

Neutralization
Buffers
Titration



How are we going to
control this equilibrium?

Add $\text{H}^{\text{+}}$ shift to the "reactants"

Remove $\text{H}^{\text{+}}$ (Add $\text{OH}^{\text{-}}$) shift to the "products"

Strong Acid/Strong Base
(only H⁺ and OH⁻)

What volume of a 0.5 M NaOH will you need to add to 200 mL of a 0.5 M solution of HCl to neutralize it?

A. 100 mL

B. 200 mL

C. 300 mL

D. 400 mL

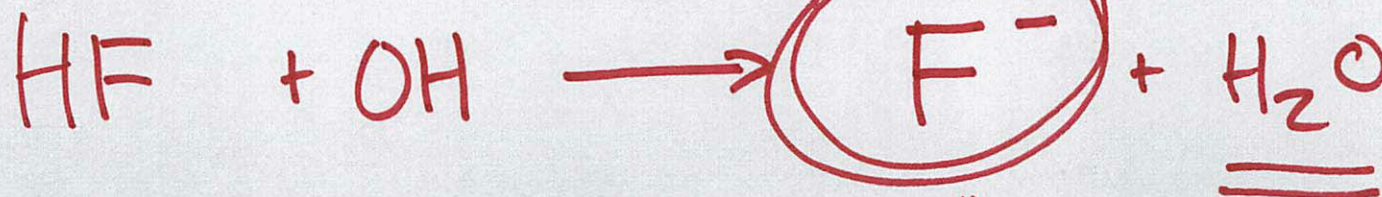
E. 500 mL

EQUAL MOLES

H⁺ is OH⁻

$$(.2\text{ L} \times .5) = \underline{\underline{.01 \text{ moles}}}$$

What is the pH of a solution that is made of equal moles of a HF and NaOH?

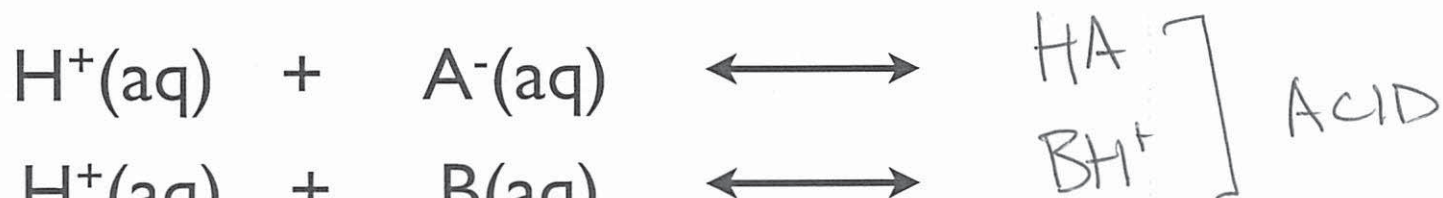
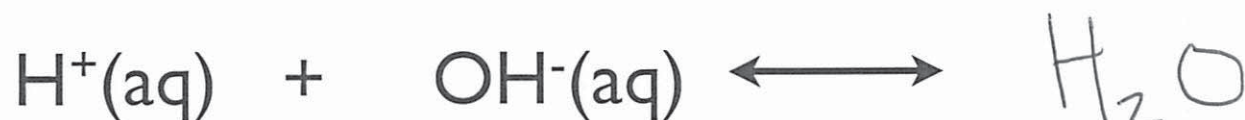


- A. neutral (pH 7)
- B. acidic (pH < 7)
- C. basic (pH > 7)

↑
BASE

I can't have OH^- and acid
I can't have H^+ and base

They will react
Neutralization reactions



} ACID



} BASE

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

A weak acid and conjugate base HA and A⁻

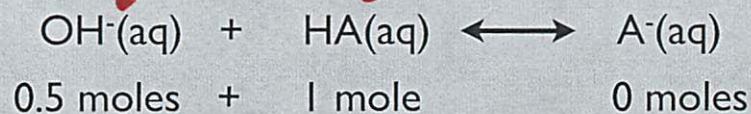
A weak base and its conjugate acid B and BH⁺

BUFFER

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⁻
- B. 1 mole H⁺ and 0.5 moles OH⁻
- C. 0.5 moles H⁺
- D. 0.5 mole HA and 0.5 moles of A⁻**
- E. 1 mole of Ha and 0.5 moles of A⁻

STRONG
BASE ACID



neutralize	- .5	- .5	+ .5
AFTER	0	.5	.5
		HA	A ⁻

First Neutralize
Second Solve the Equilibrium

Now I have a solution which initially contains both
HA and A⁻

Both HA & A⁻ Buffer

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

pH in a buffer solution

SAME

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

$$[H^+] = K_a \frac{C_A}{C_B}$$

we have approximated a small change

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

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

$$K_2 = 10^{-3.18}$$

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?

ACID

BASE

MORE

A. slightly less than 3.18

B. 3.18

C. slightly more than 3.18

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

initial conjugate base

initial weak acid

if the initial acid and base are similar in concentration than the pH is close to the pKa

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

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

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

Back to Buffers

$$\text{pK}_a = \text{pH} - \log \frac{[\text{A}^-]}{[\text{HA}]}$$

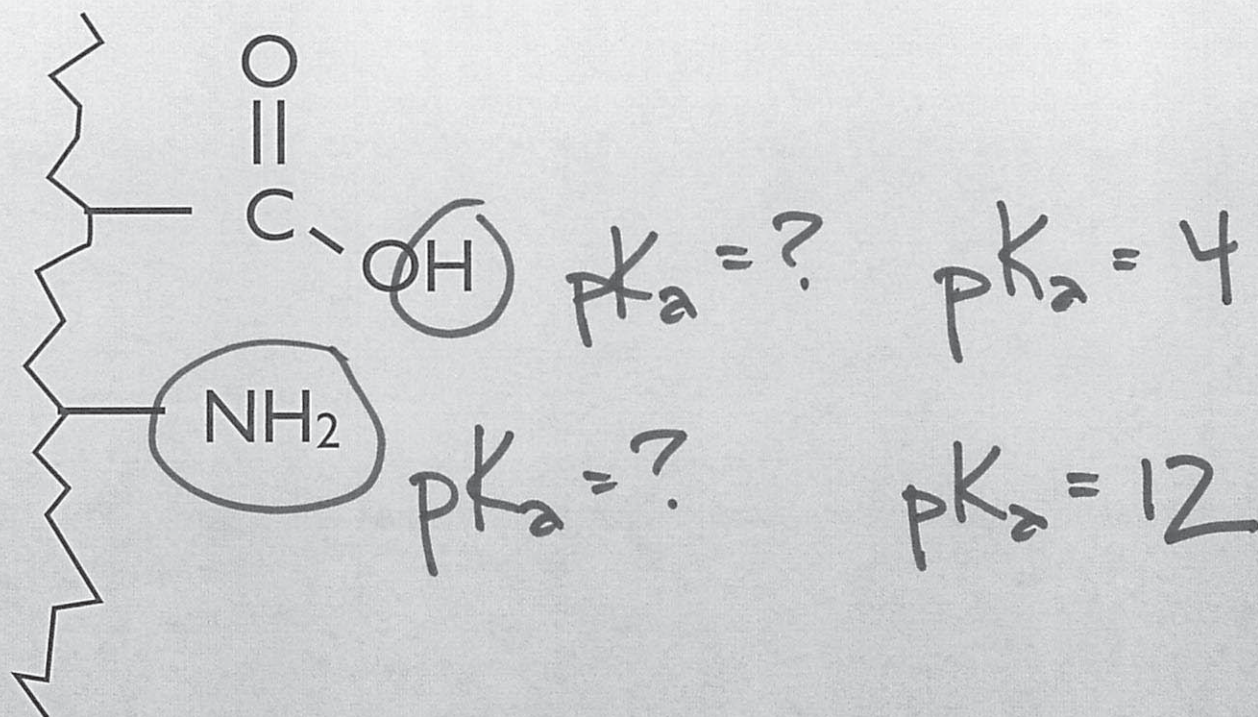
$$\text{K}_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

This is the same equation!

Let's look at the second one

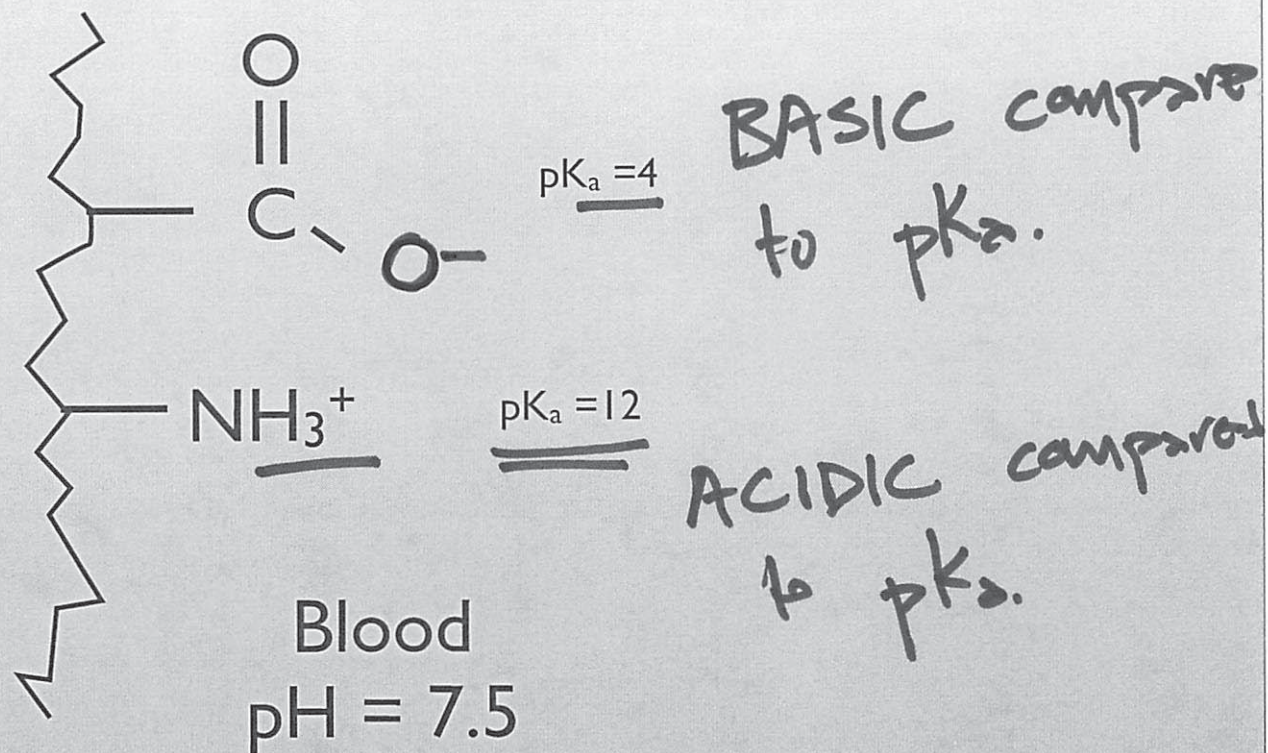
Why should I care

Proteins have lots of acid and base groups



Why should I care

Proteins have lots of acid and base groups



The pK_a of acetic acid is 4.75. What will the pH be for a solution that has equal moles sodium acetate and acetic acid?

A^-

HA

- A. much less than 4.75
- B. about 4.75**
- C. much higher than 4.75

equal

$$[A^-] = [HA]$$

$$pH = pK_a.$$

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

1 L

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

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

M

↑

↗

Quite Basic

NaOH added to buffer

1 L

initial concentration of $[HA] = 0.1 \text{ M}$

initial concentration of $[A^-] = 0.1 \text{ M}$

$$HA \quad (.1 \text{ M})(1 \text{ L}) = .1 \text{ moles}$$

$$A^- \quad (.1 \text{ M})(1 \text{ L}) = .1 \text{ moles}$$

ADDING 10^{-3} moles OH^-



$$\begin{array}{ccc} .1 & .001 & \\ -.001 & -.001 & \end{array}$$

$$.1$$

$$+.001$$

Neutral

$$.099$$

$$.101$$

$$[H^+] = K_a \frac{[0.099]}{[.101]}$$

$$pH = 4.76$$

1 L
 $\times 10^{-3}$ moles
 OH^-

Water before adding NaOH pH = 7
after adding NaOH pH = ~~3~~ 11

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^- concentrations

Buffer capacity = amount of acid(base) the buffer can “absorb”.

More HA/ A^- in solution = larger buffer capacity

Titration

Slow addition of strong base(acid)
to a solution of an acid(base)

while measuring the pH

Imagine titration of 100 mL of 0.1 M acetic acid
with 0.1 M NaOH HA

Initial point (no base added)

$$K_a = 1.8 \times 10^{-5} \quad (pK_a = 4.75)$$

pH = ?

$$[H^+] = \sqrt{K_a C_a}$$

$$pH = 2.87 \quad = \sqrt{(1.8 \cdot 10^{-5})(.1)} = 1.34 \times 10^{-3}$$

Imagine titration of 100 mL of 0.1 M acetic acid
with 0.1 M NaOH

after the addition of 10 mL of base

$$(.1 \text{ L})(.1 \text{ M}) = .01 \text{ moles HA}$$

$$(.01 \text{ L})(.1 \text{ M}) = .001 \text{ moles OH}^-$$

Volume
= 110 mL



$$[\text{H}^+] = K_a \frac{C_A}{C_B}$$

$$= 1.62 \cdot 10^{-4}$$

$$\text{pH} = 3.8$$



Imagine titration of 100 mL of 0.1 M acetic acid
with 0.1 M NaOH

after the addition of 50 mL of base

$$\text{HA } (.1\text{L})(.1\text{M}) = .01 \text{ moles HA}$$

$$\text{OH}^- (.05\text{L})(.1\text{M}) = .005 \text{ moles OH}^-$$



$$\begin{array}{ccc} .01 & .005 & 0 \end{array}$$

$$\begin{array}{ccc} \text{N} & -.005 & -.005 & +.005 \end{array}$$

$$\begin{array}{ccc} .005 & 0 & .005 \end{array}$$

$$\text{equal } [\text{HA}] = [\text{A}^-]$$

$$\text{pH} = \text{pK}_a = 4.75$$

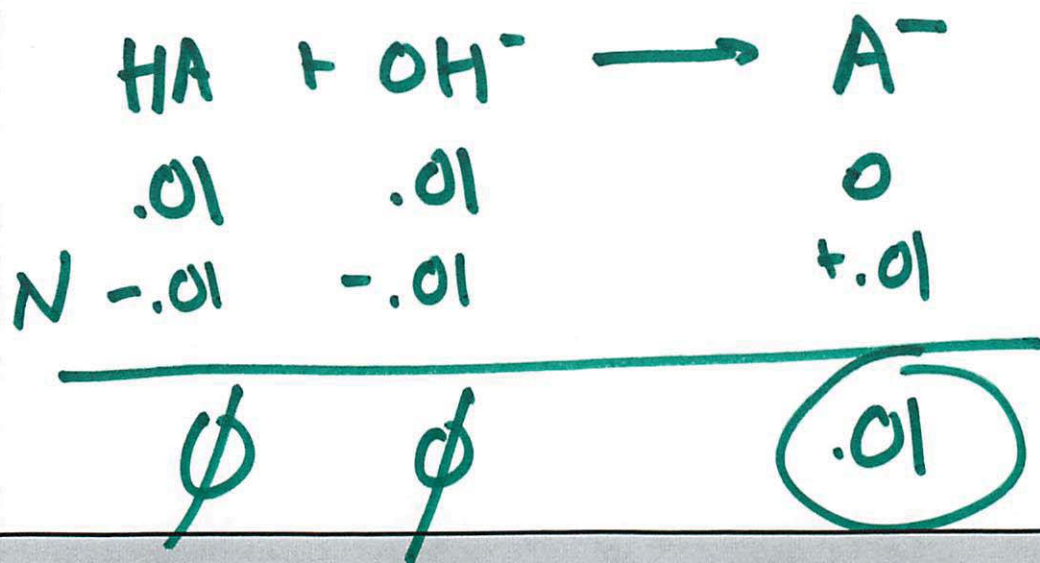
HALF-EQUIVALENCE

Imagine titration of 100 mL of 0.1 M acetic acid
with 0.1 M NaOH

after the addition of 100 mL of base

$$\text{HA} (.1\text{M})(.1\text{L}) = .01 \text{ moles HA}$$

$$\text{OH}^- (.1\text{M})(.1\text{L}) = .01 \text{ moles OH}^-$$



WEAK BASE

~~$$[\text{OH}^-] = \sqrt{K_b C_b}$$~~

$$[\text{A}^-] = \frac{.01}{.2\text{L}} = C_b$$

200 mL

Imagine titration of 100 mL of 0.1 M acetic acid
with 0.1 M NaOH

after the addition of 110 mL of base

EXCESS OH^-

STRONG BASE

Draw pH Curve

