EQUILIBRIUM CONSTANTS

WEAK ACID

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$K_a \equiv$ ACID IONIZATION CONSTANT

WEAK BASE

$$\underset{\text{BASE}}{NH_3(aq)} + H_2O(l) \rightleftharpoons \underset{\text{CONJUGATED ACID}}{NH_4^+(aq)} + OH^-(aq)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

$$K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]}$$

$$K_a K_b = [H_3O^+][OH^-] = K_w$$

PROBLEM = EXAMPLE 10.5 → FIND pH.

0.0100 mol OF NH_3 IN 1.000 L ($T = 25°C$)

$K_b = 1.8 \times 10^{-5}$

$$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

	NH_3	H_2O	NH_4^+	OH^-
I	0.0100	—	0	≈ 0
C	$-y$		$+y$	$+y$
E	$0.0100 - y$		y	y

$$\frac{y^2}{0.0100 - y} = K_b = 1.8 \times 10^{-5}$$

$$y^2 \simeq 1.00 \times 10^{-2} K_b$$

$$y = 4.15 \times 10^{-4} \Rightarrow [OH^-] = 4.15 \times 10^{-4} M$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{4.15 \times 10^{-4}}$$

$$= 2.41 \times 10^{-11} \text{ M}$$

$$pH = 10.618$$

$$CO_2(g) + H_2O(l) \overset{E}{\rightleftharpoons} H_2CO_3(aq)$$

E = Carbonic anhydrase

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

$\Rightarrow$ HCO_3^-/H_2CO_3 BUFFER

Capillaries

$$\longrightarrow CO_2(g) + H_2O(l) \xrightarrow{E} H_2CO_3(aq)$$

$$H_2CO_3(aq) + H_2O(l) \longrightarrow HCO_3^-(aq) + H_3O^+(aq)$$

$HCO_3^-(aq)$ → Plasma

$$H_3O^+(g) + HbO_2^-(aq) \rightarrow HHbO_2(aq) + H_2O(l)$$

$$HHbO_2(aq) \longrightarrow HHb(aq) + O_2(g)$$

$O_2(g)$ →

Lungs

$\rightarrow HCO_3^-(aq) + HHb(aq) \rightarrow H_2CO_3(aq) + Hb^-(aq)$

$H_2CO_3(aq) \xrightarrow{E} H_2O(l) + CO_2(g)$ ⟶

$Hb^-(aq) + O_2(g) \longrightarrow HbO_2^-(aq)$

$Hb^-(aq)$ high affinity for $O_2(g)$

$HbO_2^-(aq)$ very stable

$HHbO_2(aq)$ low affinity for $O_2(g)$

$$CO_2(g) + H_2O(l) \overset{E_1}{\rightleftharpoons} H_2CO_3(aq)$$

E_1 = Carbonic anhydrase

BUFFER HCO_3^- / H_2CO_3

$$H_2O + H_2CO_3(aq) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

HEMOGLOBIN

$$H_2O + HHb(aq) \rightleftharpoons H_3O^+(aq) + Hb^-(aq)$$

$$H_2O + HHbO_2(aq) \rightleftharpoons H_3O^+(aq) + HbO_2^-(aq)$$

Cap $\rightarrow$ $HHbO_2(aq) \rightleftharpoons HHb(aq) + O_2(aq)$

Lung $\rightarrow$ $O_2(g) + Hb^-(aq) \rightleftharpoons HbO_2^-(aq)$

BUFFERS

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

Acid — Conj. Base

BUFFER IS A SOLUTION OF

HA AND A SALT OF THE CONJ. BASE NaA

CONSIDER 1.000 mol OF HA
0.500 mol OF NaA IN 1.000 L

	$HA(aq) + H_2O(l) \rightleftharpoons$	—	$H_3O^+(aq)$ +	$A^-(aq)$
I	1.000	—	≈ 0	0.500
C	$-y$	—	$+y$	$+y$
E	$1.000 - y$	—	y	$0.500 + y$

$$K_a = \frac{y(0.500 + y)}{1.000 - y} \approx \frac{0.500 \cdot y}{1.000}$$

$y << 0.500 < 1.000$

$y \approx 2.000\, K_a$

FOR ACETIC ACID $K_a = 1.76 \times 10^{-5}$

$[H_3O^+] = 3.52 \times 10^{-5}\ M \gg 10^{-7}\ M$

$\boxed{pH = 4.453}$

ADD 0.100 mol OF HCl.

ASSUMPTION: TAKE ALL OF THE H_3^+ FROM HCl AND COMBINE THEM WITH A^- TO FORM HA. NOW RECALCULATE THE pH.

	$HA(aq)$	$+ H_2O(l) \rightleftharpoons$	$H_3O^+(aq)$	$+ A^-(aq)$
I	1.100	—	≈ 0	0.400
C	$-y$	—	y	$+y$
E	$1.100 - y$	—	y	$0.400 + y$

$$K_a = \frac{(0.400+y)\,y}{(1.100-y)} \approx \frac{0.400 \cdot y}{1.100}$$

$$y \approx \frac{1.100}{0.400} K_a = 4.84 \times 10^{-5}$$

$\boxed{pH = 4.315}$