Lecture 12 Solving buffer and neutralization problems

Deriving the Buffer Equation

You have had it hammered into your head that there are three simplified equations that can be used to calculate proton or hydroxide concentration in acid-base equilibria:
- the strong acid and base equation
- the weak acid and base equation
- the buffer equation

You have seen the strong and weak cases, now it is time to derive the buffer equation.

But first, what is a buffer? Very simply, a buffer is the mixture of

      a weak acid and conjugate base   or   a weak base and conjugate acid

Recall that the word **conjugate** means that the pair differs by a single proton. For example:

	acid	base	Buffer?
Example 1	Acetic acid $HC_2H_3O_2$	Sodium acetate $NaC_2H_3O_2$	Yes, weak acid and base differ by one proton
Example 2	Ammonium ion NH_4^+	ammonia NH_3	Yes, weak acid and base differ by one proton
Example 3	Hydrochloric acid HCl	Chloride Cl^-	No, strong acids and their cases can't be buffers
Example 4	Carbonic acid H_2CO_3	Carbonate ion $CO_3^=$	No, the acid and base differ by two protons

Derivation of the buffer equation using the RICE expression

We start with the general case of a acid equilibrium

$$HA \quad \rightleftharpoons \quad H^+ \quad + \quad A^- \quad \text{with } K_a = [H^+] [A^-]/[HA]$$
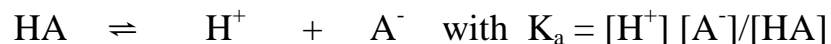
and then construct a RICE expression with the following steps:

1. Start with C_a for the amount weak acid HA and C_b for the amount of the conjugate weak base
2. We assume 0M is the amount of strong acid, H^+, to start
3. Since Q< K the reaction shifts right so we add signs to the change array accordingly
4. Assume that x is the concentration of protons that forms
5. Doing the math, at equilibrium the concentrations are C_a-x, x and C_b+x respectively

Reaction: HA $\rightleftharpoons$ H+   +   A-

Initial	C_a	0	C_b
Change	-x	+x	+x
Equilibrium	C_a -x	x	C_b + x

we get:

Substituting these amounts into the equilibrium expression

$$K_a = [x] [C_b + x]/[C_a -x]$$

But now we make an important approximation. As mentioned above, by definition, weak acids and their conjugate bases don't dissociate very much—typical values are maybe one out of a thousand or out of ten thousand. This means that x which is $[H^+]$ is very small relative to the starting concentration. And in steps:

6. Let x= $[H^+]$ and then $K_a = [H^+] [C_b + [H^+]]/[C_a -[H^+]]$
7. Approximate that $[H^+]$ is very small because this is a weak acid doesn't dissociate so $(C_a -[H^+]) \sim Ca$
8. Similarly $(C_b -[H^+]) \sim Cb$
9. Now simplified, we can rearrange the expression to obtain our famous result for the buffer equation:

$$H^+ = Ka (C_a/C_b)$$

Just as with the weak acid case, what we have done is turn a quadratic equation into a simple BUFFER problem we can do in our head by using approximation that weak acids and bases don't dissociate very much (which is true because that is the definition of a weak acid or base!!)

Wow, anyone can derive the buffer equation!! With it, let's solve a simple buffer calculation.

Example: What is pH of a 0.1 **M** acetic acid and 0.1 M sodium acetate solution if $K_a = 1 \times 10^{-3}$.

Note, we have   acetic acid which is a weak acid
                   acetate which is a conjugate base → this means we have a buffer solution and can work the buffer equation

So use buffer equation
    $H^+ = K_a\, C_a/C_b = 1 \times 10^{-5}\ (0.1/0.1) = 1 \times 10^{-5}$ and   pH=5

Note that $H^+ = K_a$ for a buffer

Also note that for buffer equation to work, same conditions for C_a, C_b and K_a apply.
    1. C_a and C_b must be large
    2. K_a in 10^{-4} to 10^{-10} range

Neutralization.

We move on to more sophisticated acid base equilibrium problems that require an additional step to find equilibrium concentrations. Note that to this point the only chemical equilibria associated with our acid base problems (assuming K_w was negligible) were the simple weak acid or weak base cases.

$$HA \quad \rightleftharpoons \quad H^+ \quad + \quad A^-$$

In which the the K value is so small that basically nothing is happening in solution.

But what happens if we were to add strong acid or base to a solution containing various other acids and bases. Now there is going to be a reaction that essentially goes to completion because the K value for strong acids and bases is essentially infinity in this course. This reaction is referred to as a
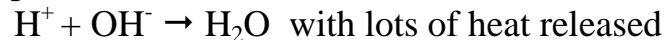
neutralization reaction

and must be accounted for before finding equilibrium concentrations of the remaining materials.

For example, what happens when I put an H^+ or OH^- in solution? Each of them look to react.
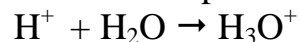
H^+ looks for most basic thing in solution
    when hydroxide is present:
        $H^+ + OH^- \rightarrow H_2O$ with lots of heat released
    and if no OH^- then the protons look for weak base
        $H^+ + A^- \rightarrow HA$ a little heat
    and if no A^- is present then the proton attaches to H_2O and makes a hydronium ion, H_3O^+
        $H^+ + H_2O \rightarrow H_3O^+$

Similarly

OH^- looks for most acidic thing in solution
    when protons are present:
        $H^+ + OH^- \rightarrow H_2O$ with lots of heat released
    and if no H^+ then the hydroxide look for weak acid
        $HA + OH^- \rightarrow A^- + H_2O$ a little heat
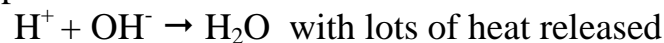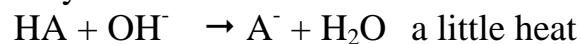
Let's watch cartoon pictures of neutralization in action as protons are added to a beaker containing weak base. Beginning with four weak bases, A⁻, we will add a proton at a time, watch a neutralization reaction happen, and then determine what the resulting equilibrium solution contains:

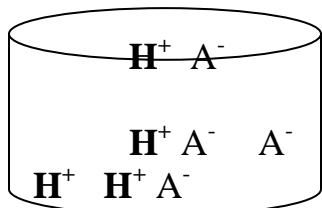## Case 1: no protons added to a beaker of four A⁻

A⁻

A⁻   A⁻
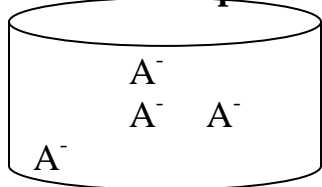
A⁻   no H⁺ added, so only A⁻ in solution, this is the weak base case, and we use $OH^- = (K_bC_b)^{1/2}$

## Case 2: add one proton to a beaker with four A⁻ so neutralization must occur

A⁻

H⁺ A⁻   A⁻
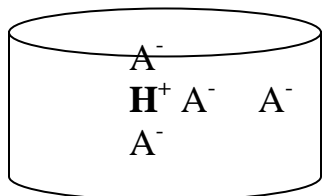
A⁻   one H⁺ added, so now HA and A⁻ are present. This is a buffer and we use $H^+ = K_a\, C_a/C_b$

Case 3: add four protons to a beaker with four A⁻ so neutralization must occur

H⁺ A⁻

H⁺ A⁻   A⁻

H⁺   **H⁺** A⁻   four H⁺ added, so now H+ and A⁻ are equal and total neutralization occurs. This is called the equivalence point and with only HA left, we solve it with the weak acid equation. $H^+ = (K_aC_a)^{1/2}$

Case 4: add five protons to a beaker with four A⁻ so neutralization must occur

H⁺ A⁻

H⁺ A⁻ **H⁺** A⁻
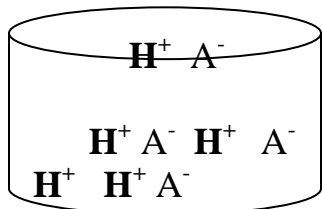
H⁺   **H⁺** A⁻   five H⁺ added, so now H+ is in excess after neutralization occurs. We assume that the H+ which is a strong acid is much more important than the weak acid and ignore the weak acid. So we perform the calculation of H+ concentration using the strong acid equation:

So how important is it to be able to perform a neutralization? Incredibly important.

Note that I will give you a siz step procedure for performing acid base reactions. Right in the middle of those six steps is the need to look for and perform a neutralization reaction. If you can learn to perform neutralization reactions, acid base chemistry becomes pretty simple. It will allow you to perform sophisticated problems involving buffer neutralization and all kinds of titrations. But if you don't learn to do the neutralization step, every acid base problem, no matter how easy, will be a challenge.

The Five Neutralization Reactions. And as a parting treat, here are the five possible neutralization reactions if you use the symbols I taught you for acid base chemistry:

Strong acid neutralizing strong base

$$H^+ \;+\; OH^- \rightleftharpoons H_2O$$

Strong acid neutralizing weak neutral base

$$H^+ \;+\; B \;\rightleftharpoons BH^+$$

Strong acid neutralizing basic salt of weak acid

$$H^+ \;+\; A^- \rightleftharpoons HA$$

Strong base neutralizing weak neutral acid

$$OH^- \;+\; HA \rightleftharpoons A^- \qquad \text{(ignore the water left over)}$$

Strong acid neutralizing acid salt of weak base

$$OH^- \;+\; BH^+ \rightleftharpoons B \qquad \text{(ignore the water left over)}$$

Note that it isn't hard to learn these. Just remember three things:

- There is always a strong acid or base in the problem
- It is always paired with a conjugate acid/base pair in the reaction
- Always make sure your mass and charge balance if you are not sure what goes where.