

How are we going to control this equilibrium?

Add HA                    shift to the "products"

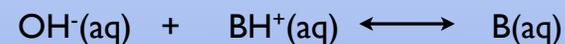
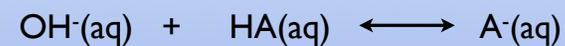
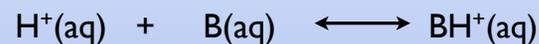
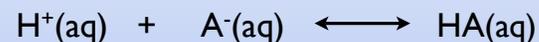
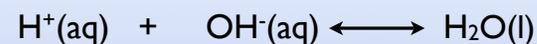
Add A<sup>-</sup>                    shift to the "reactants"

Add H<sup>+</sup>                    shift to the "reactants"

Remove H<sup>+</sup>                shift to the "products"

I can't have acid and OH<sup>-</sup>  
I can't have base and H<sup>+</sup>

They will react  
Neutralization reactions



What volume of a 0.1 M NaOH will you need to add to 200 mL of a 0.2 M solution of HCl to neutralize it?

- A. 100 mL                    There are .04 moles of H<sup>+</sup> .2M x .2L to neutralize you'll need .04 moles of OH<sup>-</sup>
- B. 200 mL
- C. 300 mL                    For that you'll need .4L of a .1M solution
- D. 400 mL                    Or you can look at it as the acid is twice as concentrated as the base
- E. 500 mL                    therefore you'll need twice as much

What can I have at the same time in a solution?

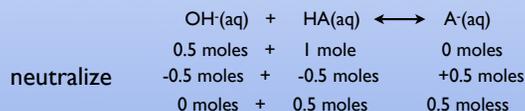
A weak acid and conjugate base HA and A<sup>-</sup>

A weak base and its conjugate acid B and BH<sup>+</sup>

What will have in solution if initially I have  
1 mole of acetic acid and I add  
0.5 mole of NaOH?

- A. 1 mole acetic acid and 0.5 mole OH<sup>-</sup>
- B. 1 mole H<sup>+</sup> and 0.5 moles OH<sup>-</sup>
- C. 0.5 moles H<sup>+</sup>
- D. 0.5 mole HA and 0.5 moles of A<sup>-</sup>
- E. 1 mole of Ha and 0.5 moles of A<sup>-</sup>

OH<sup>-</sup> will react with HA until  
one of them is gone



## First Neutralize Second Solve the Equilibrium

First find out what is mostly in solution  
Second solve for the little concentrations

Now I have a solution which initially contains both  
HA and A<sup>-</sup>

Buffer I have BOTH HA and A<sup>-</sup>



	HA	H <sup>+</sup>	A <sup>-</sup>
I	[HA] <sub>0</sub>	0	[A <sup>-</sup> ] <sub>0</sub>
C	-x	+x	+x
E	[HA] <sub>0</sub> - x	+x	[A <sup>-</sup> ] <sub>0</sub> + x

$$K_a = \frac{[\text{H}^{\text{+}}][\text{A}^{\text{-}}]}{[\text{HA}]} = \frac{(x)([\text{A}^{\text{-}}]_0 + x)}{[\text{HA}]_0 - x} = \frac{(x)([\text{A}^{\text{-}}]_0)}{[\text{HA}]_0} \quad \text{assuming } x \ll C$$

pH in a buffer solution

$$K_a \approx \frac{[\text{H}^{\text{+}}][\text{A}^{\text{-}}]_0}{[\text{HA}]_0}$$

we have approximated a small change

$$\log(K_a) \approx \log \frac{[\text{H}^{\text{+}}][\text{A}^{\text{-}}]_0}{[\text{HA}]_0} = \log[\text{H}^{\text{+}}] + \log \frac{[\text{A}^{\text{-}}]_0}{[\text{HA}]_0}$$

$$\text{pKa} = \text{pH} - \log \frac{[\text{A}^{\text{-}}]_0}{[\text{HA}]_0}$$

$$pK_a = pH - \log \frac{[A^-]_0}{[HA]_0}$$

initial conjugate base
initial weak acid

$[A^-]_0 = [HA]_0$	$[A^-]_0 < [HA]_0$	$[A^-]_0 > [HA]_0$
equal acid/base	more acid	more base
$-\log \frac{[A^-]_0}{[HA]_0} = 0$	$-\log \frac{[A^-]_0}{[HA]_0} > 0$	$-\log \frac{[A^-]_0}{[HA]_0} < 0$
$pH = pK_a$	$pH < pK_a$	$pH > pK_a$

The  $pK_a$  of HF is 3.18. What is the pH of solution of 100 mL of 0.1 M HF and 100 mL of a 0.2 M NaF?

- A. slightly less than 3.18
- B. 3.18
- C. slightly more than 3.18

$$pK_a = pH - \log \frac{[A^-]_0}{[HA]_0}$$

initial conjugate base
initial weak acid

if the initial acid and base are similar in concentration then the pH is close to the  $pK_a$

For the pH to be 1 unit different than the  $pK_a$  the difference in concentrations must be at least 10 X!

Back to Buffers

$$pK_a = pH - \log \frac{[A^-]}{[HA]}$$

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

This is the same equation!

Let's look at the second one

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

If  $[HA] = [A^-]$ , then  $[H^+] = K_a$

or we could look at it as

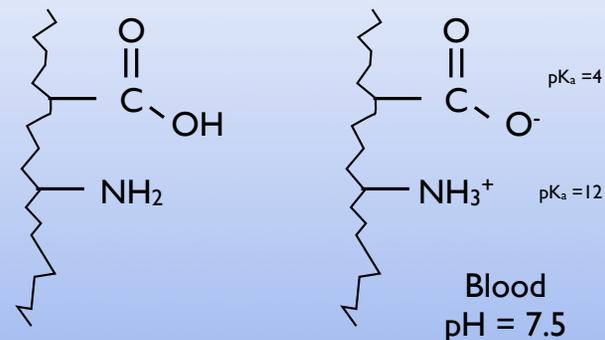
if  $[H^+] = K_a$ , then  $[HA] = [A^-]$

if  $[H^+] > K_a$ , then  $[HA] > [A^-]$  "too many" protons

if  $[H^+] < K_a$ , then  $[HA] < [A^-]$  "too few" protons

Why should I care

Proteins have lots of acid and base groups



We want to "Buffer" against pH change

demo

Add NaOH to water and the pH shoots up to 12

Add NaOH to mixture of acetic acid and sodium acetate and the pH doesn't change at all

NaOH added to water

Water. Add  $10^{-3}$  moles of  $OH^-$  to the solution

The  $[OH^-] = 10^{-3}$   $pOH = 3$   $pH = 11$

NaOH added to buffer

initial concentration of [HA] = 0.1 M  
initial concentration of [A<sup>-</sup>] = 0.1 M

add .001 moles of NaOH to 1L of solution

concentration of [HA] = .1 - .001 = 0.099  
concentration of [A<sup>-</sup>] = .1 + .001 = .101

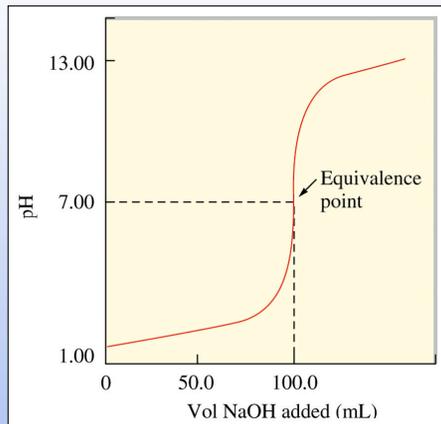
$10^{-4.75}$  → 
$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+](.101)}{0.099} \quad \text{pH} = 4.76$$

Water before adding NaOH pH = 7  
after adding NaOH pH = 3

Buffer before adding NaOH pH = 4.75  
after adding NaOH pH = 4.76

the only way to change the pH of the buffer system dramatically is to add enough acid or base to substantially change either the HA or A<sup>-</sup> concentrations

### Strong Acid/Strong Base Titration



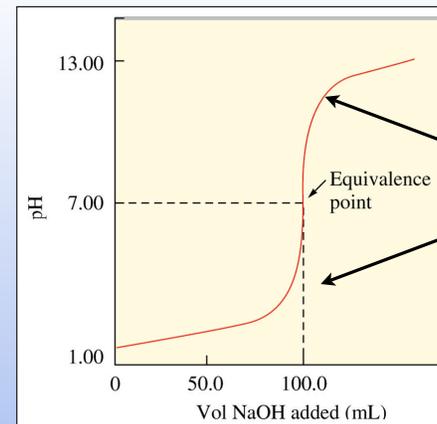
original solution 50 mL HCl  
adding .1 M NaOH  
at equivalence point

same number of moles of base  
.1L x .1M = 0.01 moles OH<sup>-</sup>

therefore the solution originally  
had 0.01 moles H<sup>+</sup>

concentration was .2 M

at the equivalence point we have  
equal number of moles of acid and base



pH changes rapidly  
because the total amount  
of H<sup>+</sup> OH<sup>-</sup> is very small  
between pH 3 and pH 11