Buffers & Henderson-Hasselbalch

<u>The three things you need to know about buffers are:</u>

1) A **buffer** consists of a weak acid with its conjugate base (or a weak base with its conjugate acid). Strong acids and bases do not form buffers.

 Examples: CH_3CO_2H / CH_3CO_2Na could be a buffer system
  NH_3 / NH_4Cl could be a buffer system
  HCl / $NaCl$ would not be a buffer system (strong acid)
  CH_3CO_2H / NH_3 would not be a buffer system (not conjugates)

2) Although you can use the "long" method using equilibrium concentrations, etc., the **Henderson-Hasselbalch equation** will almost always be much easier to utilize.

 The Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[\text{Conj. base}]}{[\text{acid}]}$$

 where pH = pH of system
  pK_a = -log K_a = - log (acid dissociation constant for weak acid in buffer)
  [Conj. base] = concentration *or* moles of base in solution
  [acid] = concentration *or* moles of acid in solution

 For the Henderson-Hasselbalch equation to be effective, the ratio of [conj. base]/[acid] must be no larger than 10 and no less than 0.1.

 Example: What is the pH of a buffer with $[CH_3CO_2H]$ = 0.700 M and $[CH_3CO_2^-]$ = 0.600 M? K_a for acetic acid = $1.8*10^{-5}$

 pK_a = -log K_a = - log $(1.8*10^{-5})$ = **4.74**
 Now use the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[\text{Conj. base}]}{[\text{acid}]} = 4.74 + \log\frac{[0.600]}{[0.700]} = \textbf{4.67}$$

3) When selecting an appropriate buffer, choose a pK_a value which is close to the desired pH of your buffer. This maintains the appropriate Henderson-Hasselbalch ratio and makes your calculations must easier.

Example: If a buffer with a pH of 4.5 was desired, acetic acid and sodium acetate would be a good system to use. As observed in #2, pK_a for acetic acid is 4.74 - this is close to pH = 4.5, so this would be a good system.

Example: If a buffer with a pH of 4.5 was desired, potassium hydrogen phosphate and potassium phosphate would ***not*** be a good system to use. The weak acid here is potassium hydrogen phosphate; the K_a is $3.6*10^{-13}$, or $pK_a = 12.44$ - too basic for our desired acidic pH of 4.5.

Buffer Calculations upon Addition of Strong Acids or Bases

The Henderson-Hasselbalch equation can give you more than just the pH of solutions; it can also tell you what the pH of the solution will be upon addition of strong acid or strong base.

Example: As we saw earlier, the pH of a buffer with $[CH_3CO_2H] = 0.700$ M and $[CH_3CO_2^{-1}] = 0.600$ M is 4.67 ($pK_a = 4.74$) What will the pH be upon the addition of 10.00 mL of 1.00 M HCl? Assume 1.00 L of buffer before addition of HCl.

Remember that the Henderson-Hasselbalch equation works equally well for concentrations as well as moles. In calculations involving the addition of strong acids or bases, it is better to use **moles**.

moles of HCl = 0.01000 L * 1.00 M = 0.0100 mol HCl
mol weak acid = 1.00 L * 0.700 M = 0.700 mol acetic acid
mol conjugate base = 1.00 L * 0.600 M = 0.600 mol acetate ion

Every mole of strong acid will eliminate one mol of the conjugate base, but it will also create one mole of the weak acid:

	$CH_3CO_2^{-1}$	$+ H^+$	->	CH_3CO_2H
initial moles:	0.600	0.0100		0.700
final moles:	0.590	0		0.710

You can then re-calculate the pH using the Henderson-Hasselbalch equation and the new concentrations:

$$pH = pK_a + \log\frac{[\text{Conj. base}]}{[\text{acid}]} = 4.74 + \log\frac{[0.590]}{[0.710]} = \textbf{4.66}$$

Note that the buffer solution become more acidic upon addition of HCl; this makes intuitive sense, since HCl is a strong acid.

For the addition of strong acids, you can re-write the Henderson-Hasselbalch equation:

$$pH = pK_a + \log \frac{\left(mol_{Conj.base} - mol_{strong.acid}\right)}{\left(mol_{weak.acid} + mol_{strong.acid}\right)}$$

Example: Calculate the pH of a 1.00 L buffer with $[CH_3CO_2H] = 0.700$ M and $[CH_3CO_2^{-1}] = 0.600$ M, $pK_a = 4.74$, if 15.00 mL of 2.10 M NaOH is added?
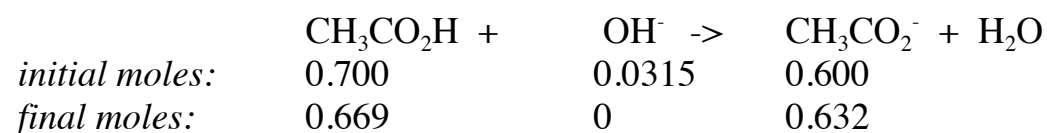
Use moles with the Henderson-Hasselbalch equation as before.

moles of NaOH = 0.01500 L * 2.10 M = 0.0315 mol NaOH
mol weak acid = 1.00 L * 0.700 M = 0.700 mol acetic acid
mol conjugate base = 1.00 L * 0.600 M = 0.600 mol acetate ion

Every mole of strong base will eliminate one mol of the weak acid, but it will also create one mole of the conjugate base:

	CH_3CO_2H +	OH^- ->	$CH_3CO_2^-$ + H_2O
initial moles:	0.700	0.0315	0.600
final moles:	0.669	0	0.632

You can then re-calculate the pH using the Henderson-Hasselbalch equation and the new concentrations:

$$pH = pK_a + \log \frac{[\text{Conj. base}]}{[\text{acid}]} = 4.74 + \log \frac{[0.632]}{[0.669]} = \mathbf{4.72}$$

Note that the buffer solution become more basic upon addition of NaOH; this makes intuitive sense, since sodium hydroxide is a strong base.

For the addition of strong base, you can re-write the Henderson-Hasselbalch equation:

$$pH = pK_a + \log \frac{\left(mol_{Conj.\ base} + mol_{strong\ base}\right)}{\left(mol_{weak\ acid} - mol_{strong\ base}\right)}$$

Buffer Calculations Using Weak Bases & Conj. Acids

The Henderson-Hasselbalch equation can be re-written to accommodate buffers which incorporate a weak base and its conjugate acid. The new expression would be:

$$pOH = pK_b - \log \frac{[\text{base}]}{[\text{Conj. acid}]}$$

The buffer calculations are similar to those above for buffers with weak acids and conjugate bases. $pK_b = -\log K_b$, etc. Remember to switch to pH from pOH if using this version of the Henderson-Hasselbalch equation.