Ⓘ

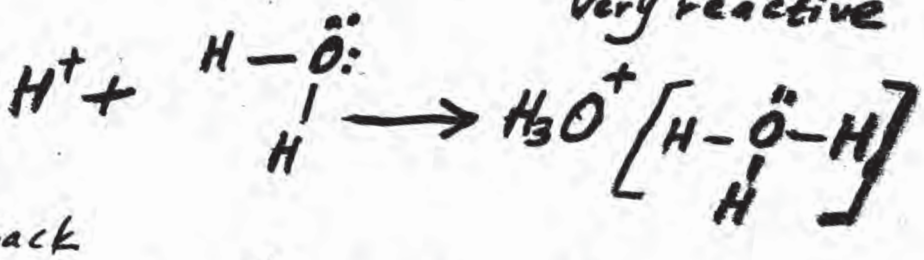
ACIDS & BASES

- Arrhenius Difinitions of Acids & Bases

- Acids in $H_2O \longrightarrow H^+$
- Bases " " $\longrightarrow OH^-$
- neutralization of acid & base → salt + H_2O

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

$$HCl \xrightarrow{\text{in } H_2O} Cl^- + \underbrace{H^+}_{\text{very reactive}}$$

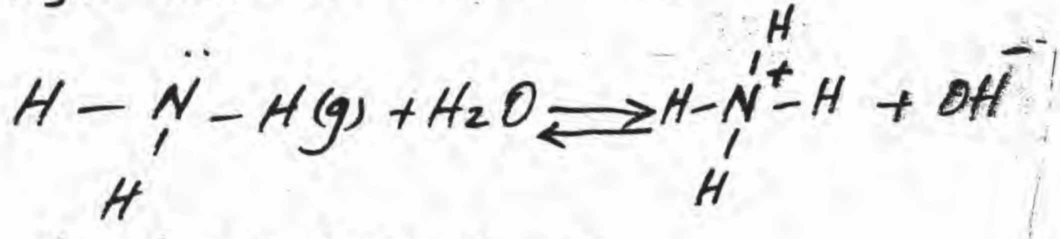


$$H^+ + H_2O \longrightarrow H_3O^+ \left[H-\ddot{O}-H\right]$$

Drawback

(1) H_3O^+ not H^+ is released

(2)



$$NH_3(g) + H_2O \rightleftarrows NH_4^+ + OH^-$$

(3) reaction is necessary in aq.

e.g. $NH_{3(g)} + HCl_{(g)}$

Common Acids & Bases

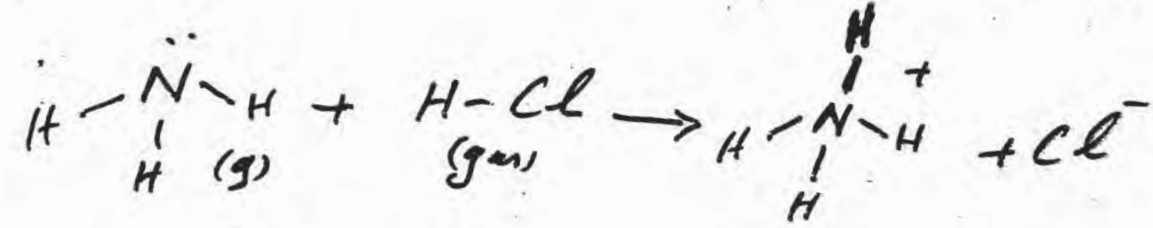
Acids:- H_2SO_4, HCl, H_3PO_4 & HNO_3, CH_3COOH

Bases:- Metal hydroxides:- $NaOH$, $Ca(OH)_2$, $Mg(OH)_2$, Ammonia (NH_3)

- Bronsted-Lowry Difinition of Acids & Bases

Acid : proton donor

Base : Proton acceptor
should have at least one non-bonding electron pair



$$H-\overset{\cdot\cdot}{\underset{\underset{H}{|}}{N}}-H_{(g)} + \underset{(gas)}{H-Cl} \longrightarrow \left[H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}-H\right]^{+} + Cl^{-}$$

$$B: + H-A \rightleftharpoons \overset{+}{B}H + A^{-}$$

$$\bar{B}: + H-A \rightleftharpoons BH + A^{-}$$

$$NH_3 + H-A \rightleftharpoons NH_4^{+} + :A^{-}$$

$$H-\ddot{\underset{\cdot\cdot}{O}}:^{-} + H-A \rightleftharpoons H_2O + A^{-}$$

$$\underset{Base}{B:} + \underset{Acid}{H-A} \rightleftharpoons \underset{Base}{:\bar{A}} + \underset{Acid}{\overset{+}{B}-H}$$

conjugate acid-base pair

Conjugate acid-base pairs:

$$\text{Conjugate acids}\left\{\begin{array}{l} CH_3\overset{O}{\overset{\|}{C}}-OH \rightleftharpoons H^+ + CH_3\overset{O}{\overset{\|}{C}}O^- \\ H_3O^+ \rightleftharpoons H^+ + H_2O \\ NH_4^+ \rightleftharpoons H^+ + NH_3 \end{array}\right\}\text{conjugate bases}$$

Water as both an Acid and a Base:

$$\underset{\text{(bases)}}{CH_3-\overset{O}{\overset{\|}{C}}-O} + \underset{\text{(acid)}}{H_2O} \rightleftharpoons \underset{\text{(acid)}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{base}}{OH^-}$$

$$\underset{\text{(base)}}{H-\underset{\underset{H}{|}}{\ddot{O}}:} + \underset{\text{acid}}{HCl} \rightarrow \underset{\underset{\text{acid}}{(H_3O)}}{H-\underset{\underset{H}{|}}{O}-H^+} + \underset{\text{(base)}}{Cl^-}$$

strong	$HClO_4$	ClO_4^-	v.v. weak or no reaction
	H_2SO_4	HSO_4^-	
	HCl	Cl^-	
weak	HNO_2	NO_2^-	v. weak bases
	CH_3COOH	CH_3COO^-	
v. weak	H_2CO_3	HCO_3^-	weak bases
	$H_2PO_4^-$	HPO_4^{2-}	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
v.v. weak	H_2O	OH^-	strong base

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Table 10.1 Relative strengths of acids and conjugate bases

TABLE 10.1 Relative Strengths of Acids and Conjugate Bases

Increasing acid strength ↑		ACID		CONJUGATE BASE			Increasing base strength ↓
	Strong acids: 100% dissociated	Perchloric acid	$HClO_4$	ClO_4^-	Perchlorate ion	Little or no reaction as bases	
		Sulfuric acid	H_2SO_4	HSO_4^-	Hydrogen sulfate ion		
		Hydriodic acid	HI	I^-	Iodide ion		
		Hydrobromic acid	HBr	Br^-	Bromide ion		
		Hydrochloric acid	HCl	Cl^-	Chloride ion		
		Nitric acid	HNO_3	NO_3^-	Nitrate ion		
		Hydronium ion	H_3O^+	H_2O	**Water**		
	Weak acids	Hydrogen sulfate ion	HSO_4^-	SO_4^{2-}	Sulfate ion	Very weak bases	
		Phosphoric acid	H_3PO_4	$H_2PO_4^-$	Dihydrogen phosphate ion		
		Nitrous acid	HNO_2	NO_2^-	Nitrite ion		
		Hydrofluoric acid	HF	F^-	Fluoride ion		
		Acetic acid	CH_3COOH	CH_3COO^-	Acetate ion		
	Very weak acids	Carbonic acid	H_2CO_3	HCO_3^-	Bicarbonate ion	Weak bases	
		Dihydrogen phosphate ion	$H_2PO_4^-$	HPO_4^{2-}	Hydrogen phosphate ion		
		Ammonium ion	NH_4^+	NH_3	Ammonia		
		Hydrocyanic acid	HCN	CN^-	Cyanide ion		
		Bicarbonate ion	HCO_3^-	CO_3^{2-}	Carbonate ion		
		Hydrogen phosphate ion	HPO_4^{2-}	PO_4^{3-}	Phosphate ion		
		Water	H_2O	OH^-	**Hydroxide ion**	Strong base	

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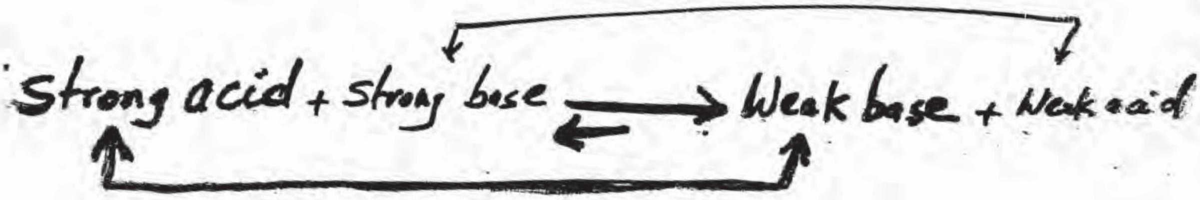
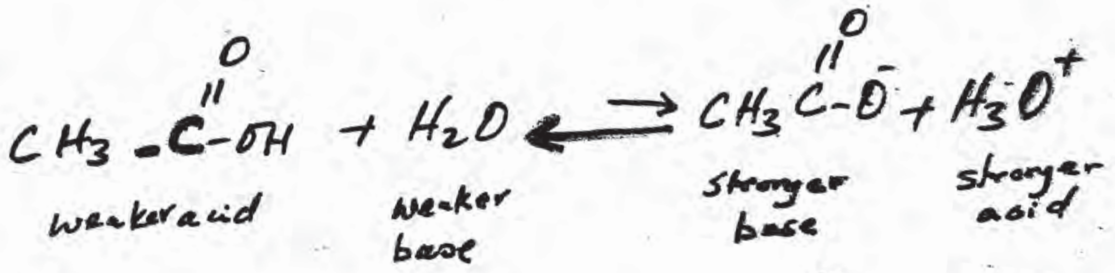
$$\underset{\text{Strong Acid}}{HA} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{weak base}}{A^-}$$

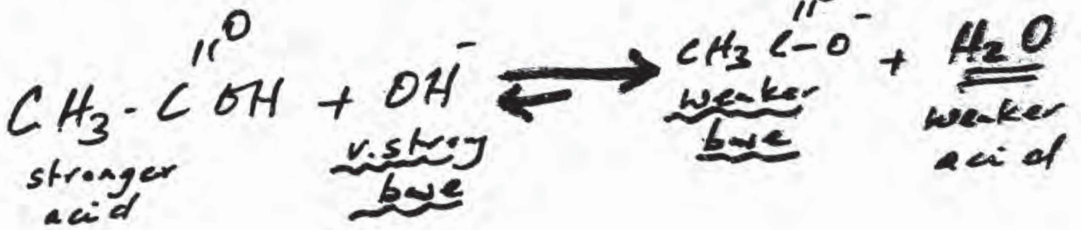
$$\underset{\text{Weak acid}}{HA} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{strong base}}{A^-}$$



$$\text{Strong acid} + \text{strong base} \rightleftharpoons \text{Weak base} + \text{Weak acid}$$



$$\underset{\text{weaker acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{weaker base}}{H_2O} \rightleftharpoons \underset{\text{stronger base}}{CH_3\overset{\overset{O}{\|}}{C}-O^-} + \underset{\text{stronger acid}}{H_3O^+}$$



$$\underset{\text{stronger acid}}{CH_3-\overset{\overset{O}{\|}}{C}OH} + \underset{\text{v. strong base}}{OH^-} \rightleftharpoons \underset{\text{weaker base}}{CH_3\overset{\overset{O}{\|}}{C}-O^-} + \underset{\text{weaker acid}}{H_2O}$$

Table 10.2 Some acid dissociation constants, K_a, at 25 °C

TABLE 10.2 Some Acid Dissociation Constants, K_a, at 25 °C

ACID	K_a	ACID	K_a
Hydrofluoric acid (HF)	3.5×10^{-4}	*Polyprotic acids*	
Hydrocyanic acid (HCN)	4.9×10^{-10}	Sulfuric acid	
Ammonium ion (NH_4^+)	5.6×10^{-10}	H_2SO_4	Large
		HSO_4^-	1.2×10^{-2}
Organic acids		Phosphoric acid	
Formic acid (HCOOH)	1.8×10^{-4}	H_3PO_4	7.5×10^{-3}
Acetic acid (CH_3COOH)	1.8×10^{-5}	$H_2PO_4^-$	6.2×10^{-8}
Propanoic acid	1.3×10^{-5}	HPO_4^{2-}	2.2×10^{-13}
(CH_3CH_2COOH)		Carbonic acid	
Ascorbic acid (vitamin C)	7.9×10^{-5}	H_2CO_3	4.3×10^{-7}
		HCO_3^-	5.6×10^{-11}

$pKa = -\log Ka$

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

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Acid Dissociation Constant

$$HA_{(aq)} + H_2O \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

$$\underset{(eq.constt.)}{K} = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \rightarrow 55.5\,M$$

Dissociation constt. $= K_a = K\,[H_2O]$

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

- Strong acids have large K_a, much greater than 1
  HNO_3, HCl H_2SO_4
- Weak acids have K_a much less than 1
  NH_4^+, CH_3COOH, H_2CO_3 4.3×10^{-7}, HCO_3^- 5.6×10^{-11}
  $\underset{6\times10^{-10}}{HCN}$, HF 3.5×10^{-4}, $HSO_4^-(1.3\times10^{-2})$
- Donation of each successive H^+ from Polyprotic acid is more difficult than the one before — K_a values becomes lower
- Most organic acid, containing $-CO_2H$ group have K_a values near 10^{-5}

II WATER & PH

- Simple and abundant
- Extraordinary physical, chemical and biological properties
- Vital to all forms of life
  70% to 85% the wt. of typical cell

Biological Roles of Water

- Biological Solvent

- Water serves as an essential buffer to regulate Temp. and PH
  High specific heat capacity

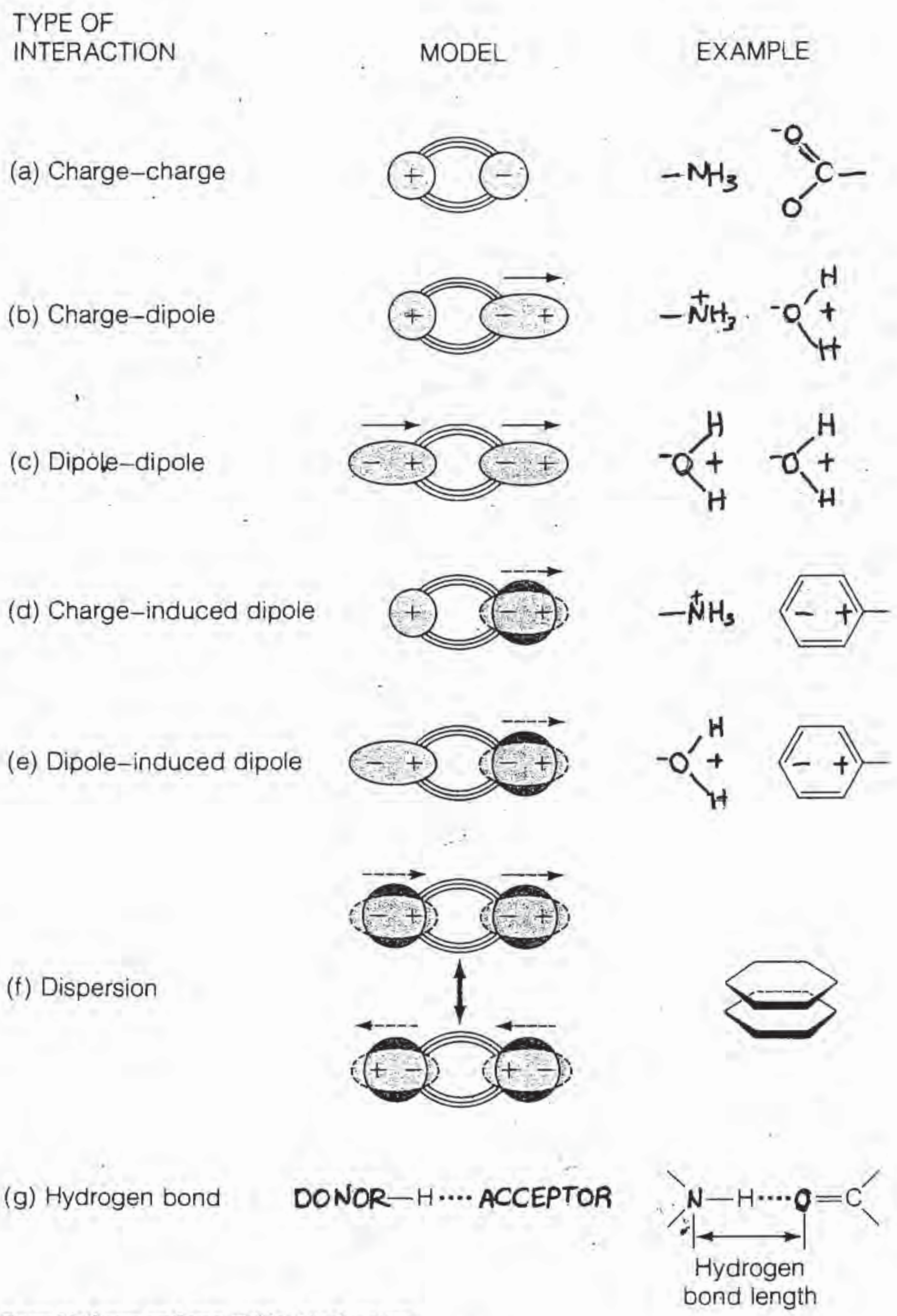
- Water is a participant in many biochemical reactions
  - Hydrolysis
  - photosynthesis

$$6CO_2 + 6H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2$$

  - Respiration - aerobic metabolism
  - others

Types of noncovalent interactions

Figure 2.1



From Mathews and van Holde: *Biochemistry*

Noncovalent Interactions in Biomolecules

- Ionic bonds
  between oppositely charged atoms or grou
  Energy 20-30 kJ/mole

- Hydrogen bonds
  - between H atom linked to electronegative atom (O, N or F) and electronegative atom
  10 - 30 kJ/mole

- van der Waals Interactions
  1-5 kJ/mole

- Hydrophobic interactions
  5-30 kj/mole

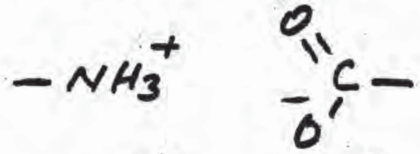
Characteristics of Non covalent Interactions:-

- relatively weak
  1-30 kJ/mole as compared to 350 kJ/mole in C-C
- Reversible
- Binding between molecules is specific

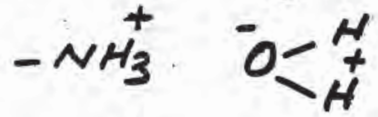
Weak Interactions in an Aqueous Environment

The nature of non-covalent interactions
(Essentially Electrostatics)

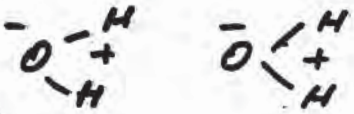
- Charge-Charge



- Charge-dipole



- Dipole-dipole

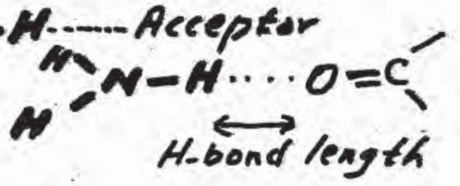


- charge-induced dipole

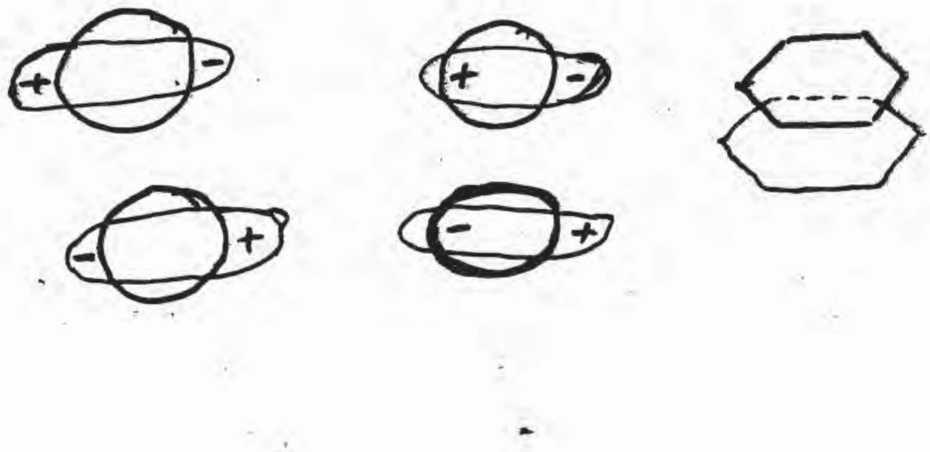
- Dipole-induced dipole

- Dispersion

- Hydrogen bond Doner—H........Acceptor



- Dispersion



Structure of Water

- electronegativity of O atom is 3.5
  H " " 2.1
- =

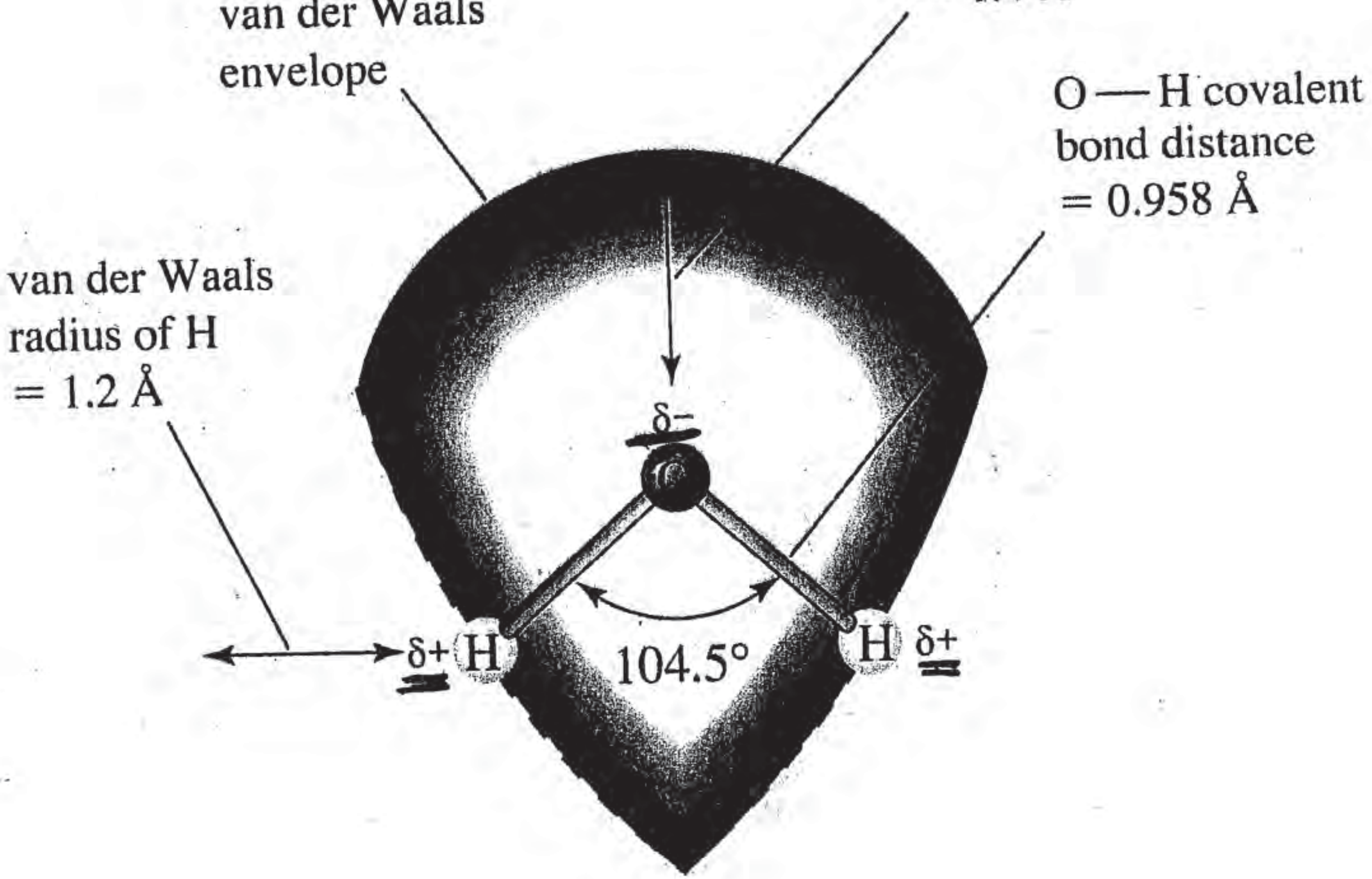


Figure 2-1a Concepts in Biochemistry, 3/e
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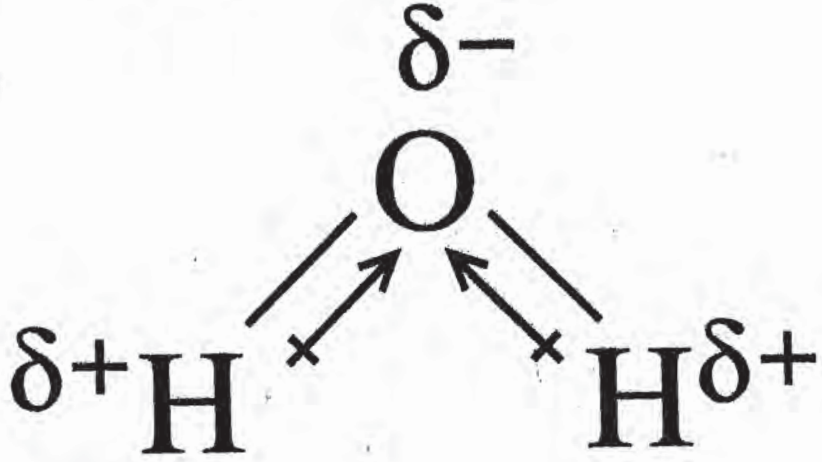
Water is electrically neutral (no net charge) but has relatively large dipole moment because of its bent geometry



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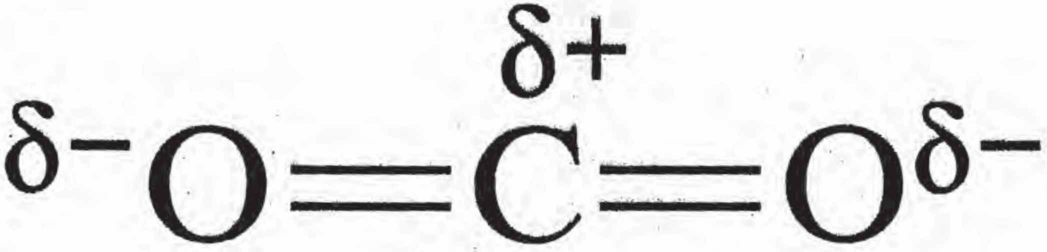
<u>CO_2</u> has polar bonds caused by electronegativity between C and O atoms but no dipole moment because it is linear



$$^{\delta-}\mathrm{O}=\overset{\delta+}{\mathrm{C}}=\mathrm{O}^{\delta-}$$

Figure 2-2 Concepts in Biochemistry, 3/e
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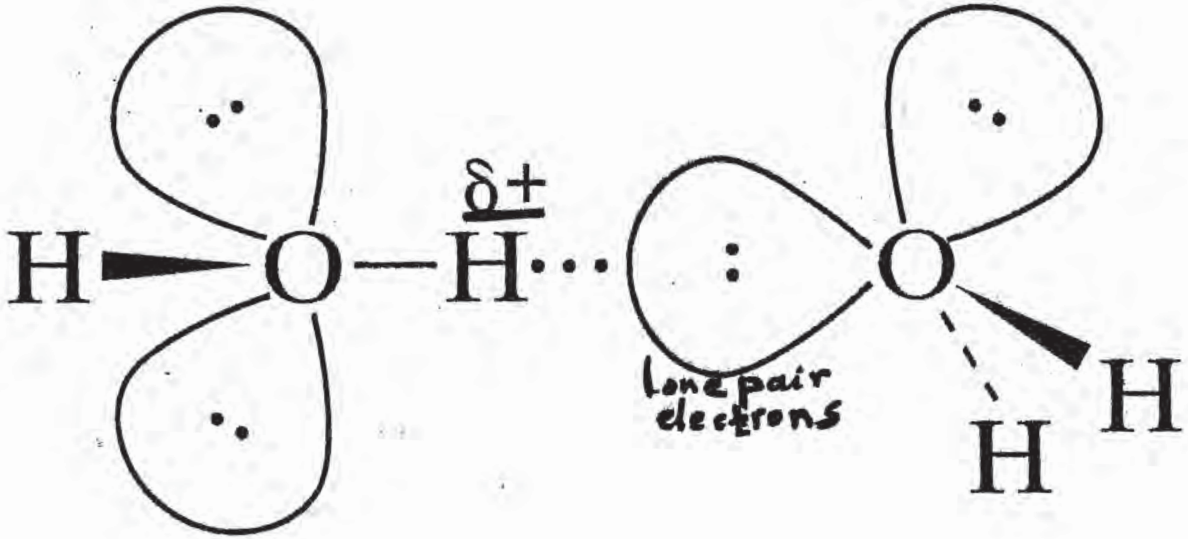
Hydrogen bond between two water molecules



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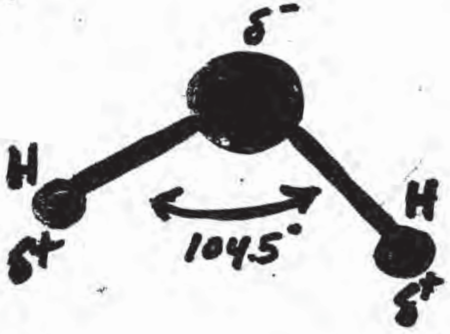
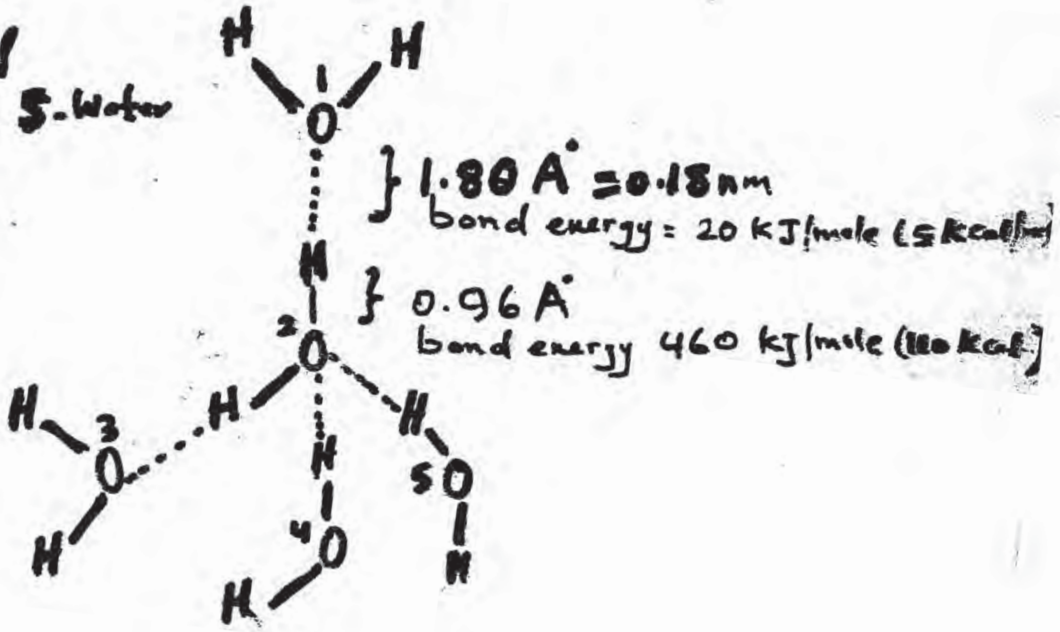
Hydrogen Bonds Between Water Molecules:-

The H–O–H bond angel



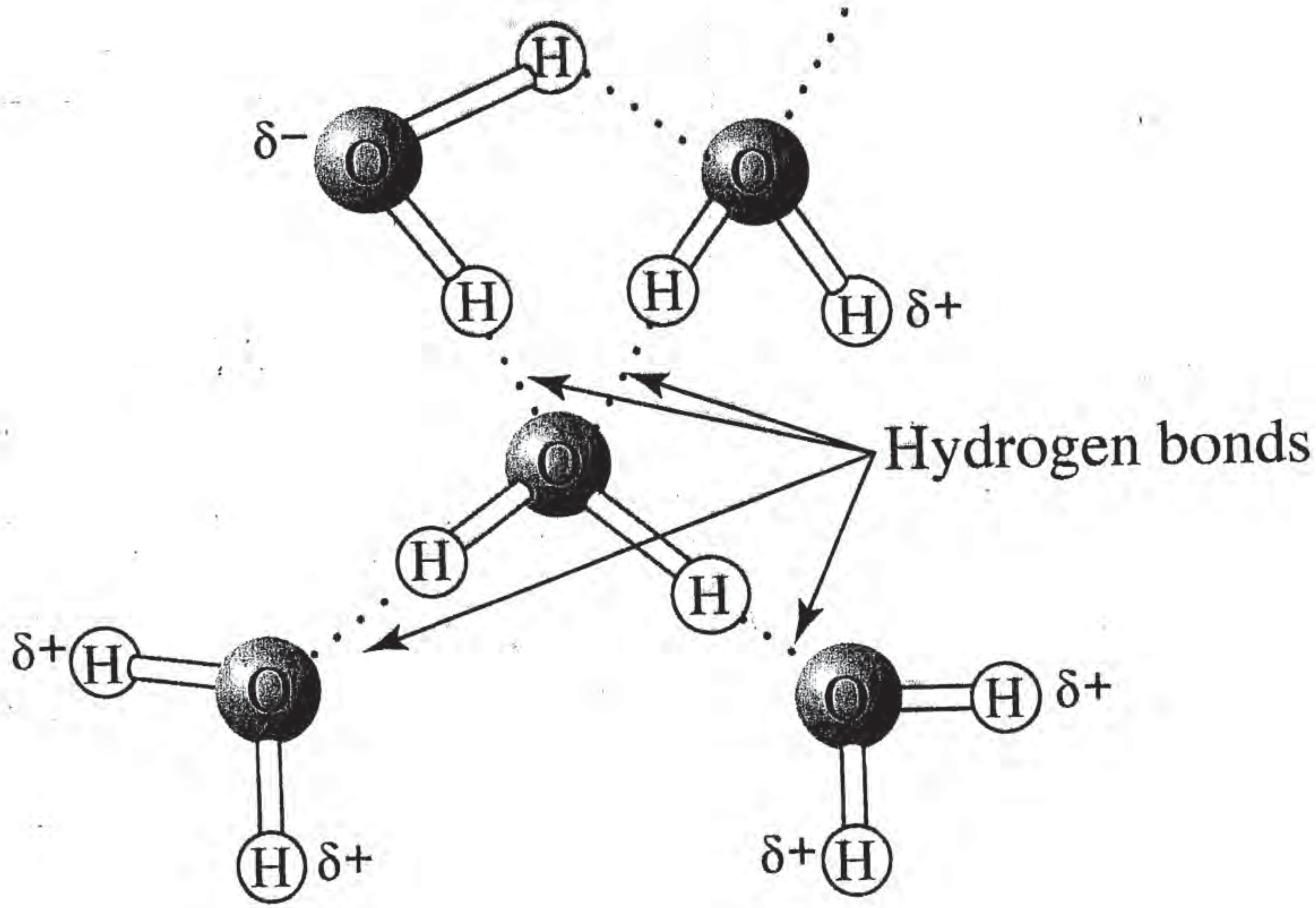
Tetrahedral H-bonding of 5-water molecules



Hydrogen bond is strongest when the three atoms X—H----A are linear

A can be oxygen, nitrogen or fluorine

X can be oxygen, nitrogen or fluorine



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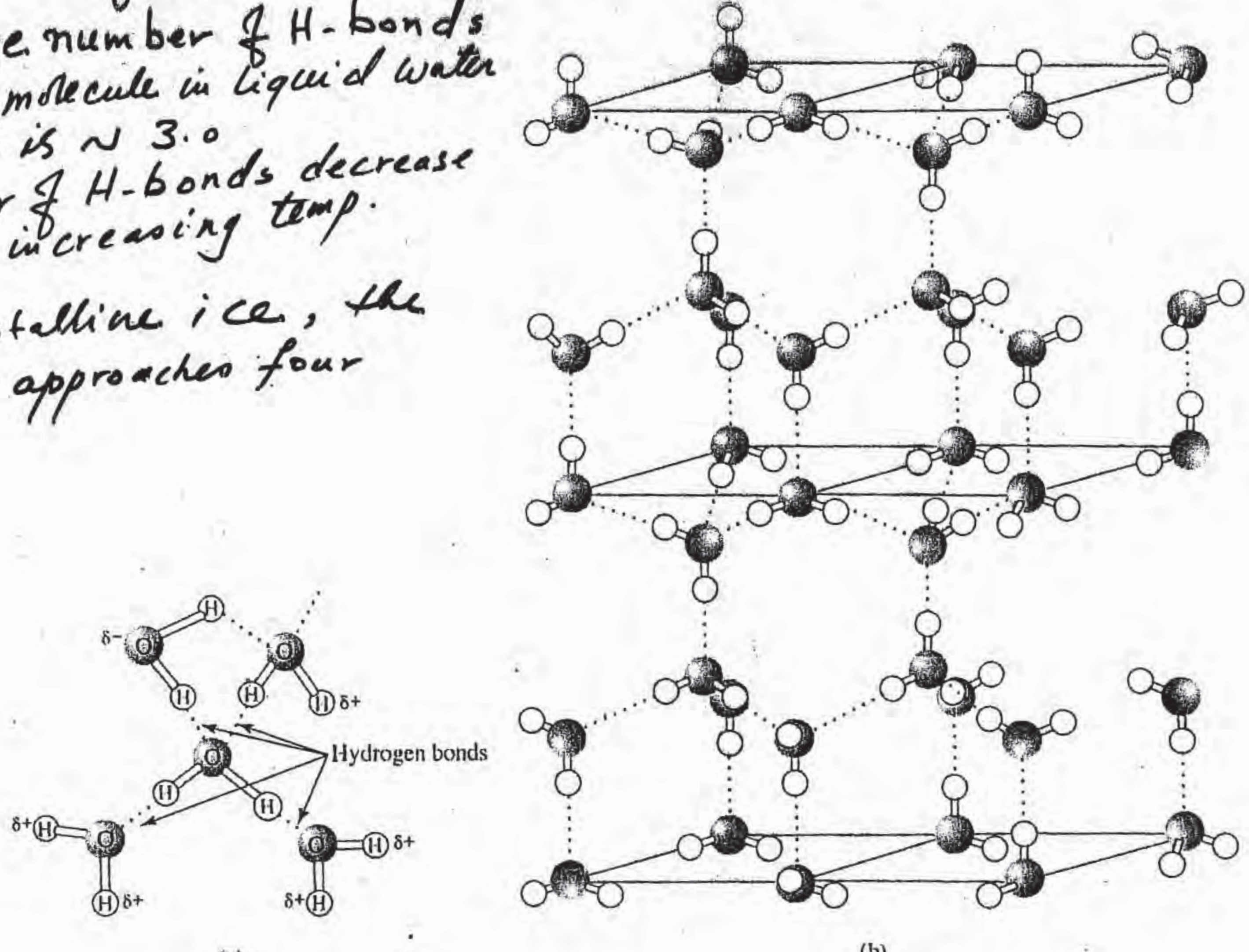
he network of Potential H-bonds in water

- Average number of H-bonds to each molecule in liquid water at 10°C is ~ 3.0
- Number of H-bonds decrease with increasing temp.
- In crystalline ice, the number approaches four



(a)

(b)

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Table 2.3
A comparison of some physical properties of water with hydrides of other nonmetallic elements: N, C, and S

Property	H_2O	NH_3	CH_4	H_2S
Molecular weight	18	17	16	34
Boiling point (°C)	100	−33	−161	−60.7
Freezing point (°C)	0	−78	−183	−85.5
Viscosity[a]	1.01	0.25	0.10	0.15

[a] Units are centipoise.

Table 2-3 Concepts in Biochemistry, 3/e

Physical Properties of Water:

- Hydrogen bonding Gives Water its unusual Properties
  - higher m.P. ; B.P. ; heat of vaporization, higher freezing , surface tension

H-O-H bond angle is 104.5°

Bond energy of H-bond is 20 kj/mole
life-time 1×10^{-9} s O-H 460 kj/mole bond energy

in liquid state each water molecule hydrogen bond with another 3.4 H_2O molecules

In Ice — $\underbrace{4\ H_2O \text{ molecules}}$
Larger vol. + less dense the ice-lattice

- Water forms Hydrogen bonds with solutes
  <u>H-bonds are not unique only to Water</u>

- Hydrogen atoms covalently bonded to carbon atoms, which are not electronegatives, do not participate in H-bonding

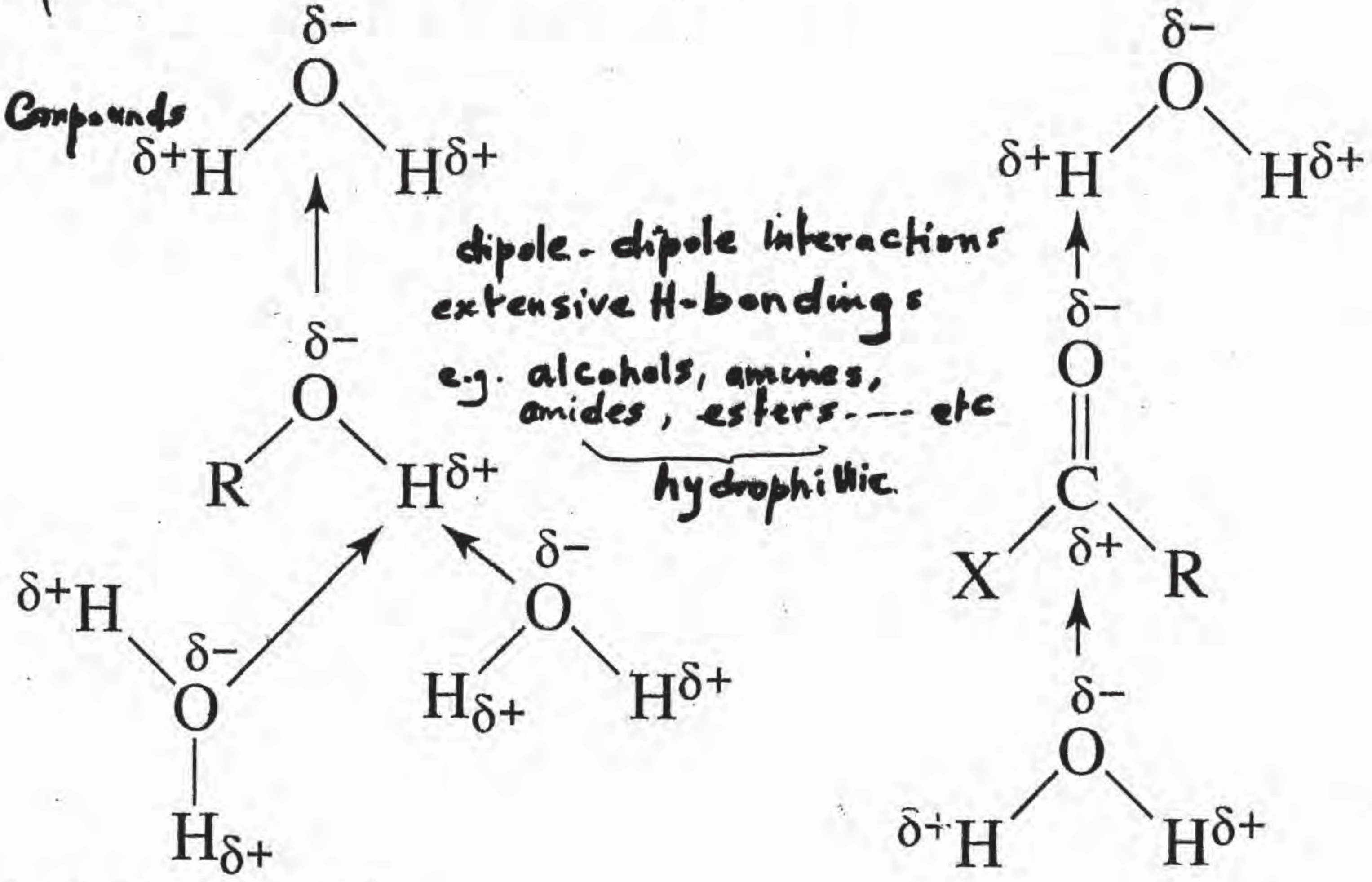
—O—H --- O=C<
—O—H --- N<
—O—H --- O<
>N—H — O=C<
>N—H --- O<
>N—H — N<

e.g.
- B.P. for butanol =117 °C
  $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$
- B.P. for butane = -0.5°C
  $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$

Water as a Solvent

Important solvent and transporter

1- Polar Compounds



dipole - dipole interactions
extensive H-bondings

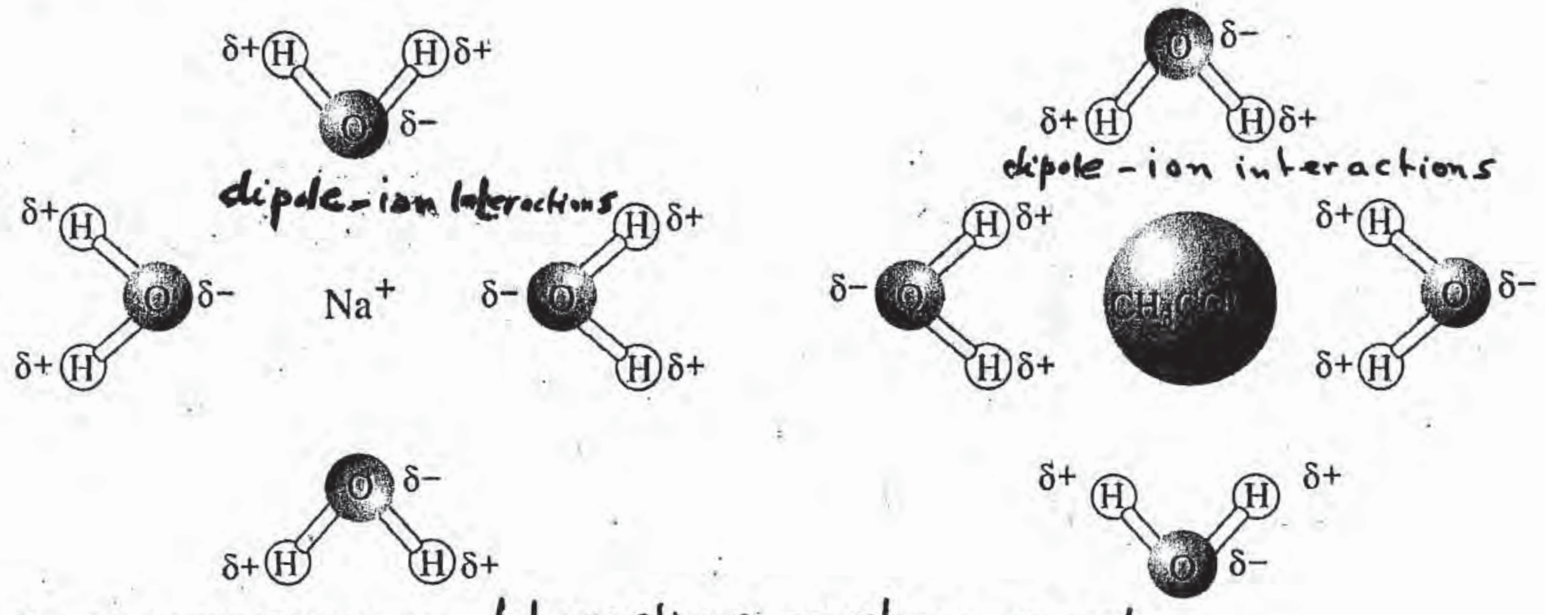
e.g. alcohols, amines, amides, esters. --- etc

hydrophillic

Figure 2-6a Concepts in Biochemistry, 3/e

2-Ionic Compounds

Individual ions are hydrated (solvated) by polar water molecules



dipole-ion Interactions

dipole-ion interactions

Figure 2-6b Concepts in Biochemistry, 3/e
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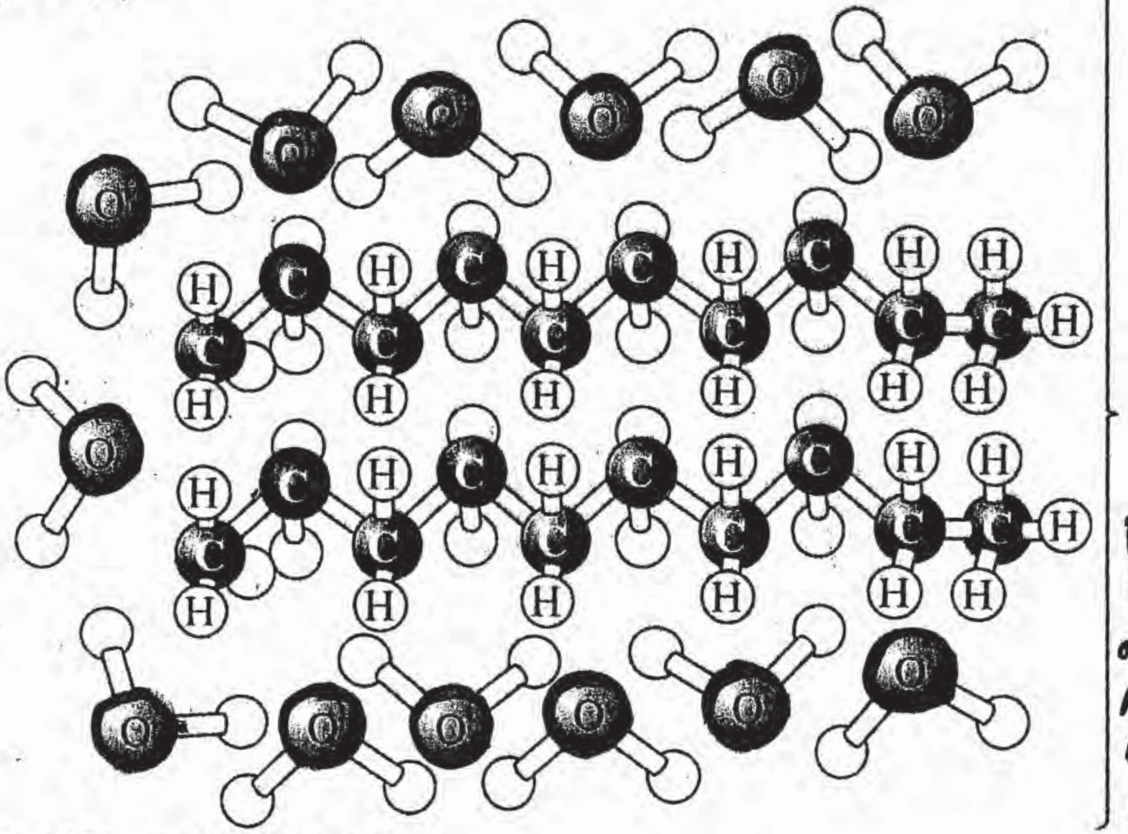
Interactions are strong enough to overcome the tendency of anions and cations to recombine

3- Nonpolar Compounds :- e.g. decane, benzene ... etc

- They do <u>not</u> contain ions or polar functional groups - Hydrophobic
- Amphiphilic e.g. sodium stearate



Water molecules in cage around hydrocarbon chain

Formation of this highly ordered cage of water requires much energy, which comes from hydrophobic interactions

Figure 2-7 Concepts in Biochemistry, 3/e
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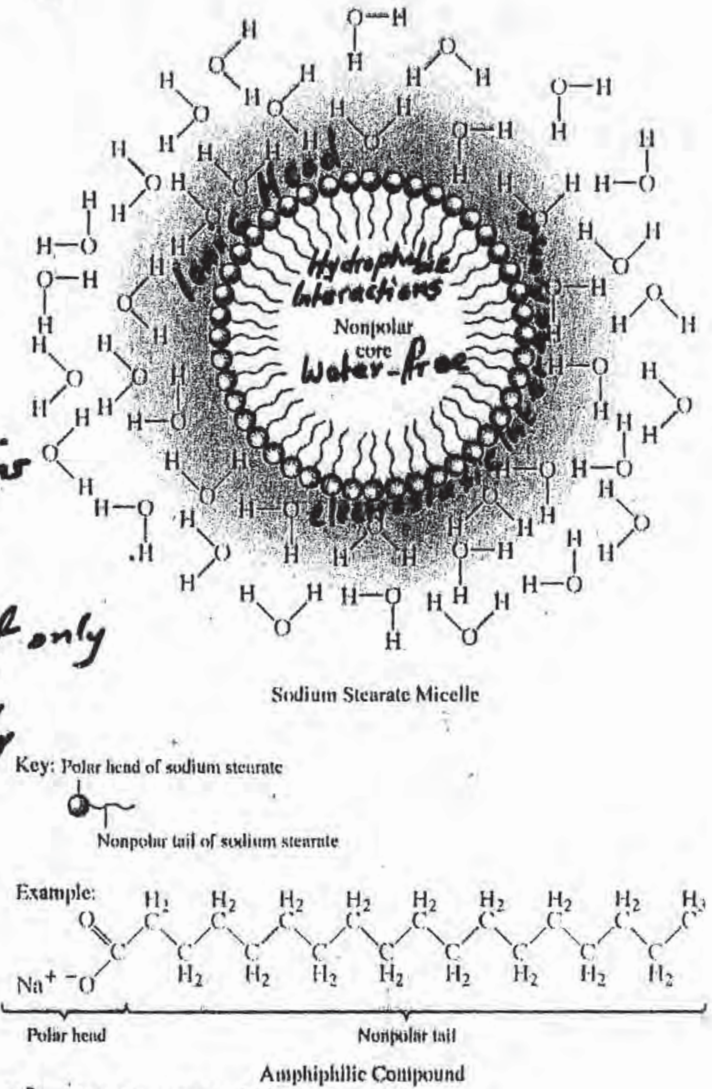
Amphiphilic Molecules

- . Soap action
- . changes in water structure by solutes
- - changes in solutes structure by water
- . Nucleic acids, proteins and some lipids are amphiphilie
- . Ordered arrangement only are often associated with biological activity



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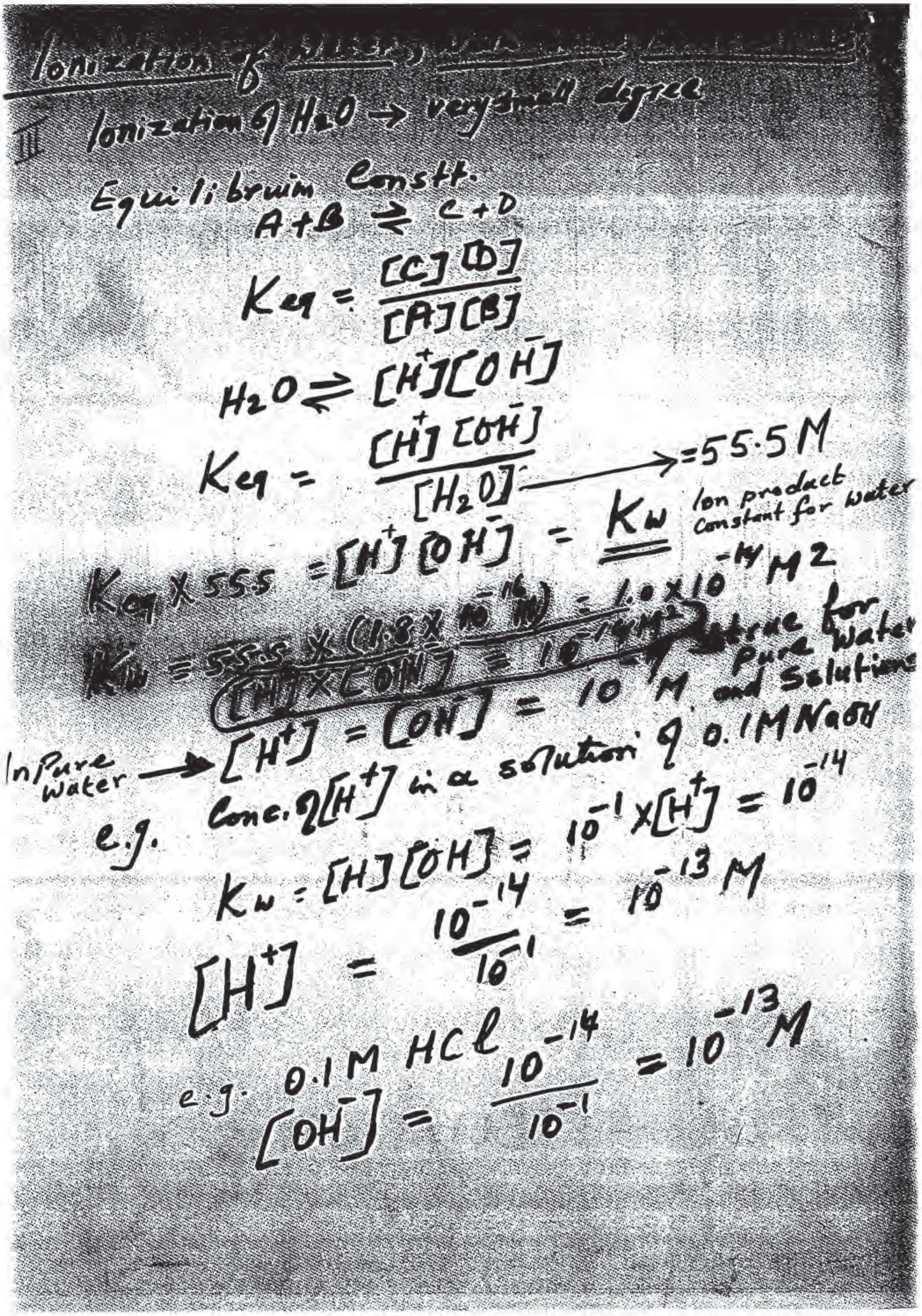


Ionization of [illegible]

III Ionization of H_2O → very small degree

Equilibrium Constt.

$$A + B \rightleftharpoons C + D$$

$$K_{eq} = \frac{[C][D]}{[A][B]}$$

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

$$K_{eq} = \frac{[H^+][OH^-]}{[H_2O]} \longrightarrow = 55.5\,M$$

$$K_{eq} \times 55.5 = [H^+][OH^-] = \underline{\underline{K_w}}$$ Ion product constant for water

$$K_w = 55.5 \times (1.8 \times 10^{-16}\,M) = 1.0 \times 10^{-14}\,M^2$$

$$\boxed{[H^+] \times [OH^-] = 10^{-14}\,M^2} \rightarrow$$ true for pure water and solutions

In Pure water → $[H^+] = [OH^-] = 10^{-7}\,M$

e.g. Conc. of $[H^+]$ in a solution of 0.1 M NaOH

$$K_w = [H][OH] = 10^{-1} \times [H^+] = 10^{-14}$$

$$[H^+] = \frac{10^{-14}}{10^{-1}} = 10^{-13}\,M$$

e.g. 0.1 M HCl

$$[OH^-] = \frac{10^{-14}}{10^{-1}} = 10^{-13}\,M$$

Acidic solution $[H_3O^+] > 10^{-7} M$ or $[OH^-] < 10^{-7}$

Neutral solution $[H_3O^+] = 10^{-7} = [OH^-]$

Basic solution $[H_3O^+] < 10^{-7}$ or $[OH^-] > 10^{-7}$

PH scale: Measuring acidity in aqueous solutions

$$pH = -\text{Log}[H_3O^+]$$

or $[H_3O^+] = 10^{-pH}$

- $[H_3O^+]$ for coffee is $10^{-5} M$

$$pH = -\log[10^{-5}] = 5$$

- Lemon juice has a $pH = 2$

$$2 = -\log[H_3O^+]$$

$$[H_3O^+] = 10^{-2}$$

- Detergent has $[OH^-] = 10^{-3} M$

$$[H_3O^+] = \frac{10^{-14}}{10^{-3}} = 10^{-11} M$$

$$pH = -\log[10^{-11}] = 11$$

The pH Scale:

$$pH = \mathrm{Log}\,\frac{1}{[H^+]} = -\log[H^+]$$

$$p[\bar{OH}] = -\mathrm{Log}[OH^+]$$

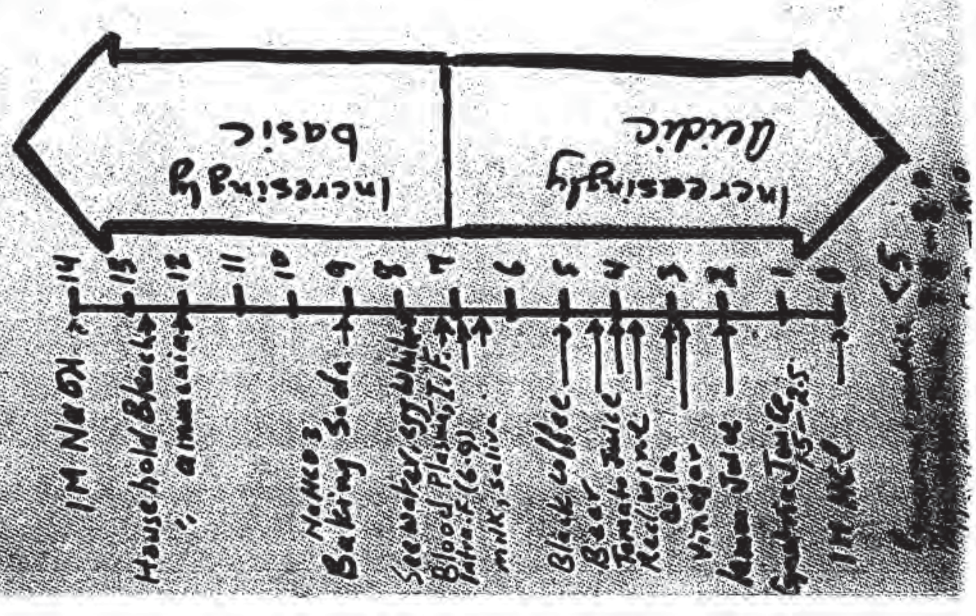
$$-\log\left[[H^+] \times [OH^-]\right] = -\log 10^{-14}$$

$$-\log[H^+] - \log[\bar{OH}] = 14$$

$$pH + pOH = 14$$

$[H^+]$ M	pH	$[OH^-]$ M	pOH M
$10^0 \dashrightarrow 1.0$	0	10^{-14}	14
$10^{-1} \dashrightarrow 0.1$	1	10^{-13}	13
$10^{-2} \dashrightarrow 0.01$	2	10^{-12}	12
$10^{-3} \dashrightarrow 0.001$	3	10^{-11}	11
10^{-4}	4	10^{-10}	10
↓			
10^{-7}	7	10^{-7}	7
↓ 10^{-12}	12	10^{-2}	2
10^{-14}	14	1	0

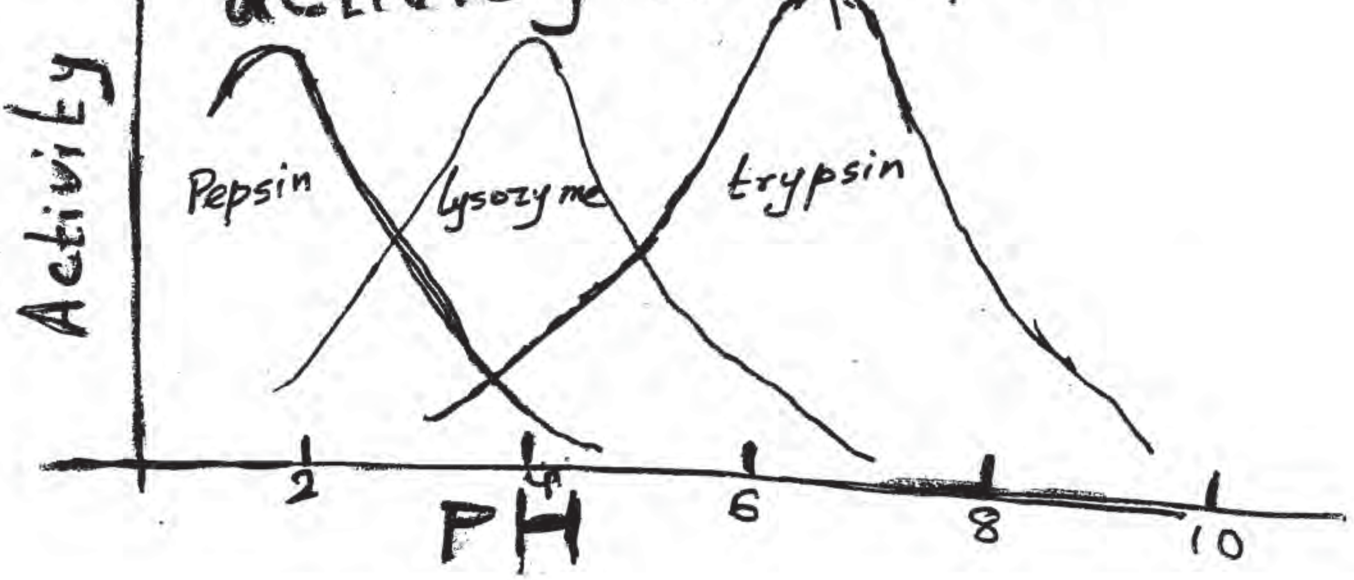
PH of Some Fluids



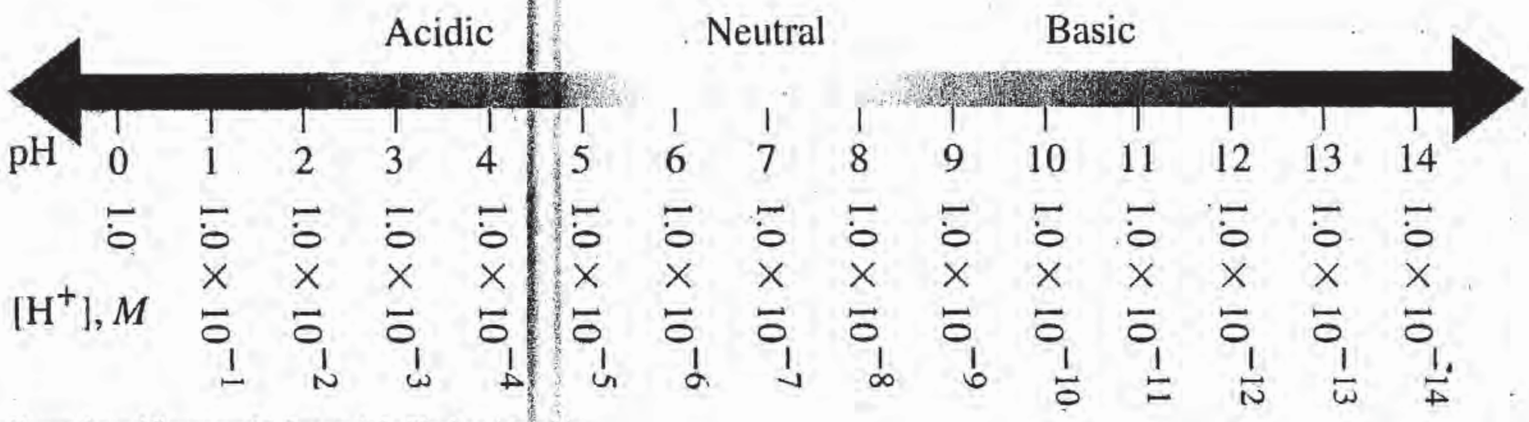
Importance of pH Regulation

- Narrow range of Cellular pH in which living organism can function

- Variation of Enzyme activity with pH



pH scale



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- Note each digit increase or decrease represents a 10-fold change in $[H^+]$

The pH values of some substances
many natural fluids have pH around neutral pH of 7.0

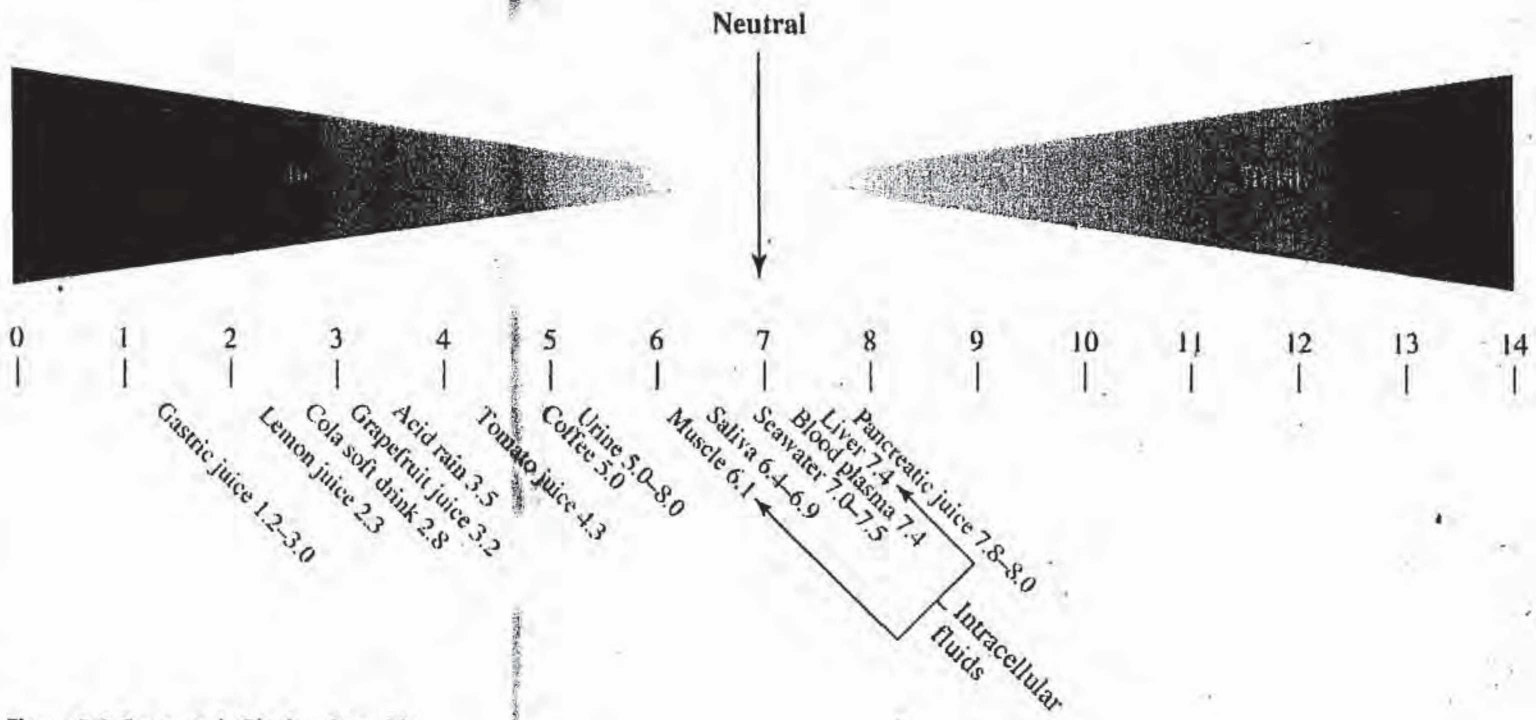

Figure 2-9 Concepts in Biochemistry, 3/e
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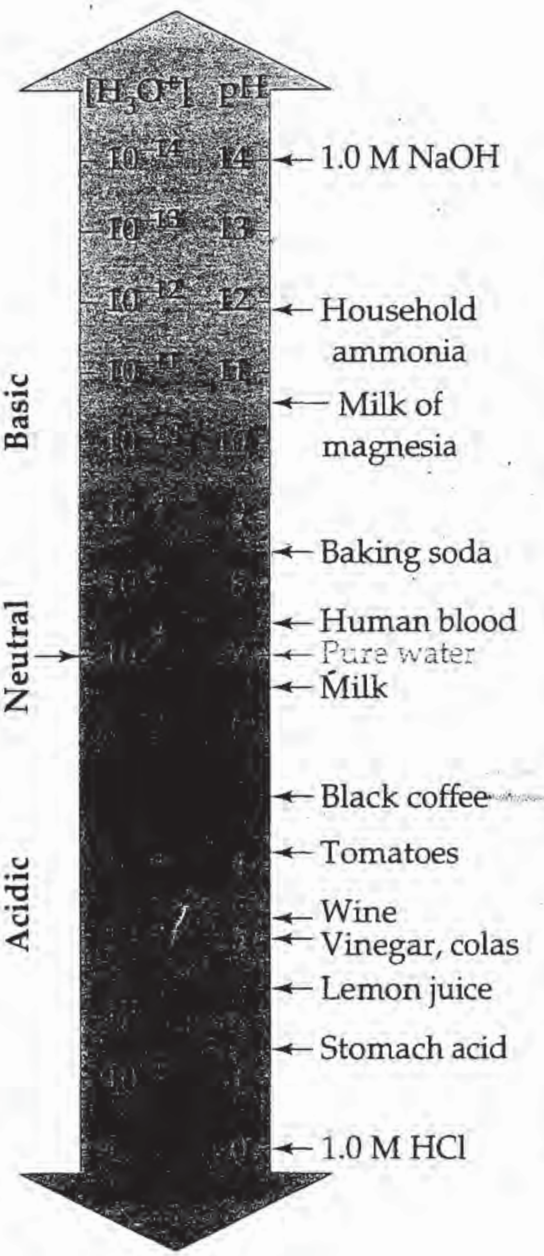
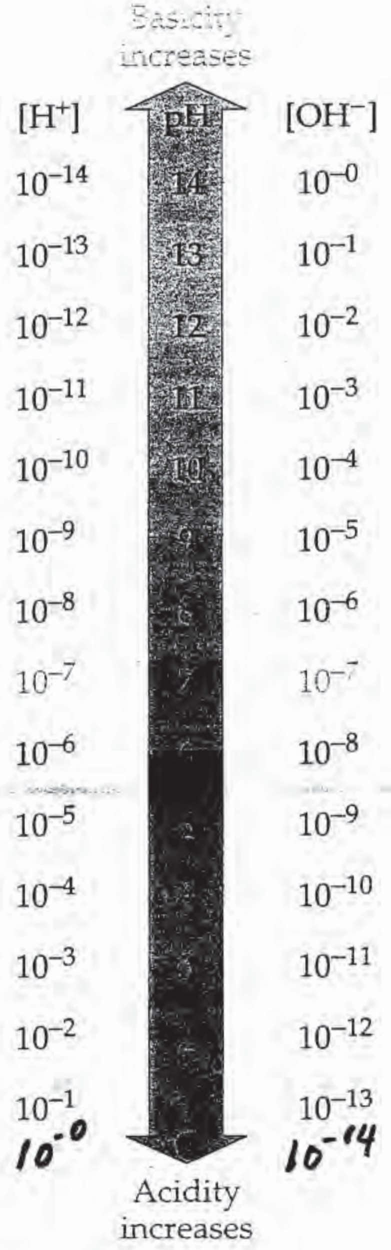
5b

T-92 Figures 10.1, 10.2 The pH scale and the pH of some common substances
The relationship of pH scale to H⁺ and OH⁻ concentrations





Fundamentals of General, Organic, and Biological Chemistry, 6e
by John McMurry, Mary Castellion, David S. Ballantine, Carl A. Hoeger, and Virginia E. Peterson

Dissociation of Acid in Aqueous solution

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

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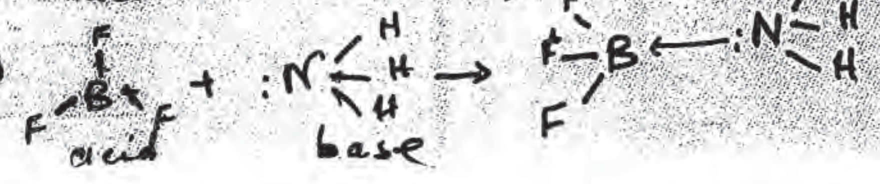
Bronsted-Lowry Acids and Bases

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{Cl^-}$$

$$\underset{\text{base}}{NH_3} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{acid}}{NH_4^+} + \underset{\text{base}}{OH^-}$$

} H_2O is **amphiprot**

Lewis Acids and Bases



[illegible]

Acid – proton donor

Base – Proton acceptor

Acid dissociation constant

$$HA_{(aq)} + H_2O \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

$$K_{eq.const} = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

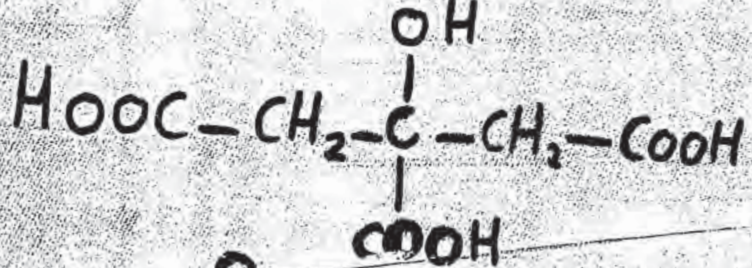
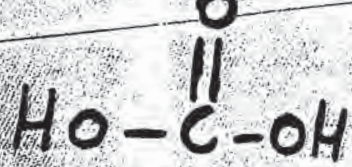
Dissociation constant $= K_a = K[H_2O]$

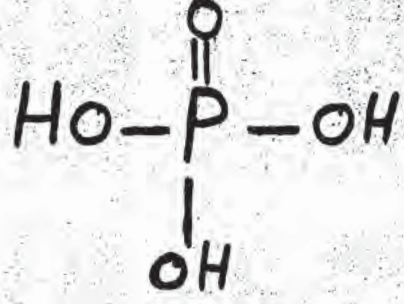
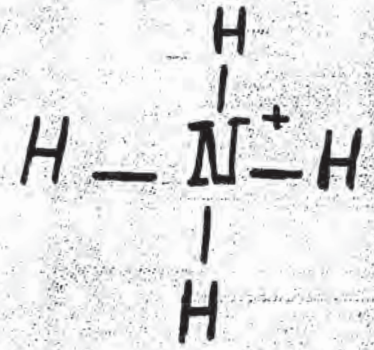
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Acid	K_a (M)	pK_a
HCOOH	1.78×10^{-4}	3.75
CH_3COOH	1.74×10^{-5}	4.76
H_3PO_4	7.25×10^{-3}	2.14
$H_2PO_4^-$	1.38×10^{-7}	6.86
HPO_4^{2-}	3.98×10^{-13}	12.4
H_2CO_3	1.7×10^{-4}	3.77
HCO_3	6.31×10^{-11}	10.2
NH_4^+	5.62×10^{-10}	9.25

$$pK_a = \log\frac{1}{K_a} = -\log K_a$$

$$PH = \log\frac{1}{[H^+]} = -\log[H^+]$$

Acid	Structur°	Ka	pKa
Formic acid	$HCOOH$	$1.78*10^{-4}$	3.75
Acetic acid	CH_3COOH	$1.74*10^{-5}$	4.76
Pyruvic acid	$CH_3COCOOH$	$3.16*10^{-3}$	2.50
Lactic acid	$CH_3CHOHCOOH$	$1.38*10^{-4}$	3.86
Malic acid	$HOOC-CH_2-CHOH-COOH$	(1) $3.98*10^{-4}$ (2) $5.50*10^{-6}$	3.40 5.26
Citric acid	 $HOOC-CH_2-\overset{OH}{\underset{COOH}{C}}-CH_2-COOH$	(1) $8.14*10^{-4}$ (2) $1.78*10^{-5}$ (3) $3.92*10^{-6}$	3.09 4.75 5.41
Carbonic acid	 $HO-\overset{O}{\overset{\|}{C}}-OH$	(1) $4.31*10^{-7}$ (2) $5.62*10^{-11}$	6.37 10.26

Acid	Structure[a]	Ka	PKa
Phosphoric acid		(1) $7.25 * 10^{-3}$ (2) $6.31 * 10^{-8}$ (3) $3.98 * 10^{-13}$	2.14 7.20 12.40
Ammonium ion		$5.62 * 10^{-10}$	9.25
H_2SO_4		Large	
HSO_4^-		1.2×10^{-2}	
HCl		Large	
HNO_3		Large	

- pH of 0.04M $Ba(OH)_2$

$[\bar{OH}] = 2 \times 0.04M = 0.08M$

$pOH = 1.1$

$pH = 14 - 1.1 = 12.9$

- pH of 0.02M weak acid (HA) is 4.0. Find Ka

$$K_a = \frac{[H^+] \times [A^-]}{HA} = \frac{[H^+]^2}{HA} = \frac{10^{-4} \times 10^{-4}}{0.02}$$

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

$$= 5 \times 10^{-7} M$$

Weak bases:

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

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

Reverse reaction for $BH^+ \rightleftharpoons B + H^+$

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

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

$$pKa + pKb = 14$$

Example

Kb for ammonia is 1.8×10^{-5} M

Find the pH of 1×10^{-2} M of Ammonia

$$Kb = \frac{[NH_4^+][OH^-]}{NH_3} \qquad NH_3 + H_2O \rightleftharpoons NH_4 + O$$

$$1.8 \times 10^{-5} = \frac{[OH^-]^2}{0.01}$$

$$OH = \sqrt{1.8 \times 10^{-7}} = 4.24 \times 10^{-4}\ M$$

$$pOH = -\log 4.24 \times 10^{-4} = 3.37$$

$$pH = 14 - 3.37 = 10.6$$

Example

The pH of 0.03M weak base solution is 10. Calculate pKb

$$pOH = 14 - 10 = 4$$

$$[OH] = 10^{-4} \qquad B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$Kb = \frac{10^{-4} \times 10^{-4}}{0.03} = 3.33 \times 10^{-7}\ M$$

$$pKb = -\log Kb = 6.48$$

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

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

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

$$pOH = -\log[OH^-]$$

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

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

MOST IMPORTANT FORMULAS
TO USE

Relation b/ pH, pK & buffer Concentration

"Henderson – Hasselbalch Equation"

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

$a \quad H^+ \quad A^-$

$a-x \quad x \quad x$

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

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

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

$pH = pK_a$ at mid point $\equiv [A^-] = [HA]$

$$pH = pK_a + \log\frac{[\text{conjugate base}]}{[\text{conjugate acid}]}$$

e.g. $pH = pK_a - 1$

base/acid $= 1/10$

$pH = pK_a + 1$

base/acid $= 10/1$

Titration Curves

1- Monoprotic acids

$$\overbrace{CH_3COOH}^{\text{weak acid}} + \overbrace{NaOH}^{\text{strong base}} \rightleftharpoons CH_3COO^-Na^+ + H_2O$$

Acid Base Conjugate base

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strong acids have weak conjugate bases
weak acid have strong conjugate bases

id Strength ↑

Acid	Conjugate base
CH_3COOH	CH_3COO^-
C_6H_5OH phenol	$C_6H_5O^-$ phenoxide
H_2O	OH^- hydroxide
C_2H_5OH ethanol	$C_2H_5O^-$ ethoxide

↓ Base strength

Titration Curve

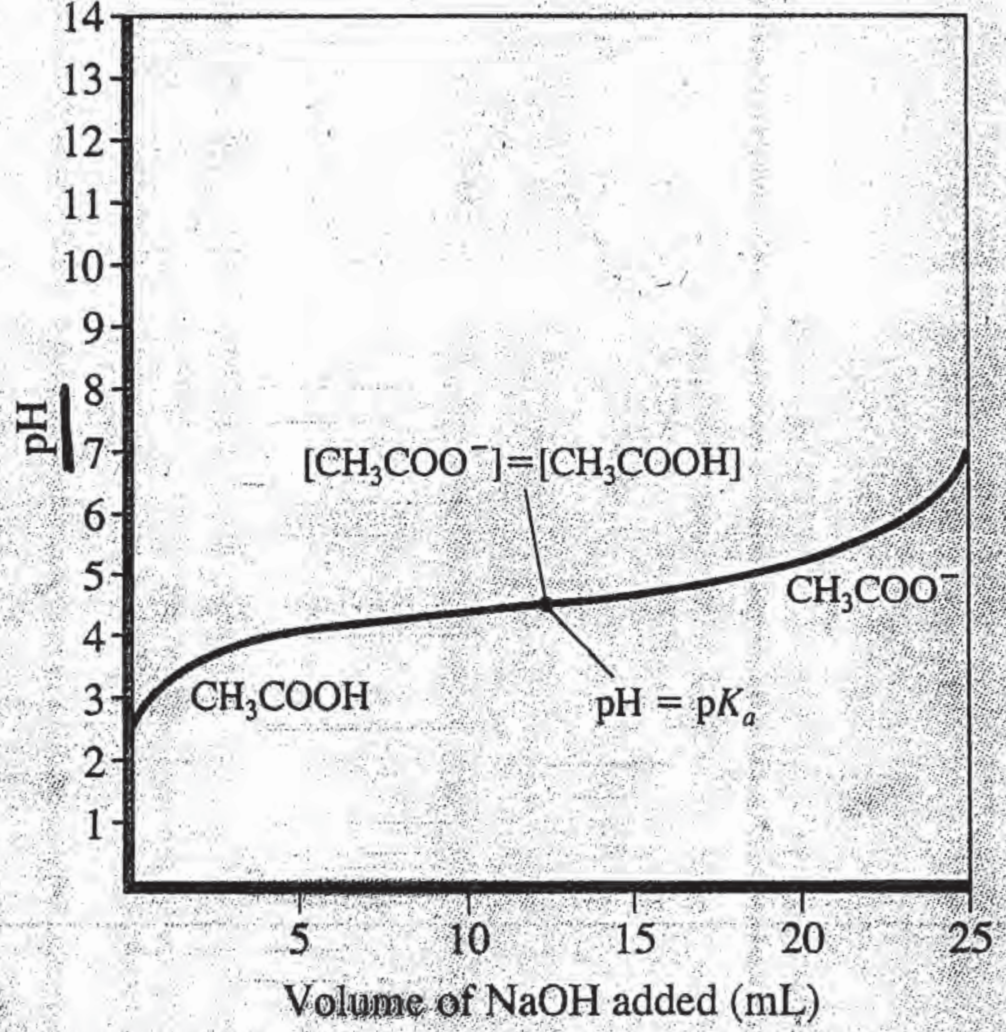
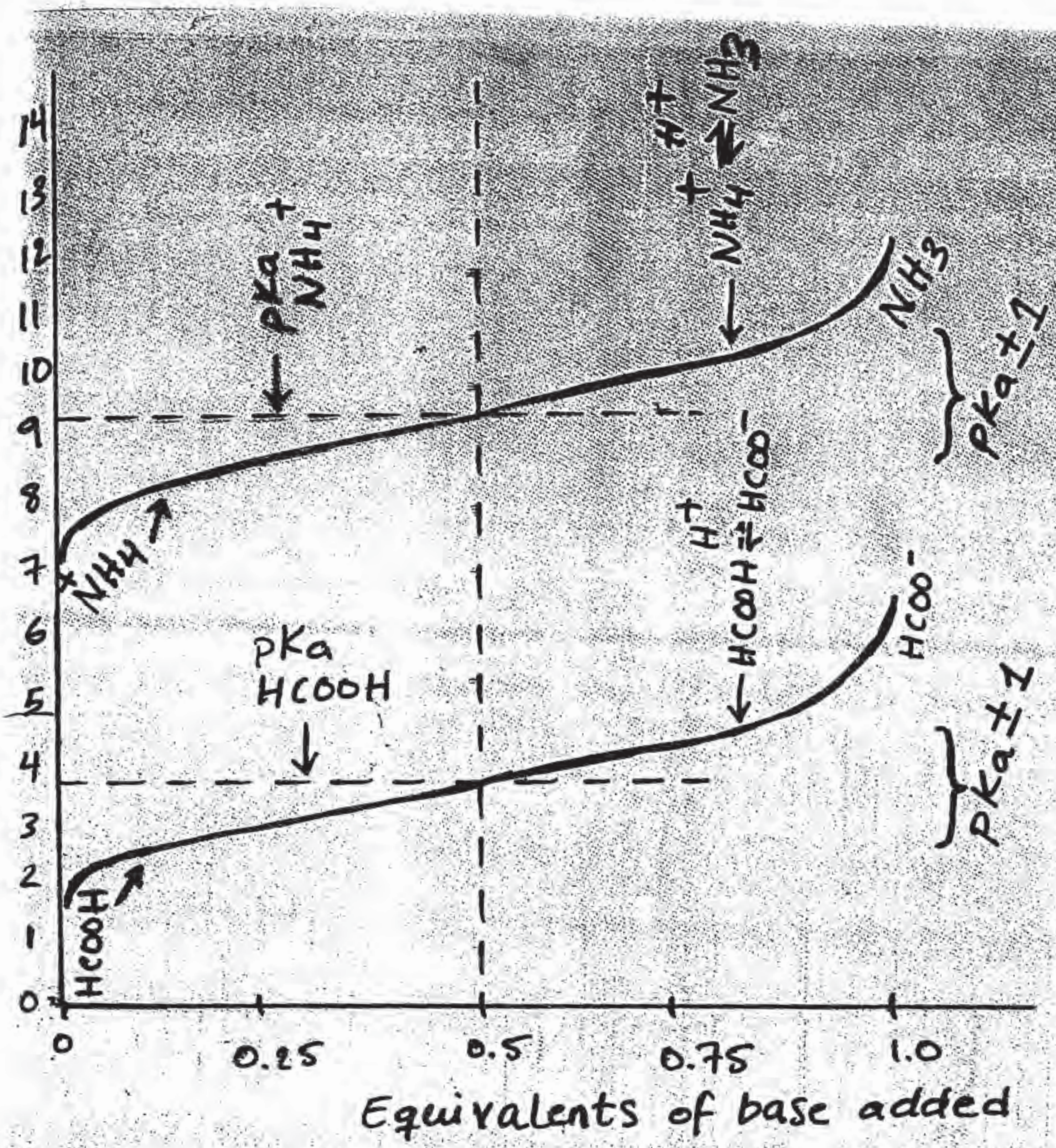
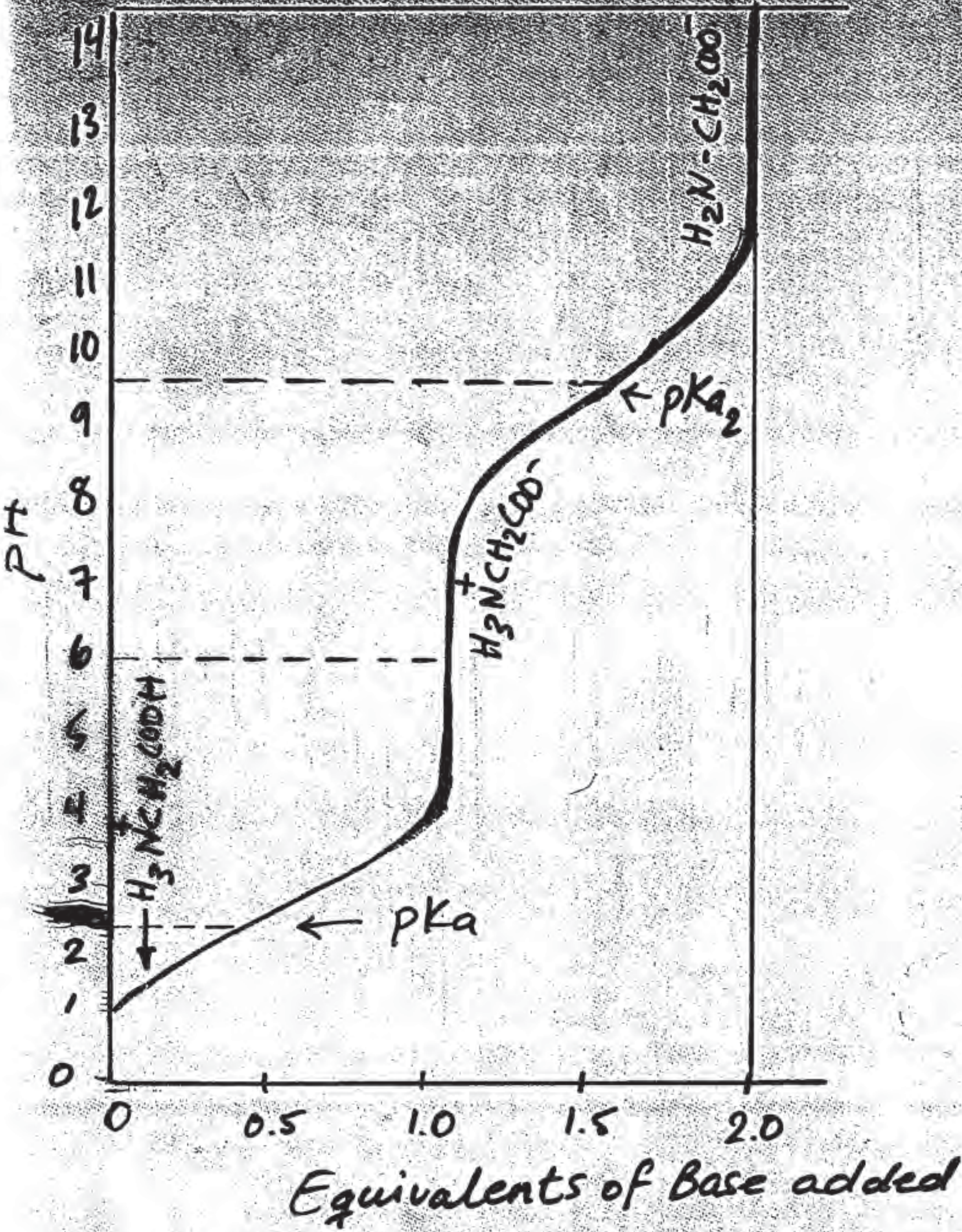


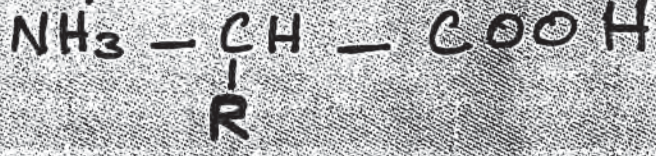
Figure 2-10 Concepts in Biochemistry/3/e


14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0
0.25
0.5
0.75
1.0
Equivalents of base added
pKa NH_4^+
$NH_4^+ \rightleftharpoons NH_3 + H^+$
NH_3
pKa ± 1
NH_4^+
pKa HCOOH
$HCOOH \rightleftharpoons HCOO^- + H^+$
$HCOO^-$
pKa ± 1
HCOOH

[illegible] Curves of Glycine



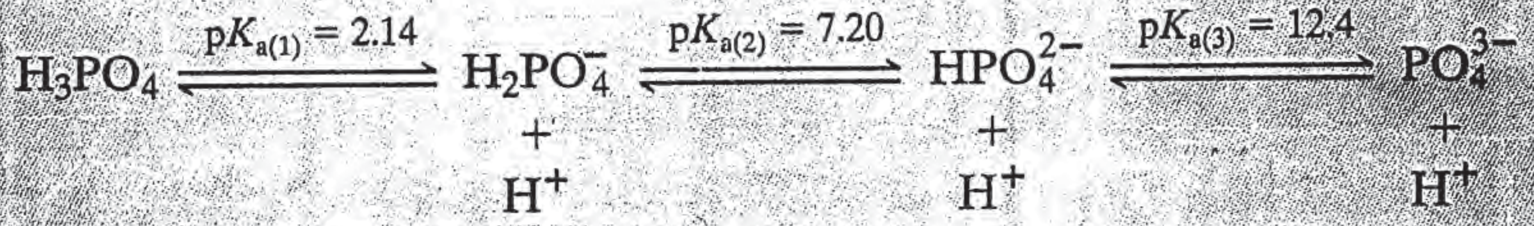
Amino acids General Formula



$$\overset{+}{N}H_3 - \underset{\displaystyle R}{\underset{|}{C}}H - COOH$$

Polyprotic Acids

e.g. malic acid, citric acid, carbonic acid, phosphoric acid



$$H_3PO_4 \underset{}{\overset{pK_{a(1)} = 2.14}{\rightleftharpoons}} H_2PO_4^- + H^+ \overset{pK_{a(2)} = 7.20}{\rightleftharpoons} HPO_4^{2-} + H^+ \overset{pK_{a(3)} = 12.4}{\rightleftharpoons} PO_4^{3-} + H^+$$

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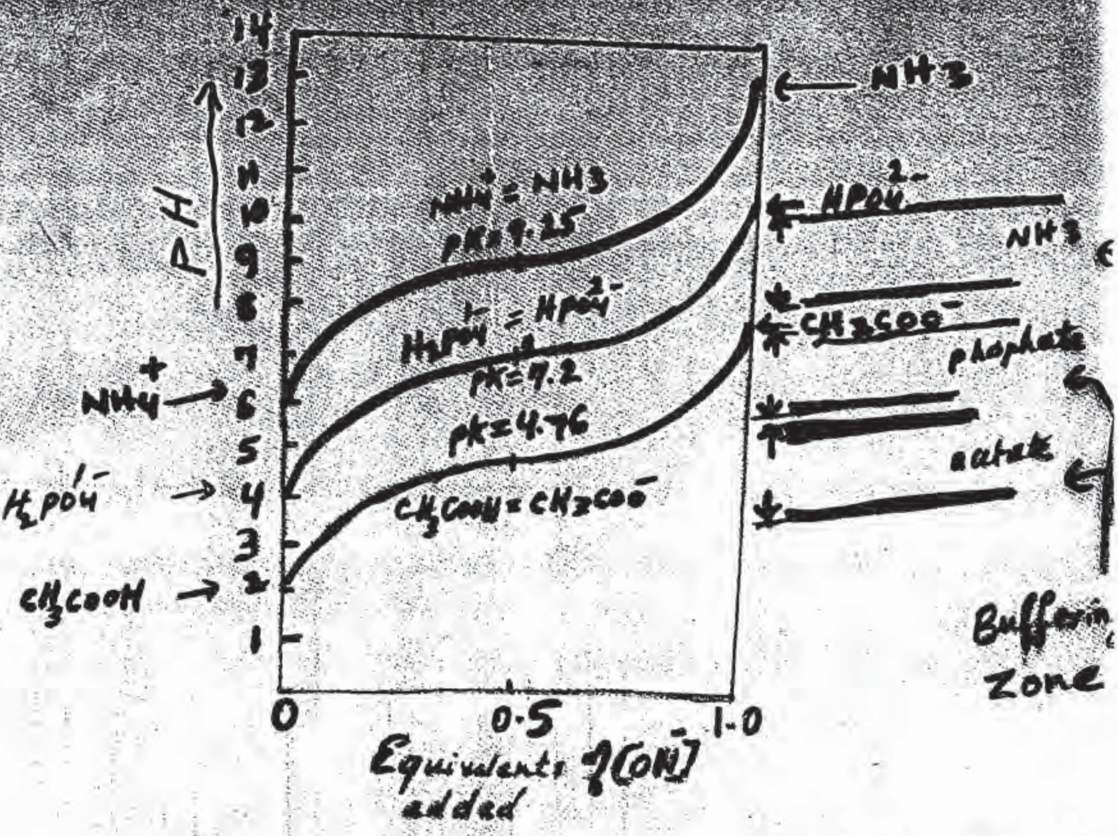

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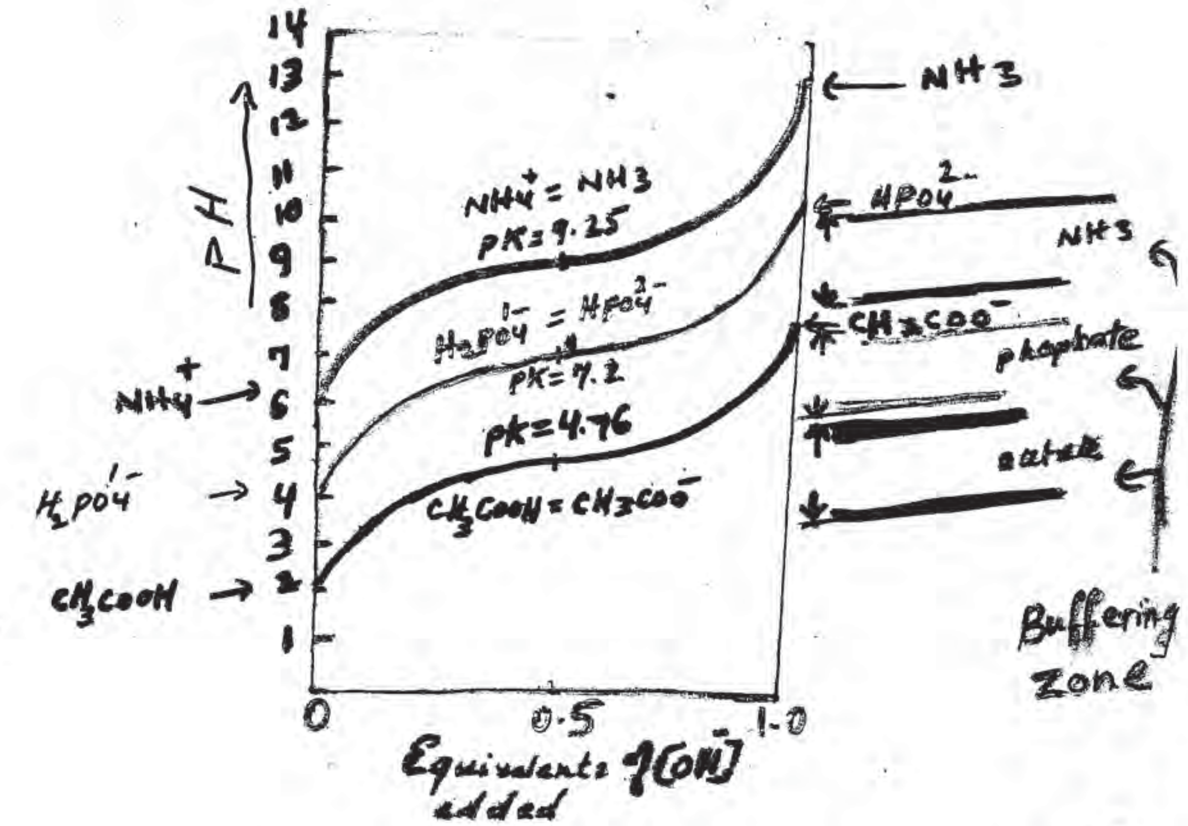
Henderson-Hasselbatch Equation

Buffer Capacity

Effective buffering range at a pH range = pKa ± 1 but better at pKa ± 0.5 only

- Ratio of $[A^-]/[HA]$
- Concentration of $[A^-]$ + $[HA]$



$$\rightarrow pH = PK_a + \log \frac{[\text{conjugate base}]}{[\text{Conjugate Acid}]}$$

Handerson-Hasselbatch Equation

Buffer Capacity

Effective buffering range at a pH range = $pka \pm 1$ but better at $pKa \pm 0.5$ only

- Ratio of $[A^-]/[HA]$
- Concentration of $[A^-] + [HA]$

Buffer Action:-

Resists changes in pH when small amount of acid or alkali are added to it

Acidic buffer = weak acid + salt of the acid (Acid + strong base)

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

- if an acid is added, the extra H^+ combines with acetate → undissociated **HAC**, so $[H^+]$ remains constt.

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

- if an alkali is added, the OH^- ions is removed by reaction with undissociated acid to form water — so $[H^+]$ remains constt

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

Prepⁿ of Buffers:-

$$\underset{\text{limiting reagent}}{NaOH} + CH_3COOH \longrightarrow \underbrace{\underset{\text{salt}}{CH_3COONa} + H_2O + \underset{\text{excess weak acid}}{CH_3COOH}}_{\text{Buffer solution}}$$

Alkali buffer :- pH > 7.0

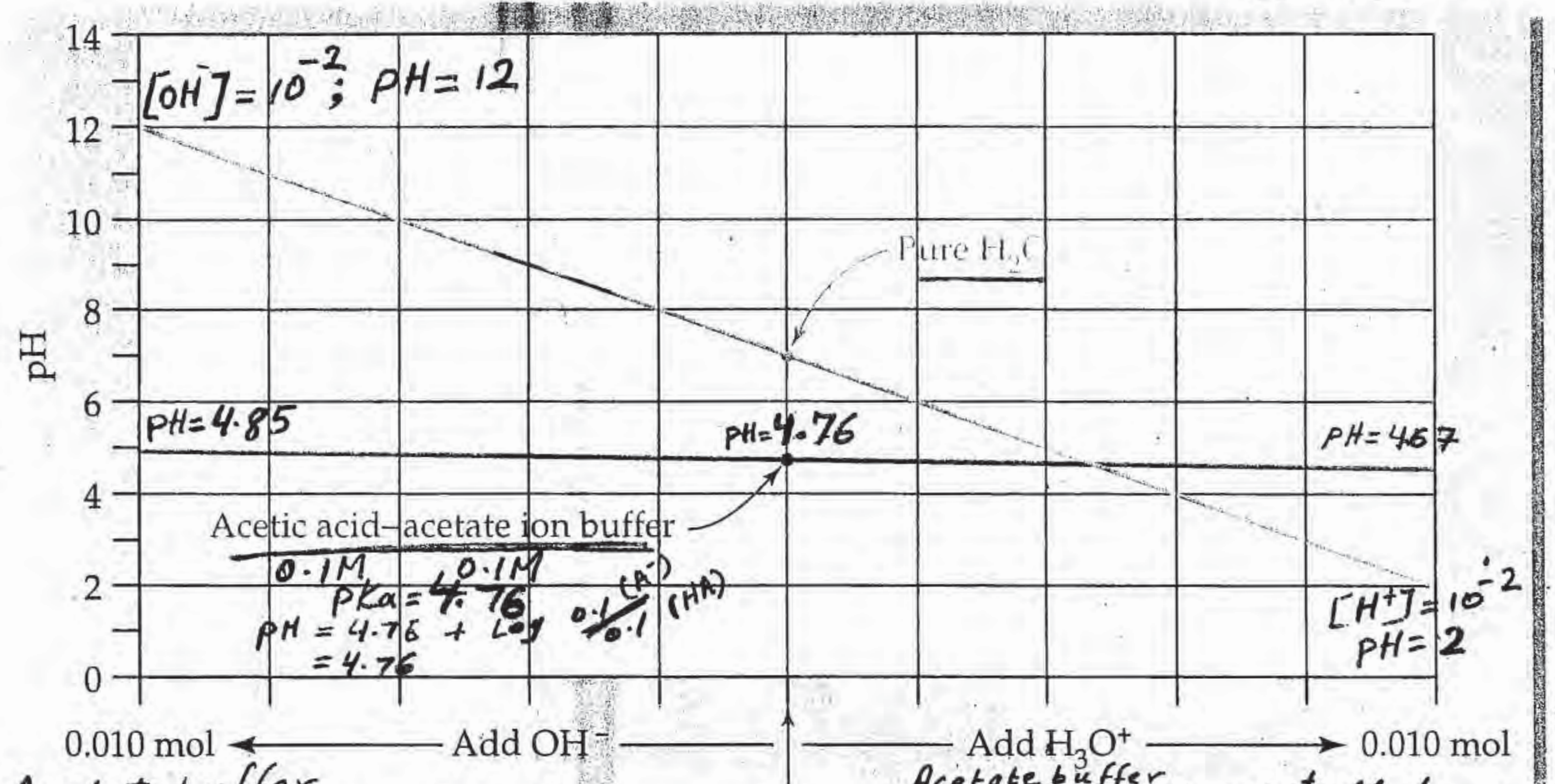
Weak base + $\underbrace{\text{salt of the base}}_{\text{(made from base + strong acid)}}$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Excess H^+ combines with OH^- ; excess OH^- combines with $NH_4^+ \longrightarrow NH_3$

Figure 10.5 The effect of a buffer solution on pH

$$pH \doteq pKa + \log \frac{[\text{Conjugate base}]}{[\text{Conjugate acid}]}$$



Acetate buffer
when 0.01 mole $[OH^-]$ added
$pH = 4.76 + \log \frac{0.11}{0.09}$
$= 4.85$

Acetate buffer
when 0.01 mole of H_3O^+ added
$pH = 4.76 + \log \frac{0.09}{0.11}$
$= 4.673$

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Buffer Calculations:-

1) Buffer consists of 0.2 mole CH_3COONa in 500ml of 0.1M CH_3COOH ($K_a = 1.8 \times 10^{-5} M$)
What is its pH?

$$pH = pK_a + \log \frac{Base}{Acid}$$

$$pH = \underbrace{-\log 1.8 \times 10^{-5}}_{pK_a} + \log \frac{\overset{2 \times 0.2}{0.4}}{0.1}$$

OR

$$K_a = \frac{[H^+] \times 0.4}{CH_3COOH} = 1.8 \times 10^{-5}$$

$$[H^+] = 4.5 \times 10^{-6} M$$

$$pH = -\log 4.5 \times 10^{-6} = 5.4$$

2) Calculate mass of sod. propionate to be dissolved in 1l of 1M propionic acid (MW=96) to give buffer of pH = 4.5 ($pK_a = 4.87$)

$pH = 4.5$ $[H^+] = 10^{-4.5}$

$pK_a = 4.87$ $K_a = 10^{-4.87}$

$$K_a = \frac{[H^+][\text{propionate}]}{\text{propionic acid}}$$

} or use Handerson-Hasselbalch Eq.

$$[\text{Propionate}] = \frac{1 \times 10^{-4.87}}{10^{-4.5}} = 0.427 M$$

0.427×96.08 (M.W.) $= 41.0$ gr.

3) Calculate pH of a buffer when 18 ml of 0.1 M HCl is added to 32 ml of 0.1 M NH_3 ($pK_b = 4.75$)

(1) Calculate excess NH_3 and salt formed

$$HCl \text{ moles} = \frac{18}{1000} \times 0.1 = 1.8 \times 10^{-3}$$

$$NH_3 \text{ moles} = \frac{32}{1000} \times 0.1 = 3.2 \times 10^{-3}$$

$$\text{Ammonium salt} = 1.8 \times 10^{-3}$$

$$\text{excess Ammonia} = 3.2 \times 10^{-3} - 1.8 \times 10^{-3} = 1.6 \times 10^{-3}$$

$$\text{Molar conc. of salt} = \frac{1.8 \times 10^{-3}}{50/1000} = 3.6 \times 10^{-2}\, M$$

$$\text{〃 〃 of } NH_3 = \frac{1.6 \times 10^{-3}}{50/1000} = 3.2 \times 10^{-2}\, M$$

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

$$10^{-4.75} = \frac{3.6 \times 10^{-2} \times OH^-}{3.2 \times 10^{-2}}$$

$$[OH^-] = 0.889 \times 10^{-4.75} = 1.58 \times 10^{-5}\, M$$

$$pOH = -\log 1.58 \times 10^{-5} = 4.8$$

$$pH = 14 - 4.8 = 9.2$$

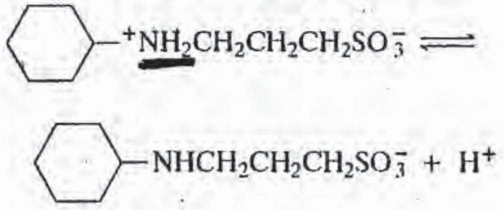
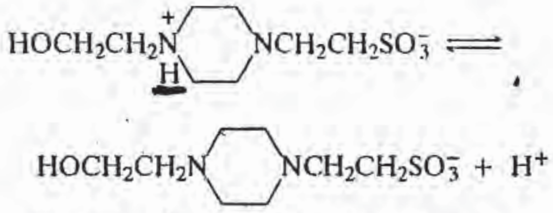
OR

$$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{Weak base}]}$$

$$pOH = 4.75 + \log \frac{3.6 \times 10^{-2}}{3.2 \times 10^{-2}}$$

$$= 4.75 + 0.05 = 4.8 \;;\; pH = 14 - 4.8 = 9.2$$

Table 2.6
Some synthetic buffers

Name (Abbreviation)	pK_a	Useful pH Range	Ionization Reaction[a]
N-(2-Acetamido)-2-aminoethanesulfonic acid (ACES)	6.9	6.4–7.4	$H_2NCOCH_2\overset{+}{N}H_2CH_2CH_2SO_3^- \rightleftharpoons H_2NCOCH_2NHCH_2CH_2SO_3^- + H^+$
3-(Cyclohexylamino)propanesulfonic acid (CHAPS)	10.5	10.0–11.0	
N-(2-Hydroxyethyl)piperazine-*N*′-2-ethanesulfonic acid (HEPES)	7.5	7.0–8.0	
Tris(hydroxymethyl)aminomethane (TRIS)	8.3	7.5–9.0	$(HOCH_2)_3C\overset{+}{N}H_3 \rightleftharpoons (HOCH_2)_3CNH_2 + H^+$

[a] Each reaction shows the two predominant forms (acid and base) present in the useful pH range.

Table 2-6 Concepts in Biochemistry, 3/e

INDICATORS

- often organic dye → different colors in acidic and alkaline sol.

- weak acid / base

$$HIn_{(aq)} \rightleftharpoons H^+ + In^-$$

For Litmus Red Blue

In presence of acid → HIn red

In presence of base → In^- blue

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

$$\frac{[HIn]}{[In^-]} = \frac{[H^+]}{K_a}$$

so, color of indicator depends on pH or $[H^+]$ and Ka.

when pH = pKa, the two colors have equal conc.

So different indicators change color over different pH ranges

e.g.

	pKa	pH range	Color in acid	Color in alkali
phenolphthaleine	9.6	8.3 – 10.00	Colorless	Pink
Methyl orange	3.7	3.1 – 4.4	Red	Yellow

In order for an indicator to be effective, color change (called the end-point) must occur rapidly at the equivalence point

e.g.

Property	"Phenolphthalein"	Methyl orange
pKa	9.6	3.7
pH range	8.3 - 10.0	3.1 - 4.4
Color in acid	Colorless	Red
〃 〃 alkali	Pink	Yellow
Useful for	Titrations involving strong bases	Titrations involving Strong Acids

[illegible] = [H] [illegible]