

## Acids and Bases

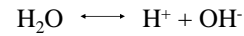
9 / 03 / 2009

### Chapter 2 Water

1. How is the molecular structure of water related to physical and chemical behavior?
2. What is a Hydrogen Bond?
3. What are Acids and Bases?
4. What is pH, and what does it have to do with the properties of Water?
5. What are Titration Curves?
6. What are buffers, and why they are important?

## Ionization of water

- Neutral water has a tendency to ionize



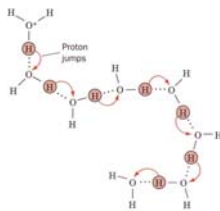
- The free proton is associated with a water molecule to form the **hydronium ion**



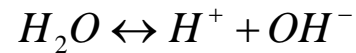
## Proton Jumping

### Large proton and hydroxide mobility

- $\text{H}_3\text{O}^+$  :  $362.4 \times 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$
- $\text{Na}^+$ :  $51.9 \times 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$
- Hydronium ion migration; hops by switching partners at  $10^{12}$  per second



## Equilibrium expression



- Described by:  $K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$

*Where K is the dissociation constant*

- Considering  $[\text{H}_2\text{O}]$  constant yields  $K_w = [\text{H}^+][\text{OH}^-]$

## $K_w$

$$K_w = [\text{H}^+][\text{OH}^-]$$

- Where  $K_w$  is the ionization constant of water
- For pure water ionization constant is  $10^{-14} \text{ M}^2$  at  $25^\circ$
- For pure water

$$[\text{H}^+] = [\text{OH}^-] = (K_w)^{1/2} = 10^{-7} \text{ M}$$

## Acids and bases

- For pure water (neutral)

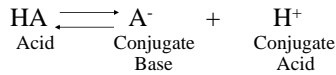
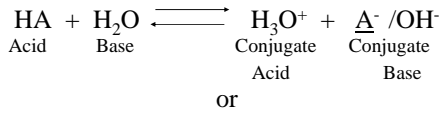
$$[\text{H}^+] = [\text{OH}^-] = (K_w)^{1/2} = 10^{-7} \text{ M}$$

- Acidic if  $[\text{H}^+] > 10^{-7} \text{ M}$
- Basic if  $[\text{H}^+] < 10^{-7} \text{ M}$

## Acids and Bases

Lowery definition:

- Acid is a substance that can donate a proton.
- Base is a substance that can accept a proton.



If you establish equilibrium, changes in  $[\text{H}^+]$  will shift the ratio of HA and  $\text{A}^-$ .

By adding more  $\text{H}^+$ ,  $\text{A}^-$  will be consumed forming HA.

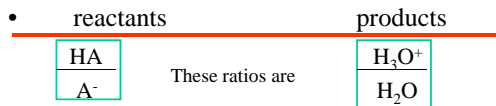
★ If there is sufficient  $[\text{A}^-]$ , the extra  $\text{H}^+$  will also be consumed and the  $[\text{H}^+]$  will not change. ★

Acid strength is specified by its dissociation constant

Molar concentration

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

for:  $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$



a measure of relative proton affinities for each conjugate acid base pair.

## What about the water

The concentration of  $\text{H}_2\text{O}$  remains almost unchanged especially in dilute acid solutions.

What is the concentration of  $\text{H}_2\text{O}$ ?

Remember the definition: Moles per liter

$$1 \text{ mole of } \text{H}_2\text{O} = 18 \text{ g} = 18 \text{ ml}$$

$$1 \text{ g} \equiv 1 \text{ ml}$$

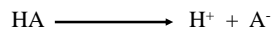
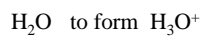
$$\frac{1000 \text{ g/liter}}{18 \text{ g/mol}} = 55.5 \text{ M}$$

$$K_a = K[\text{H}_2\text{O}] = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

From now on we will drop the a, in  $K_a$

- ★ Weak acids ( $K < 1$ )
- ★ Strong acids ( $K > 1$ )

Strong acid completely dissociates: Transfers all its protons to



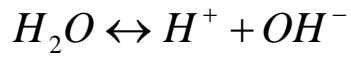
## Weak Acids

Weak acids do not completely dissociate:  
They form an equilibrium:



If we ADD more  $\text{H}^+$ , the equilibrium shifts to form more HA using up  $\text{A}^-$  that is present.

### Dissociation of H<sub>2</sub>O



Water also dissociates  $[H_2O] = 55.5$

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

$$K_w = [H^+][OH^-] = 10^{-14} M^2$$

Ionization constant for water

Since there is equal amounts of [H<sup>+</sup>] and [OH<sup>-</sup>]

$$[H^+] = [OH^-] = 1 \times 10^{-7} M$$

This is neutral

At [H<sup>+</sup>] above this concentration the solution is **ACIDIC**

$$[H^+] = 1 \times 10^{-2}$$

At [H<sup>+</sup>] below this concentration the solution is **BASIC**

$$[H^+] = 1 \times 10^{-9}$$

[H <sup>+</sup> ]	pH
10 <sup>-7</sup>	= 7
10 <sup>-3</sup>	= 3
10 <sup>-2</sup>	= 2
10 <sup>-10</sup>	= 10
5x10 <sup>-4</sup>	= 3.3
7x10 <sup>-6</sup>	= 5.15
3.3x10 <sup>-8</sup>	= 7.48

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

Relationship between pH and [H<sup>+</sup>] / [OH<sup>-</sup>] concentration

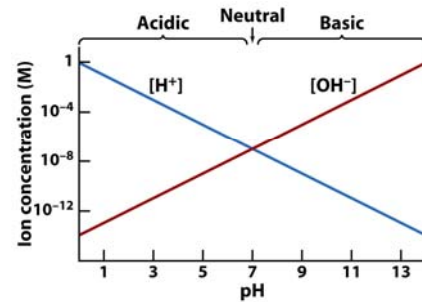


Figure 2-18 Fundamentals of Biochemistry, 2/e  
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### Henderson - Hasselbalch equation

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

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

Take (-)Log of each 
$$pH = -\log K + \log \frac{[A^-]}{[HA]}$$

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

### Buffers

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

$$\frac{[A^-]}{[HA]} \text{ ratio varies from } \frac{1}{10} \Rightarrow \frac{10}{1}$$

Above and below this range there is insufficient amount of conjugate acid or base to combine with the base or acid to prevent the change in pH.

For weak acids

$$\text{HA} \rightleftharpoons \text{A}^- + \text{H}^+$$

This equilibrium depends on concentrations of each component.

If  $[\text{HA}] = [\text{A}^-]$  or 1/2 dissociated

Then  $\log \frac{[\text{A}^-]}{[\text{HA}]} = \log 1 = 0 : \text{pH} = \text{pK}$

By definition the pK is the pH where  $[\text{HA}] = [\text{A}^-]$

**Table 2-3 pH Values of Some Common Substances**

Substance	pH
1 M NaOH	14
Household ammonia	12
Seawater	8
Blood	7.4
Milk	7
Saliva	6.6
Tomato juice	4.4
Vinegar	3
Gastric juice	1.5
1 M HCl	0

Table 2-3 Fundamentals of Biochemistry, 2/e  
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**Buffers**

A buffer can resist pH changes if the pH is at or near a its pK.

Buffer range: the pH range where maximum resistance to pH change occurs when adding acid or base. It is  $\pm 1$  pH from the weak acid pK

If pK is 4.8 the buffering range is 3.8 to 5.8

Why?

The buffer effect can be seen in a titration curve.

To a weak acid salt,  $\text{CH}_3\text{COO}^-$  add HCl while monitoring pH vs. the number of equivalents of acid added.

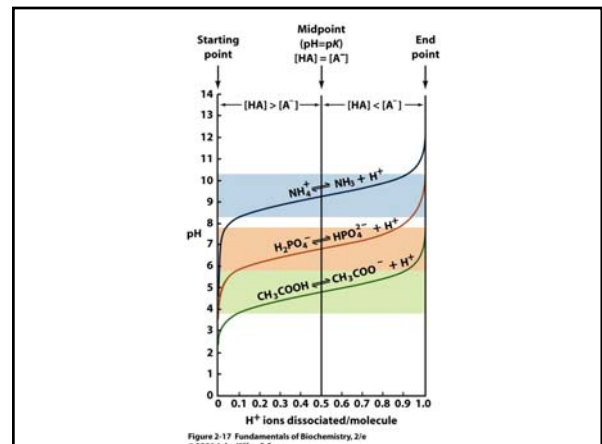
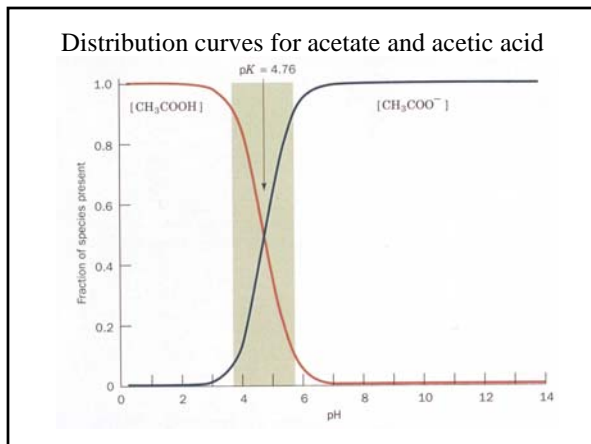
or

do the opposite with base.

Buffer capacity: the molar amount of acid which the buffer can handle without significant changes in pH.

i.e

1 liter of a .01 M buffer can not buffer 1 liter of a 1 M solution of HCl  
but  
1 liter of a 1 M buffer can buffer 1 liter of a .01 M solution of HCl



### Titration curve for phosphate

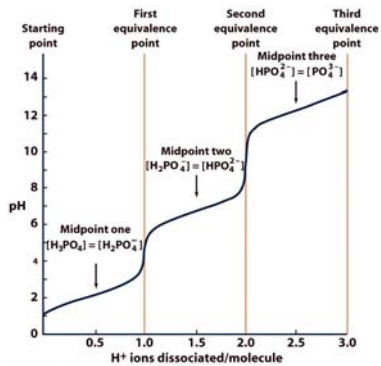


Table 2-4 Dissociation Constants and pK Values at 25°C of Some Acids

Acid	K	pK
Oxalic acid	$5.37 \times 10^{-2}$	1.27 (pK <sub>1</sub> )
H <sub>2</sub> PO <sub>4</sub>	$7.08 \times 10^{-3}$	2.15 (pK <sub>1</sub> )
Formic acid	$1.78 \times 10^{-4}$	3.75
Succinic acid	$6.17 \times 10^{-5}$	4.21 (pK <sub>1</sub> )
Oxalate <sup>-</sup>	$5.37 \times 10^{-8}$	4.27 (pK <sub>2</sub> )
Acetic acid	$1.74 \times 10^{-5}$	4.76
Succinate <sup>-</sup>	$2.29 \times 10^{-6}$	5.64 (pK <sub>2</sub> )
2-(N-Morpholino)ethanesulfonic acid (MES)	$8.13 \times 10^{-7}$	6.09
H <sub>2</sub> CO <sub>3</sub>	$4.47 \times 10^{-7}$	6.35 (pK <sub>1</sub> ) <sup>a</sup>
Piperazine-N,N'-bis(2-ethanesulfonic acid) (PIPES)	$1.74 \times 10^{-7}$	6.76
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	$1.51 \times 10^{-7}$	6.82 (pK <sub>2</sub> )
3-(N-Morpholino)propanesulfonic acid (MOPS)	$7.08 \times 10^{-8}$	7.15
N-2-Hydroxyethylpiperazine-N'-2-ethanesulfonic acid (HEPES)	$3.39 \times 10^{-8}$	7.47
Tris(hydroxymethyl)aminomethane (Tris)	$8.32 \times 10^{-9}$	8.08
NH <sub>4</sub> <sup>+</sup>	$5.62 \times 10^{-10}$	9.25
Glycine (amino group)	$1.66 \times 10^{-10}$	9.78
HCO <sub>3</sub> <sup>-</sup>	$4.68 \times 10^{-11}$	10.33 (pK <sub>2</sub> )
Piperidine	$7.58 \times 10^{-12}$	11.12
HPO <sub>4</sub> <sup>2-</sup>	$4.17 \times 10^{-13}$	12.38 (pK <sub>3</sub> )

Source: Dawson, R.M.C., Elliott, D.C., Elliott, W.H., and Jones, K.M., *Data for Biochemical Research* (3rd ed.), pp. 424-425, Oxford Science Publications (1986); and Good, N.E., Winget, G.D., Winter, W., Connolly, T.N., Izawa, S., and Singh, R.M.M., *Biochemistry* 5, 467 (1966).  
<sup>a</sup>The pK for the overall reaction  $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ ; see Box 2-2.

Table 2-4 Fundamentals of Biochemistry, 2/e  
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### Blood Buffering System

- Bicarbonate most significant buffer
- Formed from gaseous CO<sub>2</sub>

$$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$$

$$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$$
- Normal value blood pH 7.4
- Deviations from normal pH value lead to acidosis

### Henderson - Hasselbalch type problems:

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

You may be asked the pH, pK, the ratio of acid or base or solve for the final concentrations of each.

### The 6 step approach

1. Write the Henderson + Hasselbalch equation.
2. Write the acid base equation
3. Make sure either an H<sup>+</sup> or OH<sup>-</sup> is in the equation.
3. Find out what you are solving for
4. Write down all given values.
5. Set up equilibrium conditions.
6. Plug in H + H equation and solve.

What is the pH of a solution of that contains 0.1M CH<sub>3</sub>COO<sup>-</sup> and 0.9 M CH<sub>3</sub>COOH?

$$1) \text{pH} = \text{pK} + \log \frac{[\text{A}^-]}{[\text{HA}]}$$



3) Find pH

$$4) \text{pK} = 4.76 \quad \text{A}^- = 0.1 \text{ M} \quad \text{HA} = 0.9 \text{ M}$$

5) Already at equilibrium

$$6) \quad X = 4.76 + \log \frac{0.1}{0.9}$$

$$\log 0.111 = -.95 \quad X = 4.76 + (-.95) \quad X = 3.81$$

What would the concentration of  $\text{CH}_3\text{COO}^-$  be at pH 5.3 if 0.1M  $\text{CH}_3\text{COOH}$  was adjusted to that pH.

- 1)  $\text{pH} = \text{pK} + \text{Log} \frac{[\text{A}^-]}{[\text{HA}]}$
- 2)  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$
- 3) Find equilibrium value of  $[\text{A}^-]$  i.e.  $[\text{CH}_3\text{COO}^-]$
- 4)  $\text{pH} = 5.3$ ;  $\text{pK} = 4.76$
- 5) Let  $X$  = amount of  $\text{CH}_3\text{COOH}$  dissociated at equilibrium

$$\begin{aligned} [\text{A}^-] &= [X] \\ [\text{HA}] &= [0.1 - X] \end{aligned}$$

- 6)  $5.3 = 4.76 + \text{Log} \frac{[X]}{[0.1 - X]}$

Now solve.

**Lecture 5**  
**Tuesday 9/08/09**  
**Amino Acids**