Acid Base Equilibria

Critical for most aqueous chemistry
(if you've missed it biochemistry is mostly aqueous chemistry)

$$H_2O(l) \longleftrightarrow H^+(aq) + OH^-(aq)$$

$$2H_2O(l) \longrightarrow H_3O^+(aq) + OH^-(aq)$$

$$H_3O^+ = H^+$$ short hand

For this reaction which has a higher entropy?

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$$

A. the products

B. the reactants

C. they are the same

For this reaction which has a lower enthalpy?

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$$

A. the products

B. the reactants

C. they are the same

Bond Breaks

$\Delta_R H^\circ > 0$

For this reaction which has a lower free energy?

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$$

VERY STABLE

A. the products

B. the reactants

C. they are the same

$\Delta_R G^\circ > 0$

$K \ll 1$

Liquid Water
will spontaneously dissociate to a small extent

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$$

$$K = \frac{[H^+][OH^-]}{\cancel{a}_{H_2O}}$$

$$K_w = [H^+][OH^-] = 10^{-14} \quad 25^\circ C$$

In pure water what is the concentration of $[H^+]$ at 25 °C when $K_w = 10^{-14}$?

$$H_2O(l) \longleftrightarrow H^+(aq) + OH^-(aq)$$

$$K_w = [H^+][OH^-] = 10^{-14}$$

Pure Water

ignore H_2O

	H^+	OH^-
I	0	0
C	+x	+x
E	+x	+x

SAME

$$K_w = 10^{-14} = [H^+][OH^-] = (x)(x) = x^2$$

$$x = \sqrt{K_w} = \sqrt{10^{-14}} = 10^{-7} M$$

Acid/Base we are dealing with the balance of H^+ and OH^-

Definition of "Neutral"

$[H^+] = [OH^-]$

Definition of "Acidic"

$[H^+] > [OH^-]$

Definition of "Basic"

$[H^+] < [OH^-]$

pH

Log scale.
Useful when dealing with very small
or very large number (big ranges of numbers)
every "pH" unit is 10x larger or smaller $[H^+]$

$$pH = -\log[H^+]$$

$[H^+] = 10^{-13}$

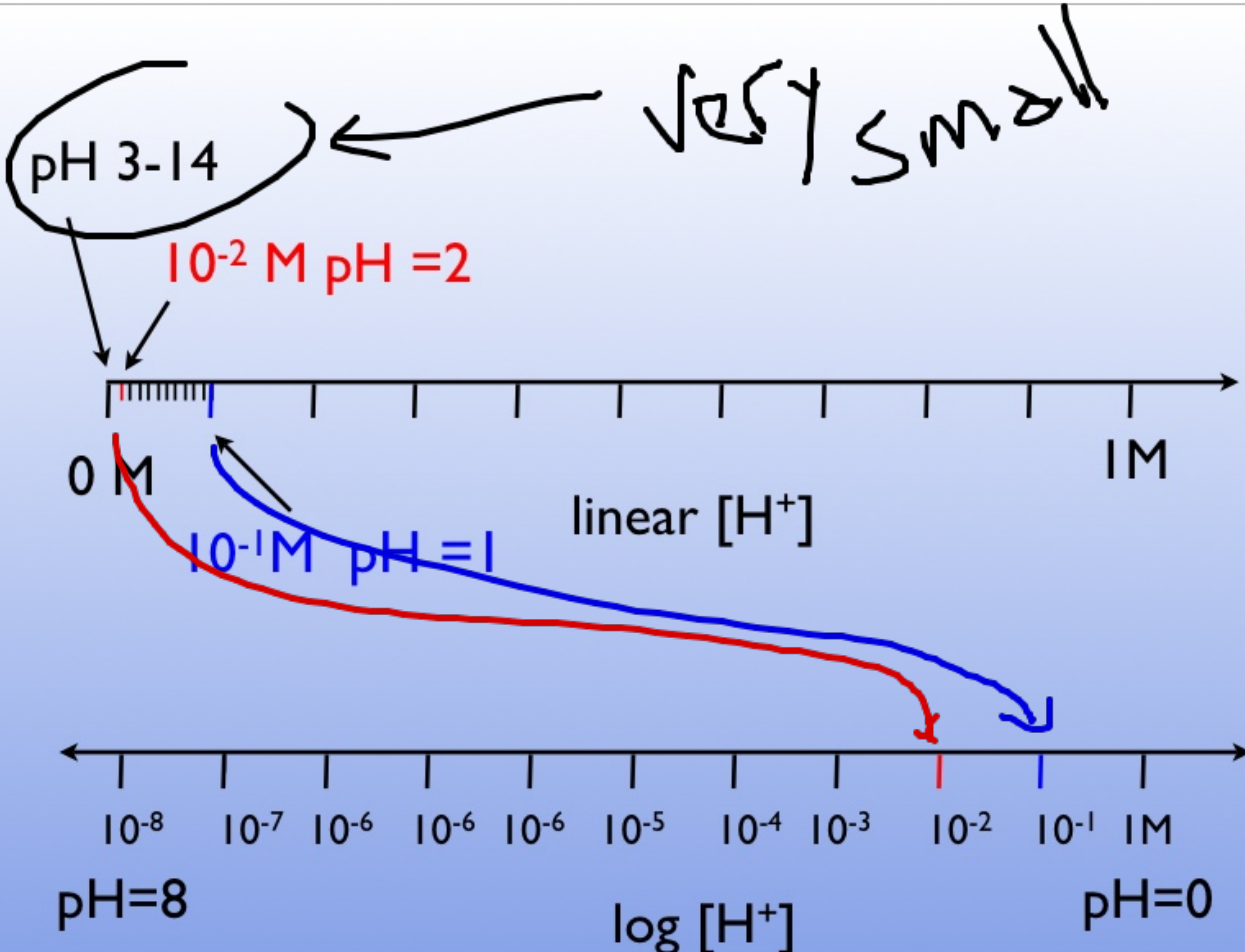
pH = 13

$[H^+] = 10^{-7}$

pH = 7

$[H^+] = 10^{-2}$

pH = 2



very small
pH 3-14
10-2 M pH =2
0 M
1M
linear [H+]
10-1M pH =1
10-8
10-7
10-6
10-6
10-6
10-5
10-4
10-3
10-2
10-1
1M
pH=8
log [H+]
pH=0

$pOH = -\log_{10}[OH^-]$

pH of pure water at 25°C

$x = 10^{-7}$ $[H^+]=[OH^-]=10^{-7}$

$$pH = -\log_{10}([H^+]) = -\log_{10}(10^{-7}) = 7$$

Neutral	Acidic	Basic
$[H^+]=[OH^-]$	$[H^+]>[OH^-]$	$[H^+]<[OH^-]$
at 25°C	at 25°C	at 25°C
$pH = 7$	$pH < 7$	$pH > 7$
$pOH = 7$	$pOH > 7$	$pOH < 7$

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$$

This reaction is endothermic.
Given that information what do you think the pH is for pure water at 60°C?

A. 6.5

B. 7

C. 7.5

$\Delta H > 0$

$T \uparrow$ $K \uparrow$

$K \uparrow$ $[H^+] \uparrow$

If pure water has a pH = 6.5 at 60°C is it Acidic?

A. Yes

B. No

$[H^+] = [OH^-] \neq 10^{-7}$

SAME

$10^{-6.5}$

Acids and Bases

Brønsted-Lowry Definition

ACID

Acid is a proton (H^+) donor

BASE

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

Base is a proton (H^+) acceptor

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

BASE

ACID

Strong Acids and Bases

"Strong" means one thing

The substance dissociates 100% in water

Strong Acid

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

$$K_a = \frac{[H^+][Cl^-]}{[HCl]} = \infty$$

Strong Electrolyte

$$NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)$$

$$K_{sp} = [Na^+][Cl^-] = \infty$$

Strong Acids

Hydrochloric	HCl
Hydrobromic	HBr
Hydroiodic	HI
Perchloric	$HClO_4$
Chloric	$HClO_3$
Sulfuric	H_2SO_4
Nitric	HNO_3

All Dissociate 100%

What is the pH of a 0.1 M solution of Nitric Acid

$$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$$

0.1 M acid makes a solution with $[H^+]$ = 0.1

$$[H^+] = 10^{-1} M \quad pH = -\log(10^{-1}) = 1$$

What is the pH of a 0.5M solution of HBr?

$>1M$

A. -0.2

10^{-1}

B. 1

C. 0.3

$1M$

D. 0

E. ~~12~~

BASIC

$[H^+] \quad 0.1 < .5 < 1$

$pH \quad 1 > .3 > 0$

Generally Scheme for Acids

$$HA(aq) \longleftrightarrow H^+(aq) \quad A^-(aq)$$

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

We can ignore the conjugate base of a strong acid

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

$$K_a = \frac{[H^+][Cl^-]}{[HCl]} \approx \infty$$

equilibrium constant is so large, even if we add Cl^- the shift back to HCl will be negligible

TABLE 7.1 Various Ways to Describe Acid Strength

Property	Strong Acid	Weak Acid
K_a value	K_a is large	K_a is small
Position of the dissociation equilibrium	Far to the right	Far to the left
Equilibrium concentration of H^+ compared with original concentration of HA	$[H^+] \approx [HA]_0$	$[H^+] \ll [HA]_0$
Strength of conjugate base compared with that of water	A^- much weaker base than H_2O	A^- much stronger base than H_2O

almost no dissociation

assume all H^+ from HA

Weak Acid

10^{-7}

$$HA(aq) \longrightarrow H^+(aq) + A^-(aq)$$

	$HA(aq)$	$H^+(aq)$	$A^-(aq)$
I	C_A	0	0
C	$-x$	$+x$	$+x$
E	$C_A - x$	$+x$	$+x$

$$K_a = \frac{(x)(x)}{C_A - x} = \frac{x^2}{C_A} = $$

TINY

assuming x << C

$$x = \sqrt{K_A C_A}$$

Weak Base

$$A^-(aq) + H_2O(l) \longrightarrow HA(aq) + OH^-(aq)$$

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

identical result as before (same assumptions)

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

What is an Acid? What is a Base?

Generic Naming HA

$$HA \longrightarrow A^- + H^+$$

$$BH^+ \longrightarrow B + H^+$$

Generic Naming B

$$B + H_2O \longrightarrow BH^+ + OH^-$$

$$A^- + H_2O \longrightarrow HA + OH^-$$

What is the approximate pH of a 1M solution of Glutamic Acid?
$K_a = 5 \times 10^{-5}$

A. 2

B. -2

C. 7

D. 5

E. 12

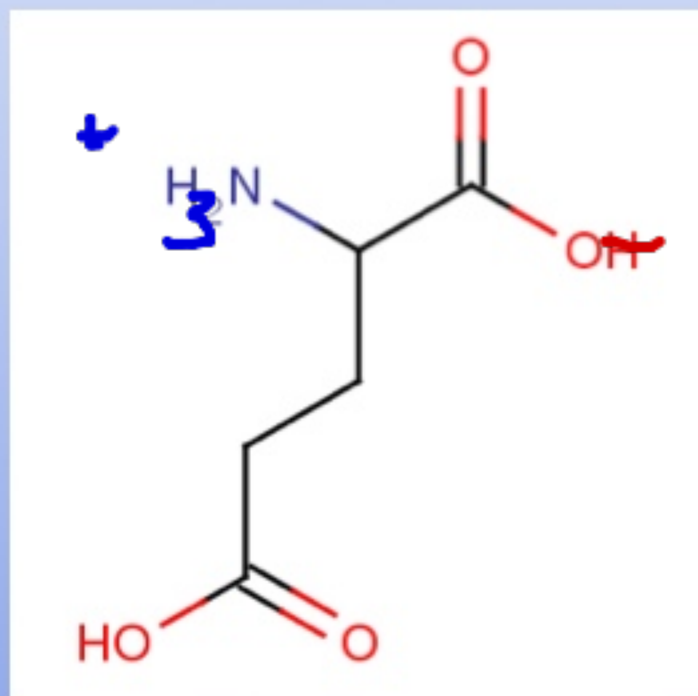
$$[H^+] = \sqrt{K_A C_A} = \sqrt{5 \cdot 10^{-5} \times 1}$$

$$[H^+] \approx 10^{-2}$$

$$pH = 2$$

Think about pH = 4
why would we care?

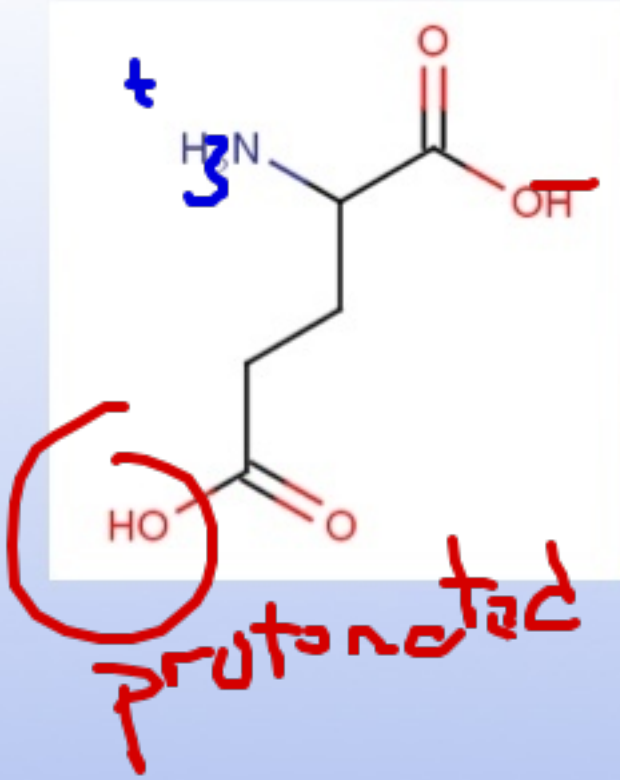
$[H^+] = 10^{-4}$ very small



Glutamic Acid
$K_a = 5 \times 10^{-5}$
$pK_a = 4.3$

What concentration of $[H^+]$ is $[HA] = [A^-]$

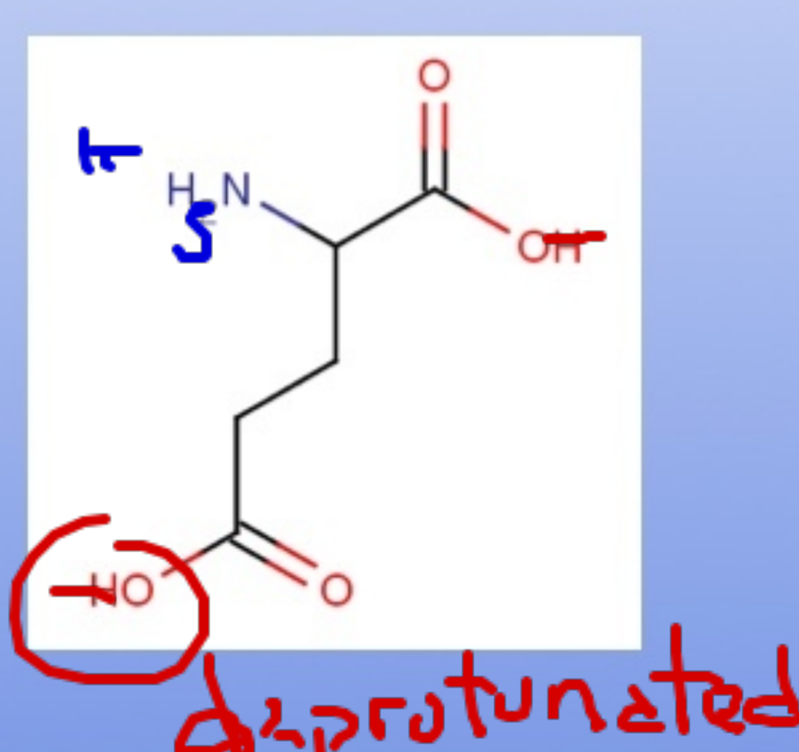
$$K_a = \frac{[H^+]\cancel{[A^-]}}{\cancel{[HA]}} \quad 1$$



So if the pH is < 4.3

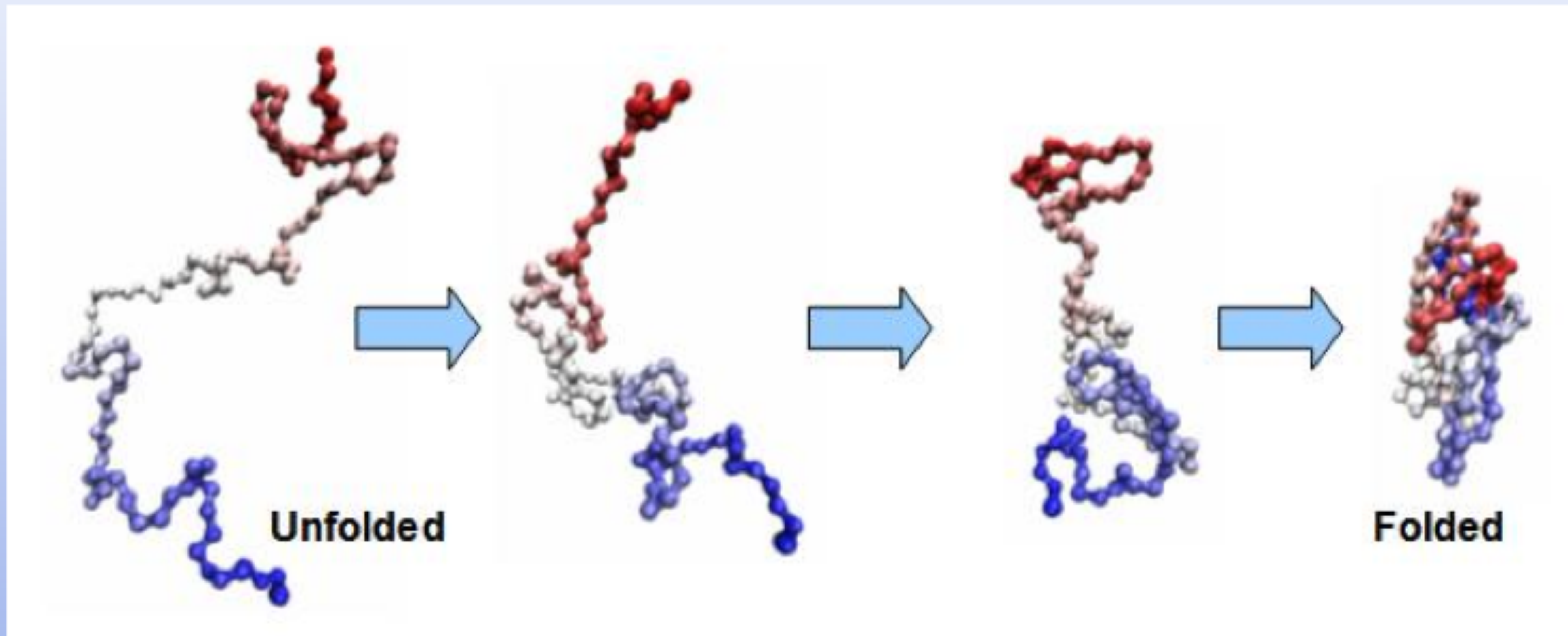
neutral charge

if the pH is > 4.3



negatively charged

Protein Function is derived from its structure



Structure results from interactions of the amino acids that make up the protein

Change the charge and you dramatically alter the structure