Acids and Bases

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Lecture 1

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Required material and further reading

Required:

Handout

Text books:

Biochemistry. Campbell Chapter 2

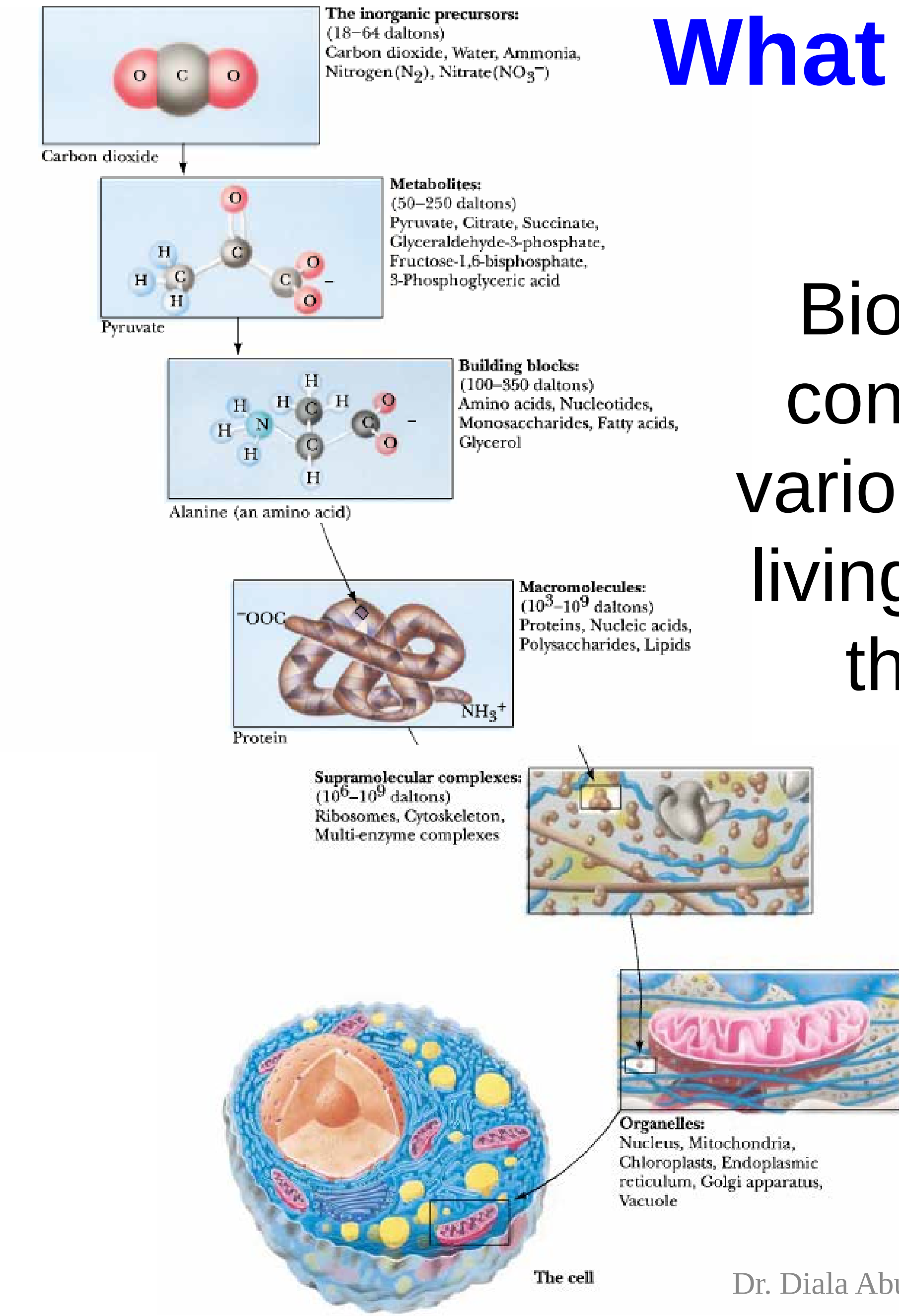
Fundamentals of General, Organic, and Biological Chemistry. McMurry. Chapter 10

softcopy will be sent

Outline

- Introduction- The Science of Biochemistry
- Definitions of acids and bases
- Acid and base strength
- The dissociation constant
- Conjugate pair strength
- Water dissociation

What is Biochemistry?



Biochemistry is the science concerned with studying the various molecules that occur in living cells and organisms and their chemical reactions.

Garret *et al*

Why Biochemistry is important to Human Biology?

1. Biochemistry is an intrinsically beautiful and fascinating body of knowledge. “Lubert Stryer”
Because it unravels the details of the most fundamental processes in biological systems.

2. Biochemistry massively influences medicine and treatment development, ex. sickle-cell anemia, cystic fibrosis, hemophilia, etc.

3. By advances in biochemistry, researchers can tackle many questions in biology and medicine, ex. Biochemical changes in diseases, causes of diseases, lab tests..etc.

Benefits of studying biological systems at the molecular and biochemical level

When we unravel the molecular and biochemical details of biological molecules:

1. Molecular and biochemical basis of diseases become clear.

2. Manipulate the biochemical processes and simulating them in vivo and in vitro.

3. Molecules of life can be prepared on the bench

What makes biomolecules special?

Table 1.1

Functional Groups of Biochemical Importance

Class of Compound	General Structure	Characteristic Functional Group	Name of Functional Group	Example
Alkenes	$RCH{=}CH_2$ $RCH{=}CHR$ $R_2C{=}CHR$ $R_2C{=}CR_2$	$C{=}C$	Double bond	$CH_2{=}CH_2$
Alcohols	ROH	$—OH$	Hydroxyl group	CH_3CH_2OH
Ethers	ROR	$—O—$	Ether group	CH_3OCH_3
Amines	RNH_2 R_2NH R_3N	$—N<$	Amino group	CH_3NH_2
Thiols	RSH	$—SH$	Sulfhydryl group	CH_3SH
Aldehydes	$R—C({=}O)—H$	$—C({=}O)—$	Carbonyl group	$CH_3C({=}O)H$
Ketones	$R—C({=}O)—R$	$—C({=}O)—$	Carbonyl group	$CH_3C({=}O)CH_3$
Carboxylic acids	$R—C({=}O)—OH$	$—C({=}O)—OH$	Carboxyl group	$CH_3C({=}O)OH$
Esters	$R—C({=}O)—OR$	$—C({=}O)—OR$	Ester group	$CH_3C({=}O)OCH_3$
Amides	$R—C({=}O)—NR_2$ $R—C({=}O)—NHR$ $R—C({=}O)—NH_2$	$—C({=}O)—N<$	Amide group	$CH_3C({=}O)N(CH_3)_2$
Phosphoric acid esters	$R—O—P({=}O)(OH)—OH$	$—O—P({=}O)(OH)—OH$	Phosphoric ester group	$CH_3—O—P({=}O)(OH)—OH$
Phosphoric acid anhydrides	$R—O—P({=}O)(OH)—O—P({=}O)(OH)—OH$	$—P({=}O)(OH)—O—P({=}O)(OH)—$	Phosphoric anhydride group	$HO—P({=}O)(OH)—O—P({=}O)(OH)—OH$

-The cellular apparatus of living organisms is made up of carbon compounds.

Different Definitions of Acids and Bases

- Arrhenius

- Bronsted-Lowry

- Lewis

Arrhenius Definition of Acids and Bases and Their Reactions

Arrhenius Acids and Bases Acids are

- Acids in H_2O are H^+ donors
- Bases in H_2O are OH^- donors

Neutralization of acids and bases produces salt and water.

Arrhenius 1903

Nobel Prize

$$NaOH \xrightarrow{H_2O} Na^+ + OH^-$$

$$HCL \xrightarrow{H_2O} Cl^- + H^+$$

$$H^+ + H{-}\ddot{O}{:}\ (\text{with } {-}H \text{ on O}) \longrightarrow H_3O^+$$

Drawbacks:

1. Reactions has to happen in aqueous solutions
2. H_3O^+ is released but not H^+

Bronsted-Lowry Definition of Acids and Bases and Their Reactions

Bronsted-Lowry Acids and Bases (1923)

- Acids donate H^+
- Bases accept H^+ (non-bonding pairs)

Conjugate acid-base pair

$$B: + H-A \rightleftharpoons BH^+ + A^-$$

Base Acid Acid Base

Conjugate acid-base pair

Lewis Definition of Acids and Bases and Their Reactions

- Acids accept electrons
- Bases donate electrons (non-bonding pairs)

$$BF_3 + :NH_3 \longrightarrow F_3B\cdots\cdots:NH_3$$

Acid **base**

Common Acids

- HCl- hydrochloric- stomach acid
- H_2SO_4- sulfuric acid - car batteries
- HNO_3 – nitric acid - explosives
- $HC_2H_3O_2$- acetic acid - vinegar
- H_2CO_3-carbonic acid – sodas
- H_3PO_4- phosphoric acid -flavorings

Common Bases

- NaOH- sodium hydroxide (LYE) soaps, drain cleaner
- Mg $(OH)_2$ - magnesium hydroxide-antacids
- $Al(OH)_3$-aluminum hydroxide-antacids, deodorants
- NH_4OH-ammonium hydroxide- “ammonia”

Water as both an acid and a base

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

base acid acid base

$$H_2O + HCl \rightleftharpoons H_3O^+ + Cl^-$$

base acid acid base

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

(strong acid) (weak base)

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

(weak acid) (strong base)

Strong acid + strong base $\rightleftharpoons$ weak base + weak acid

Amphoterism - an ion or molecule can act as an acid or base depending upon the reaction conditions

Water in NH_3 serves as an acid

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

H_2O	NH_3	NH_4^+	OH^-
acid	base	acid	base

Water in acetic acid serves as a base

$$H_2O + CH_3CO_2H \rightleftharpoons H_3O^+ + CH_3CO_2^-$$

H_2O	CH_3CO_2H	H_3O^+	$CH_3CO_2^-$
base	acid	acid	base
		Conjugate acid of H_2O	Conjugate base of acetic acid

Measuring concentrations

Molarity: the number of moles in a liter of solution

Unit: Mole/Liter = M

mM = 10^{-3} M, uM = 10^{-6} M

Symbol: [X]

$$\text{Concentration} = \frac{\text{Amount of solute}}{\text{Amount of solvent}}$$

Dissolve 2 moles of glucose in 5 liters of H_20. what is the concentration?

[Glucose] = 2/5 = 0.4 M

Acid and Base Strength

- Some acids can cause burns if come in contact with skin, other acids are safe. why?
- How easy can the acid produce proton

  - Strong acid: gives up H^+ easily (100% dissociated in water)

    $$HCl \longrightarrow H^+ + Cl^-$$

  - Weak acid: gives up H^+ with difficulty (less than 100% dissociated)

    $$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

Acid dissociation constant, K_a

– The general ionization of an acid is as follows:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

So the acid dissociation constant is as follows:

$$K_a = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$[H_2O]$ = 55.5 M and is constant in all equations

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

Acid dissociation constant

– The general ionization of an acid is as follows:

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

So the acid dissociation constant is as follows:

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

There are many orders of magnitude spanned by K_a values, so pK_a is used instead:

$$pK_a = \log 1/K_a = -\log_{10} K_a$$

The larger the value of the pK_a, the smaller the extent of dissociation.

The equilibrium constant, Ka

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

Acid

Conjugate base

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

Larger K_a means:

More dissociation

Smaller pK_a

Stronger acid

Increase acid strength

Decrease acid strength

TABLE 8-2	Acidity Constants in Water at 25°C			
Acid	**Formula**	**Conjugate Base**	**K_a**	**pK_a**
Hydriodic	HI	I^-	$\approx 10^{11}$	≈ -11
Hydrobromic	HBr	Br^-	$\approx 10^{9}$	≈ -9
Perchloric	$HClO_4$	ClO_4^-	$\approx 10^{7}$	≈ -7
Hydrochloric	HCl	Cl^-	$\approx 10^{7}$	≈ -7
Chloric	$HClO_3$	ClO_3^-	$\approx 10^{3}$	≈ -3
Sulfuric (1)	H_2SO_4	HSO_4^-	$\approx 10^{2}$	≈ -2
Nitric	HNO_3	NO_3^-	≈ 20	≈ -1.3
Hydronium ion	H_3O^+	H_2O	1	0.0
Urea acidium ion	$(NH_2)CONH_3^+$	$(NH_2)_2CO$ (urea)	6.6×10^{-1}	0.18
Iodic	HIO_3	IO_3^-	1.6×10^{-1}	0.80
Oxalic (1)	$H_2C_2O_4$	$HC_2O_4^-$	5.9×10^{-2}	1.23
Sulfurous (1)	H_2SO_3	HSO_3^-	1.5×10^{-2}	1.82
Sulfuric (2)	HSO_4^-	SO_4^{2-}	1.2×10^{-2}	1.92
Chlorous	$HClO_2$	ClO_2^-	1.1×10^{-2}	1.96
Phosphoric (1)	H_3PO_4	$H_2PO_4^-$	7.5×10^{-3}	2.12
Arsenic (1)	H_3AsO_4	$H_2AsO_4^-$	5.0×10^{-3}	2.30
Chloroacetic	$ClCH_2COOH$	$ClCH_2COO^-$	1.4×10^{-3}	2.85
Hydrofluoric	HF	F^-	6.6×10^{-4}	3.18
Nitrous	HNO_2	NO_2^-	4.6×10^{-4}	3.34
Formic	$HCOOH$	$HCOO^-$	1.8×10^{-4}	3.74

Acid dissociation constant

Acid Dissociation Constants and pK_a Values for Some Weak Electrolytes (at 25°C)

Acid	K_a (M)	pK_a
HCOOH (formic acid)	1.78×10^{-4}	3.75
CH_3COOH (acetic acid)	1.74×10^{-5}	4.76
CH_3CH_2COOH (propionic acid)	1.35×10^{-5}	4.87
$CH_3CHOHCOOH$ (lactic acid)	1.38×10^{-4}	3.86
$HOOCCH_2CH_2COOH$ (succinic acid) pK_1*	6.16×10^{-5}	4.21
$HOOCCH_2CH_2COO^-$ (succinic acid) pK_2	2.34×10^{-6}	5.63
H_3PO_4 (phosphoric acid) pK_1	7.08×10^{-3}	2.15
$H_2PO_4^-$ (phosphoric acid) pK_2	6.31×10^{-8}	7.20
HPO_4^{2-} (phosphoric acid) pK_3	3.98×10^{-13}	12.40
$C_3N_2H_5^+$ (imidazole)	1.02×10^{-7}	6.99
$C_6O_2N_3H_{11}^+$ (histidine–imidazole group) pK_R†	9.12×10^{-7}	6.04
H_2CO_3 (carbonic acid) pK_1	1.70×10^{-4}	3.77
HCO_3^- (bicarbonate) pK_2	5.75×10^{-11}	10.24
$(HOCH_2)_3CNH_3^+$ (*tris*-hydroxymethyl aminomethane)	8.32×10^{-9}	8.07
NH_4^+ (ammonium)	5.62×10^{-10}	9.25
$CH_3NH_3^+$ (methylammonium)	2.46×10^{-11}	10.62

*These pK values listed as pK_1, pK_2, or pK_3 are in actuality pK_a values for the respective dissociations. This simplification in notation is used throughout this book.

†pK_R refers to the imidazole ionization of histidine.

Data from *CRC Handbook of Biochemistry*, The Chemical Rubber Co., 1968.

Base dissociation constant

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

$$K_b = \frac{[BH+][OH^-]}{[B]}$$

Reverse the reaction:

$$BH^+ \rightleftharpoons B + H^+$$

$$K_a = \frac{[B][H^+]}{[BH^+]}$$

Weak Bases

TABLE 7.3 Values of K_b for Some Common Weak Bases

Name	Formula	Conjugate Acid	K_b
Ammonia	NH_3	NH_4^+	1.8×10^{-5}
Methylamine	CH_3NH_2	$CH_3NH_3^+$	4.38×10^{-4}
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3^+$	5.6×10^{-4}
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3^+$	3.8×10^{-10}
Pyridine	C_5H_5N	$C_5H_5NH^+$	1.7×10^{-9}

Strong Acids

- Dissociate readily
- Ka is very large
- Examples: Hydrochloric, Nitric; Sulfuric

Ex. $HCl \rightarrow H^+ + Cl^-$

$$Ka = \frac{[H^+]\,[Cl^-]}{[HCl]}$$

$$[H^+] = [acid]$$

Ex.1 M solution of HCl has a $[H^+]$ of 1 M

1 mM HCl solution has a $[H^+]$ of 1 mM

0.1 M H_2SO_4 solution has a $[H^+]$ of 0.2 M

Weak Acids

- Dissociate slightly
- Ka is smaller than strong acids
- Examples: Acetic, Boric, Nitrous, Phosphoric, Sulfurous

Ex. $CH_3COOH + H_2O \longleftrightarrow CH_3COO^- + H_3O^+$

$$Ka = \frac{[H+]\,[CH_3COO^-]}{[CH_3COOH]}$$

What is the H+ of a 0.1 M solution of acetic acid?

$Ka = 1.74 \times 10^{-5}$

$1.74 \times 10^{-5} = x^2/[0.1 - x]$

$x^2 = 1.74 \times 10^{-6}$, or $x = 1.32 \times 10^{-3}$ M

Conjugate pair strength

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

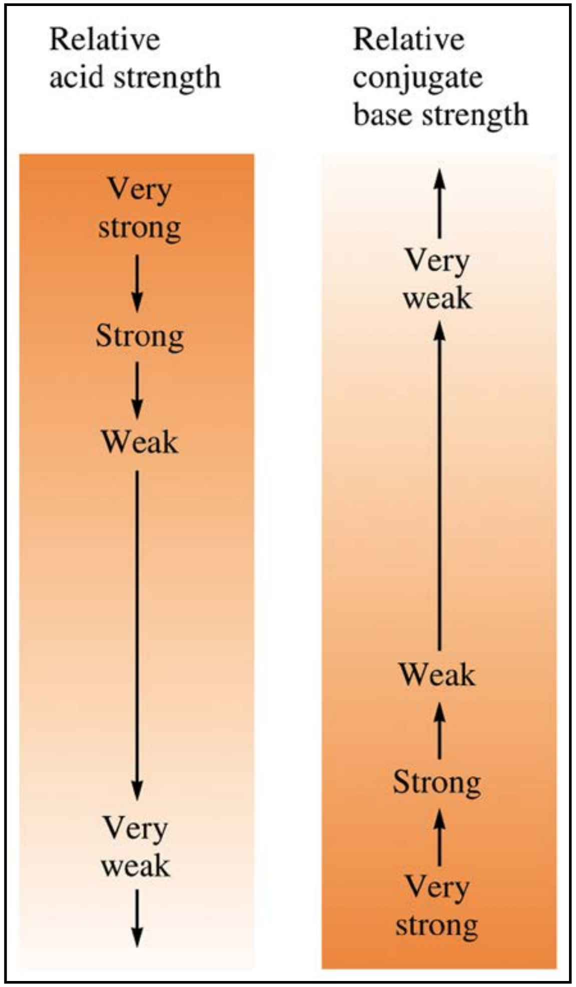
$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Weak acid   weak base   strong base   strong acid

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

Stronger acid   strong base   weak base   weak acid



Strong acid + strong base $\rightleftharpoons$ Weak base + Weak acid

Equilibrium constant and the pH of water

H_2O dissociates to a slight extent to form hydrogen (H^+) and hydroxyl (OH^-) ions.

$$H_2O \rightleftharpoons H^+ + OH^-$$

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

$$K_{eq} = \frac{(10^{-7})(10^{-7})}{55.5} = 1.8 \times 10^{-16}$$

Because the concentration of H_2O in pure water is essentially constant, a new constant, K_w, **the ion product of water,** can be written as

$$K_w = 55.5\ K_{eq} = 10^{-14} = [H^+][OH^-]$$

[H+] of pure water is only 0.0000001 M

Dissociation of water

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

Example: A solution has an $[OH^-] = 10^{-9}$ M

$[H_3O^+] = 10^{-5}$ M

Problem solving

Example:

What is the $[H^+]$ of a 0.01 M NaOH solution?

$Kw = [H^+] \times [OH^-] = [H^+] \times 10^{-2} = 10^{-14}$

$[H^+] = 10^{-12}$ M

Example:

What is the $[OH^-]$ of a 0.01 M HCl solution?

$Kw = [H^+] \times [OH^-] = 10^{-2} \times [OH^-] = 10^{-14}$

$[OH^-] = 10^{-12}$ M

Example:

Find the K_a of a 0.04 M weak acid HA whose $[H^+]$ is 1×10^{-4}?

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

$K_a = [A^-]\,[H^+] / [HA] = [H^+]^2 / [HA] = 10^{-4} \times 10^{-4} / 0.04 = 2.5 \times 10^{-7}$

Example 2:

What is the $[H^+]$ of a 0.05 M $Ba(OH)_2$?

$Ba(OH)_2 \rightleftharpoons Ba + 2OH^-$

$[OH^-] = 2x\ 0.05 = 0.10\ M = 1 \times 10^{-1}$

$[H^+] = 1x\ 10^{-13}$

Example 4:

The $[H^+]$ of a 0.03 M weak base solution is 1×10^{-10} M. Calculate pKb?

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

$[OH^-] = 10^{-4}$

$K_b = (10^{-4} \times 10^{-4}) / 0.03 = 3.33 \times 10^{-7}$ M

$pK_b = -\log K_b = 6.48$