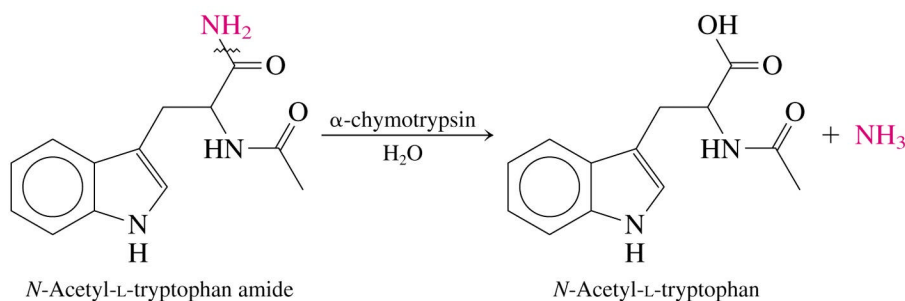


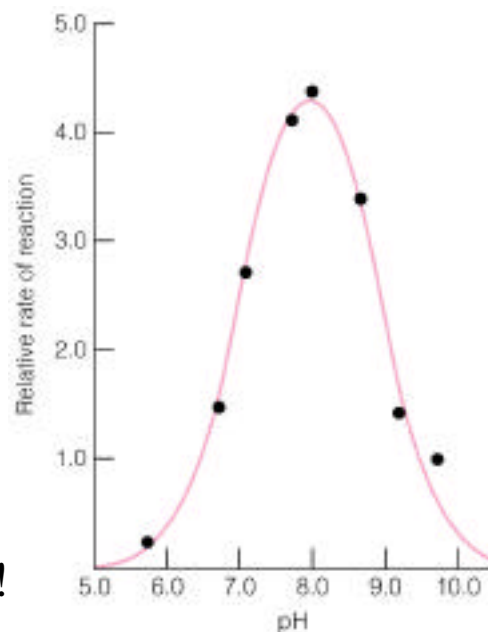
# Principles of Buffers

buffer--a solution that resists pH change---

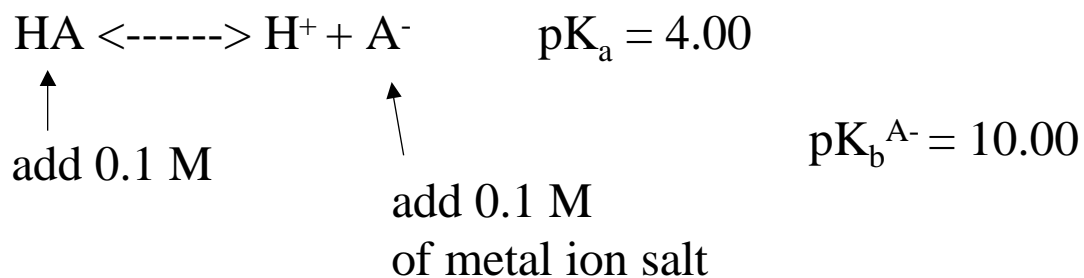
Important for many reactions---e.g., enzymatic methods of analysis, etc.---



ammonia is a base---so pH will increase as reaction proceeds; unless soln is buffered!



If instead of adding weak acid to solution---we add given concentrations of both the acid and its conjugate base---we create a buffer!!



for forward dissociation reaction---we can calculate fraction of dissociation--in absence of A<sup>-</sup> added--

$$x^2 / (F-x) = 10^{-4} ; \quad x = 3.1 \times 10^{-3} \quad (\text{by quadratic or succ. approx.})$$

$$[\text{A}^-] = [\text{H}^+] = 3.1 \times 10^{-3} \text{ M} ; \quad \text{fraction dissociated} = 0.0031/0.1 = 0.031 \text{ or } 3.1\%$$

if soln was made with 0.1 M NaA only -fraction associated =  $3.2 \times 10^{-5}$

so --basic chemical instincts tell you that very little changes when you add the two species together to water--to make the solution 0.1 M with respect the acid and the conjugate anionic base and then wait for equilibrium!!

Key to understanding what the pH of this solution would be---is the **Henderson-Hasselbalch Eqn.**

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

take logarithm of both sides:

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

swap-- $\log K_a$  and  $\log[H^+]$  to opposite sides of eqn:

$$-\log K_a = -\log[H^+] + \log \frac{[HA]}{[A^-]}$$
$$pK_a = pH + \log \frac{[A^-]}{[HA]} \quad \longleftarrow \quad \text{HH-eqn.}$$

If you want to make buffer using weak base (B) and a salt of its conjugate acid (BH<sup>+</sup>)----same basic equation applies:

$$pH = pK_a + \log \frac{[B]}{[BH^+]} \leftarrow pK_a \text{ of this conjugate acid used in equation!}$$

Whether using weak acid or weak base conjugate pairs to create buffer---the pH of the final buffer solution is controlled by ratio of the two species you add to create buffer---

- weak acid/conjugate base salt
- weak base/conjugate acid salt

**back to initial problem---where we have 0.1 M HA, and 0.1 M A<sup>-</sup> and  $pK_a = 4.00$ ;  $pH = 4.00 + \log (0.1 / 0.1) = 4.00$**

Example problem:

Suppose you want to make a pH 5.00 buffer---using acetic acid (HA) and sodium acetate (A<sup>-</sup>)

pK<sub>a</sub> of acetic acid = 4.76;

What ratio of HA and A should be used?

$$5.00 = 4.76 + \log x; \quad \text{where } x = ([A^-]/[HA])$$

$$0.24 = \log x$$

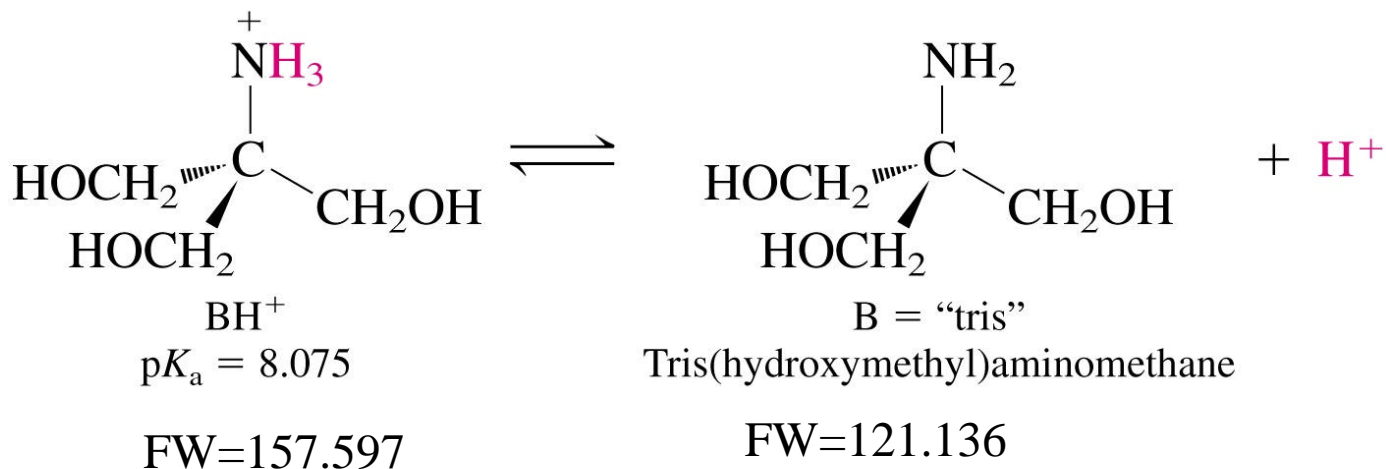
$$10^{0.24} = x = 1.74 = \text{ratio of moles conjugate base to acid in solution}$$

e.g., 0.174 M sodium acetate/0.100 M acetic acid

or 0.100 M sodium acetate/0.0575 M acetic acid

Concentration used of each species will determine “**Buffer Capacity**” and “**ionic strength**” of the buffer solution!

**note:** volumes cancel in log term of HH---pH does not depend on volume-- only ratio of moles!- (not always true!!!)



very popular buffer---can obtain Tris-HCl salt, and Tris in pure forms;  
 what is pH of solution when 12.43 g of Tris is mixed with 4.67 g of  
 Tris-HCl (BH<sup>+</sup>) a diluted to 1.00 liter?

calculate molarity of each species:

$$[\text{B}] = [\text{Tris}] = (12.43 \text{ g/L}) / (121.136 \text{ g/mol}) = 0.1026 \text{ M}$$

$$[\text{BH}^+] = [\text{Tris-H}] = (4.67 \text{ g/L}) / (157.597 \text{ g/mol}) = 0.0296 \text{ M}$$

$$\text{pH} = \text{pK}_a + \log ([\text{B}]/[\text{BH}^+]) = 8.075 + \log (0.1026/0.0296) = 8.61$$

**Secret of buffers**---what happens when strong acid added to previous Tris buffer solution? ---

as you add HCl to solution--the following reaction takes place:

$B + HCl \rightarrow BH^+Cl^-$ ; this decreases conc. of B and increases concentration of  $BH^+$ ; this will change the ratio in the HH eqn!

suppose you add 12 mL of a 1.00 M acid;  $= 0.012 \text{ L} \times 1 \text{ M} = 0.012$  moles

Therefore---this will decrease the moles of B present by 0.012 moles and increase the concentration of  $BH^+$  by 0.012 moles

$$\text{Hence---pH} = 8.075 + \log \frac{0.1026 - 0.012}{0.0296 + 0.012}$$

**pH = 8.41**-----only a change of 0.2 even though concentrated acid was added-----

If you added NaOH base--you would decrease  $BH^+$  and increase B conc.

Can also prepare buffers by starting with only one form of the two species---and then adding a given amount of acid or base to form the conjugate acid or base needed to provide the buffer system!

e.g., how many mL of 0.500 M NaOH should be added to 10 g of Tris-HCl salt to yield pH of 7.60 buffer in final volume of 250 mL

how many moles of Tris-HCl = moles of BH<sup>+</sup> = 10 g / (157.597 g/mol)  
= 0.0635 moles

for pH 7.60----HH says:

$$7.60 = 8.075 + \log x$$

$$\log x = -0.475$$

$$x = 0.335 = \text{ratio of B moles/BH}^+ \text{ moles}$$

but total moles of B + BH<sup>+</sup> = 0.0635; then 0.335 = y/(0.0635-y)

$$0.0213 - 0.335 y = y$$

y = moles of NaOH required

$$1.335 y = 0.0213$$

$$\mathbf{0.500 \times V = 0.0159 ; \quad V = 0.0318 \text{ L or } 31.8 \text{ ml} \quad y = 0.0159}$$



Buffer capacity = resistance to pH change from addition of acid or base!

- depends on concentration of buffer species---higher concentration more buffer capacity!---a 0.10 M Tris buffer would have more buffer capacity than a 0.01 M Tris buffer!
- depends on pH of buffer; if pH is at the  $pK_a$  of the buffering species then the buffer capacity is highest, since changes in the moles of base in the numerator, or acid in the denominator---of HH eqn have less effect on the log term value---when the ratio of the fraction is 1.0! (go back to earlier problem with added HCl --same amount, and calculate how much of a pH change would have occurred if the buffer was initially at the  $pK_a$  value!
- There is little buffer capacity when pH is  $> \pm 1.0$  pH unit of the  $pK_a$

