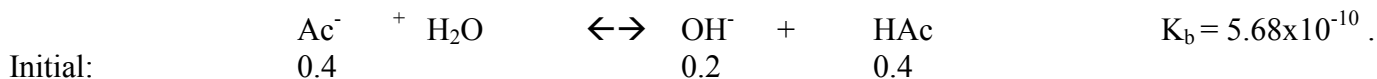
Adding a base to a buffer

This time, we will take our 100ml of buffer with $[HAc]=[Ac^-] = 0.5$M, and add 25 ml of 1M NaOH.

The dilution gives us:
    $[HAc]=[Ac^-] = 0.5$M (100/125) = 0.4M $[NaOH] = 1 (25/125)=0.2$M

NaOH is a strong base and so it produces 0.2M $[OH^-]$. Since the initial conditions involve HA, A^- and OH^-, we will choose the reaction that involves these species, the hydrolysis reaction,

	Ac^-	+	H_2O	←→	OH^-	+	HAc	$K_b = 5.68 \times 10^{-10}$.
Initial:	0.4				0.2		0.4	

Since K<<1, we want to start off by pushing the reaction all the way to the left (←),

Good start:	0.6		0		0.2
Change:	-x		+x		+x
Eq:	0.6-x		x		0.2+x
Assume x<<0.2:	0.6		x		0.2

If we plug the assume line into the equilibrium expression and solve for x, we get $x=1.70 \times 10^{-9}$. This value for x is <<0.2, so our assumption was valid. $[OH^-]=1.70 \times 10^{-9}$ means the pOH = 8.76. The pH is then 5.23.

Aside: When the base was added, the HAc absorbed the 0.2M of OH^- and got converted to Ac^-. This changed the concentrations to $[HAc]=0.2$M, $[Ac^-] = 0.6$M. If you plug this into the H-H equation, you would find a pH of 5.23. Note, however, that this "shortcut" approach implicitly assumes that x in the above solution method is <<0.2. Such assumptions will be valid if we haven't broken the buffer, i.e. if there are still substantial amounts of both HA and A^- present in the solution.