Acids, Bases, Water and Buffers

- Weak acids and bases
- strong acids
- The dissociation constant Ka and pKa
- Water, the biological solvent
  - Biological Roles of Water
  - The structure of Water
  - Noncovalent Interactions in biomolecules
  - The Importance of Hydrogen bond
  - physical properties of Water
  - Ionization of Water
- The Handerson-Hasselbalch Equation
  - The pH of a solution is the negative log of its $[H^+]$.
  - Relationship between pH, pKa and extent of acid dissociation
  - Monoprotic, diprotic and Polyprotic acids
  - selection of calculations on Ka, pKa, $[H^+]$ and pH

- The Concept of Buffers
  - Buffers Composition
  - How do buffers work
  - Buffers Capacity
  - How do we choose a buffer
  - How do we make a buffer in the laboratory + Calculations
- Normal metabolism generates metabolic acids, Inorganic acids and CO_2 - Volatile acids and Non-volatile acids
- Physiological Buffers
  Bicarbonate, phosphate and Proteins
- Mechanism of action of physiological buffers
- Acid-Base Disturbances

ACIDS & BASES

- Arrhenius Difinitions of Acids & Bases

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

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

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

$$H^+ + H-\ddot{O}:-H \longrightarrow H_3O^+ \left[H-\ddot{O}-H \atop \quad | \atop \quad H\right]$$

Drawback

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

(2) $H-\ddot{N}(H)-H_{(g)} + H_2O \rightleftharpoons H-N^+(H)(H)-H + OH$

(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

$$NH_{3\,(g)} + H{-}Cl_{(gas)} \longrightarrow NH_4^+ + Cl^-$$

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

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

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

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

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

conjugate acid-base pair

Table 10.1 Relative strengths of acids and conjugate bases

TABLE 10.1 Relative Strengths of Acids and Conjugate Bases

Increasing acid strength (↑) **Increasing base strength** (↓)

	ACID		CONJUGATE BASE		
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

Conjugate acid-base pairs:

Conjugate acids { $CH_3C(=O)-OH \rightleftharpoons H^+ + CH_3C(=O)O^-$ } conjugate bases

$H_3O^+ \rightleftharpoons H^+ + H_2O$

$NH_4^+ \rightleftharpoons H^+ + NH_3$

Water as both an Acid and a Base:

H_2O is Amphoteric or Amphoprotic

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

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

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

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

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

Strong acid + strong base ⇌ Weak base + Weak acid

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

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

Knowing the relative strength of different acids makes it possible to predict the direction of proton-transfer reactions.

Acid Dissociation Constant

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

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

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}
  HCN 6×10^{-10}, HF 3.5×10^{-4}, HSO_4^{-1} (1.3×10^{-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}

T-91 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 (CH_3CH_2COOH)	1.3×10^{-5}	HPO_4^{2-}	2.2×10^{-13}
		Carbonic acid	
Ascorbic acid (vitamin C)	7.9×10^{-5}	H_2CO_3	4.3×10^{-7}
		HCO_3^-	5.6×10^{-11}

$pKa = -\log Ka$

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

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

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

Noncovalent Interactions in Biomolecules

- Ionic bonds
  between oppositely charged atoms or group
  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)

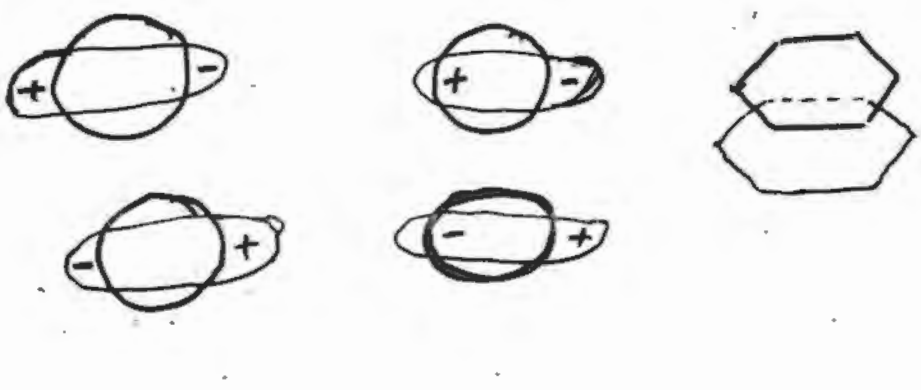
- Charge - Charge $-NH_3^+$ $\quad {}^{-}O-C(=O)-$
- Charge - dipole $-NH_3^+$ $\quad {}^{-}OH_2^{+}$
- Dipole - dipole ${}^{-}OH_2^{+}$ $\quad {}^{-}OH_2^{+}$
- charge - induced dipole $-NH_3^+$ 
- Dipole - induced dipole ${}^{-}OH_2^{+}$ 
- Dispersion

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

$H_2N-H\cdots O=C<$

$\longleftrightarrow$
H-bond length

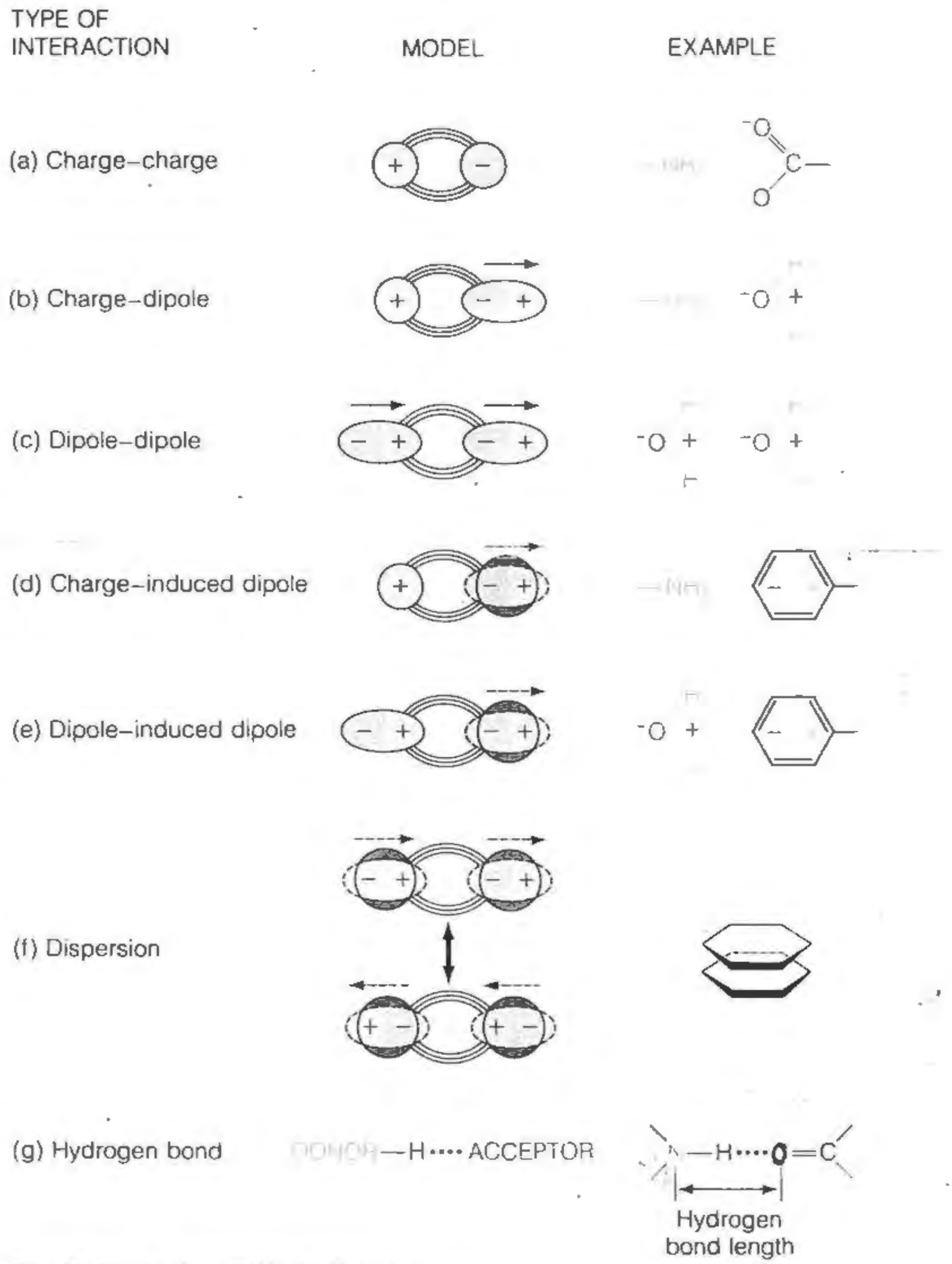
- Dispersion



3b

Types of noncovalent interactions

Figure 2.1



Structure of Water

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

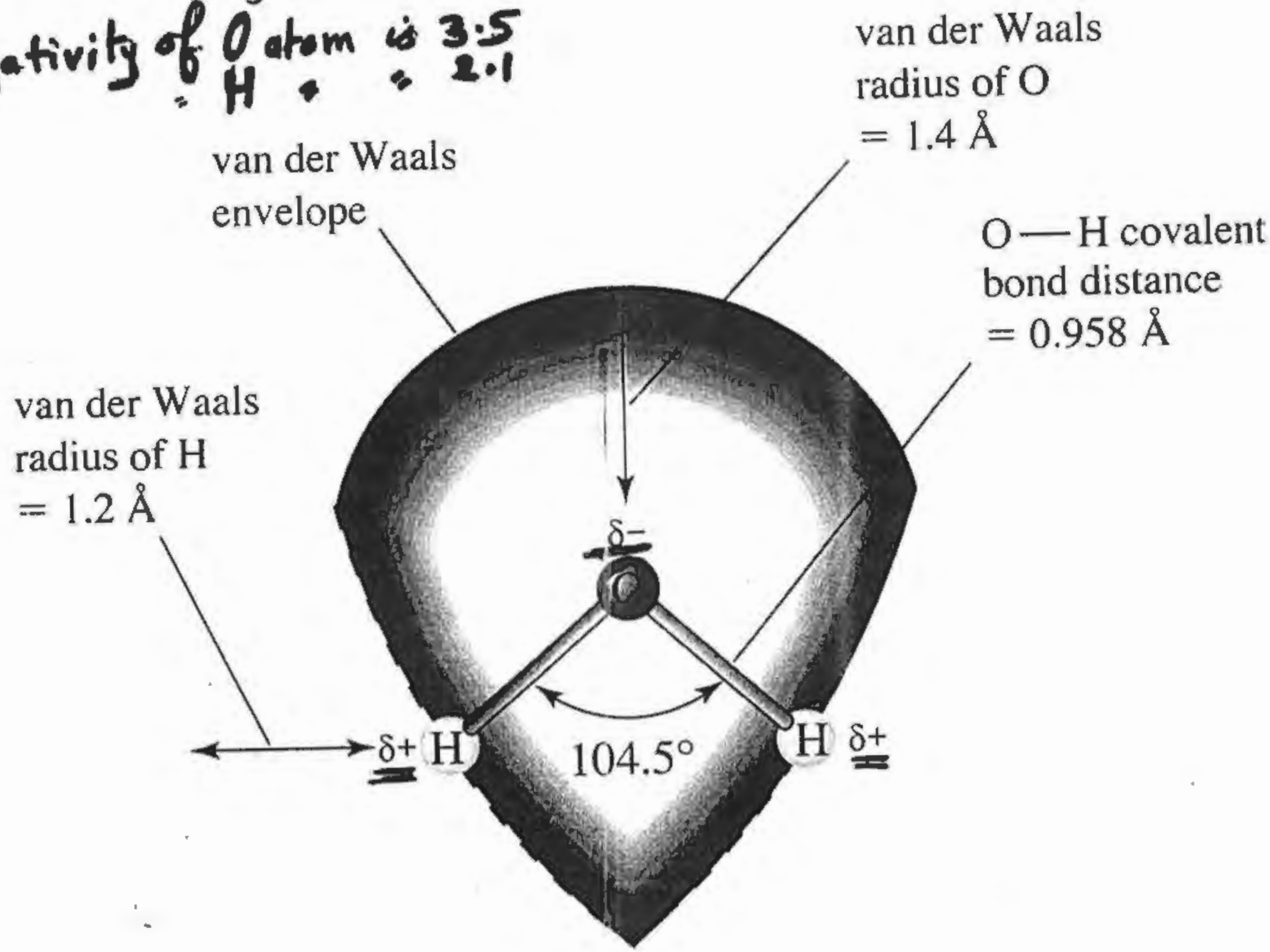


Figure 2-1a Concepts in Biochemistry, 3/e

Water is electrically neutral (no net charge) but has relatively large dipole moment because of its bent geometry

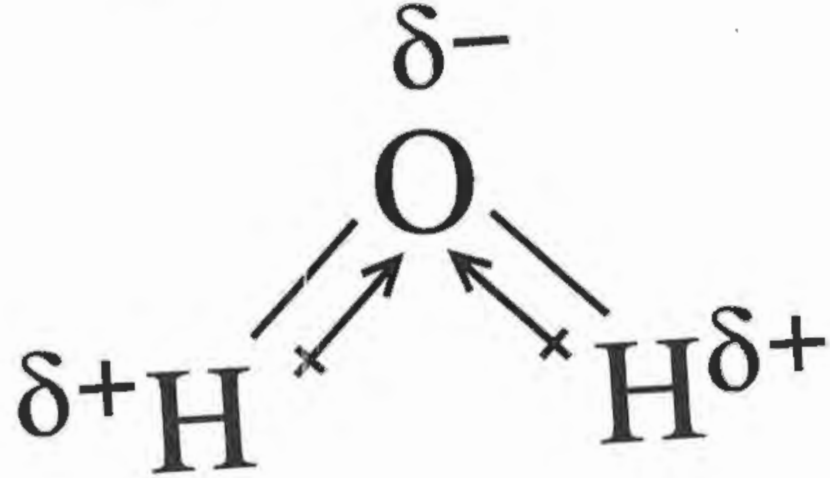


Figure 2-1b Concepts in Biochemistry, 3/e

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

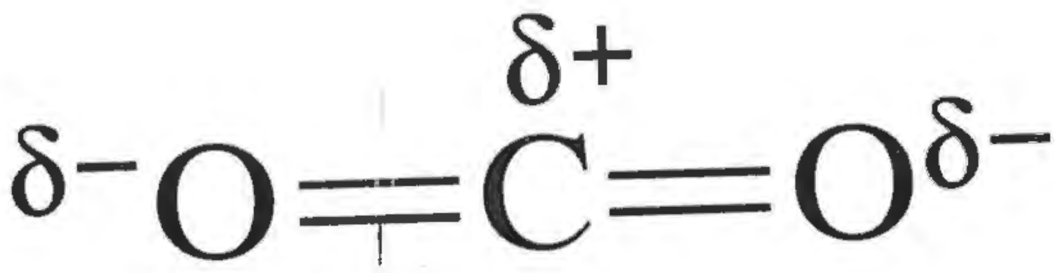


Figure 2-2 Concepts in Biochemistry, 3/e

Hydrogen bond between two water molecules

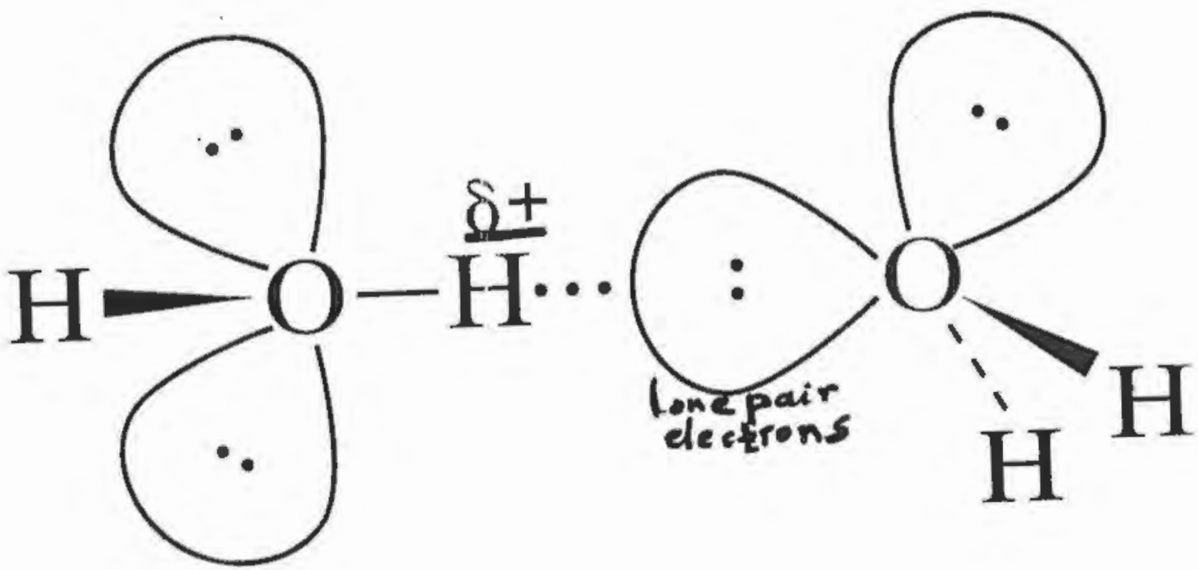
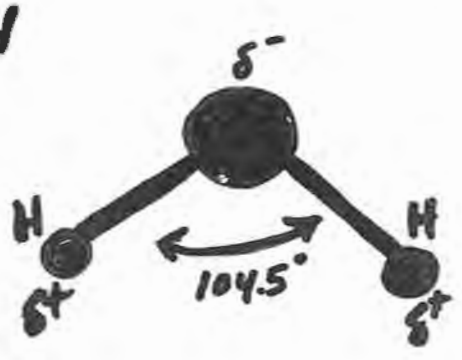


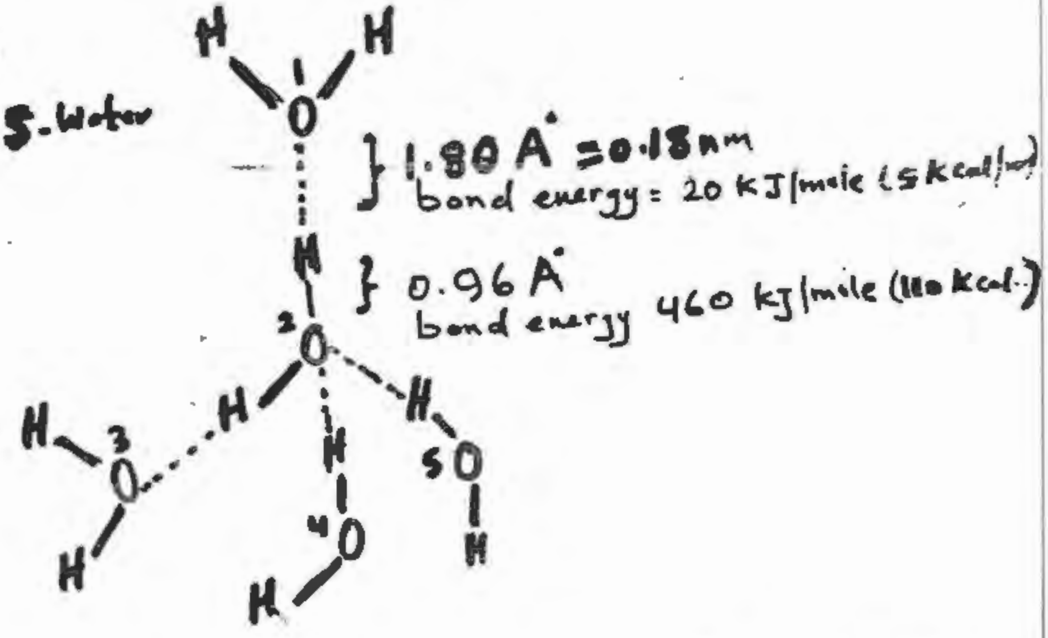
Figure 2-3 Concepts in Biochemistry, 3/e

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

- Many biomolecules have atoms that can hydrogen bond with: - Water, themselves & other molecules

Functional groups that participate in H-bonding include:

- -OH gr in alcohols, org. acids & carbohydrate
- Carbonyl groups in aldehydes, Ketones, acids, amides & esters
- N-H groups in Amines & Amides

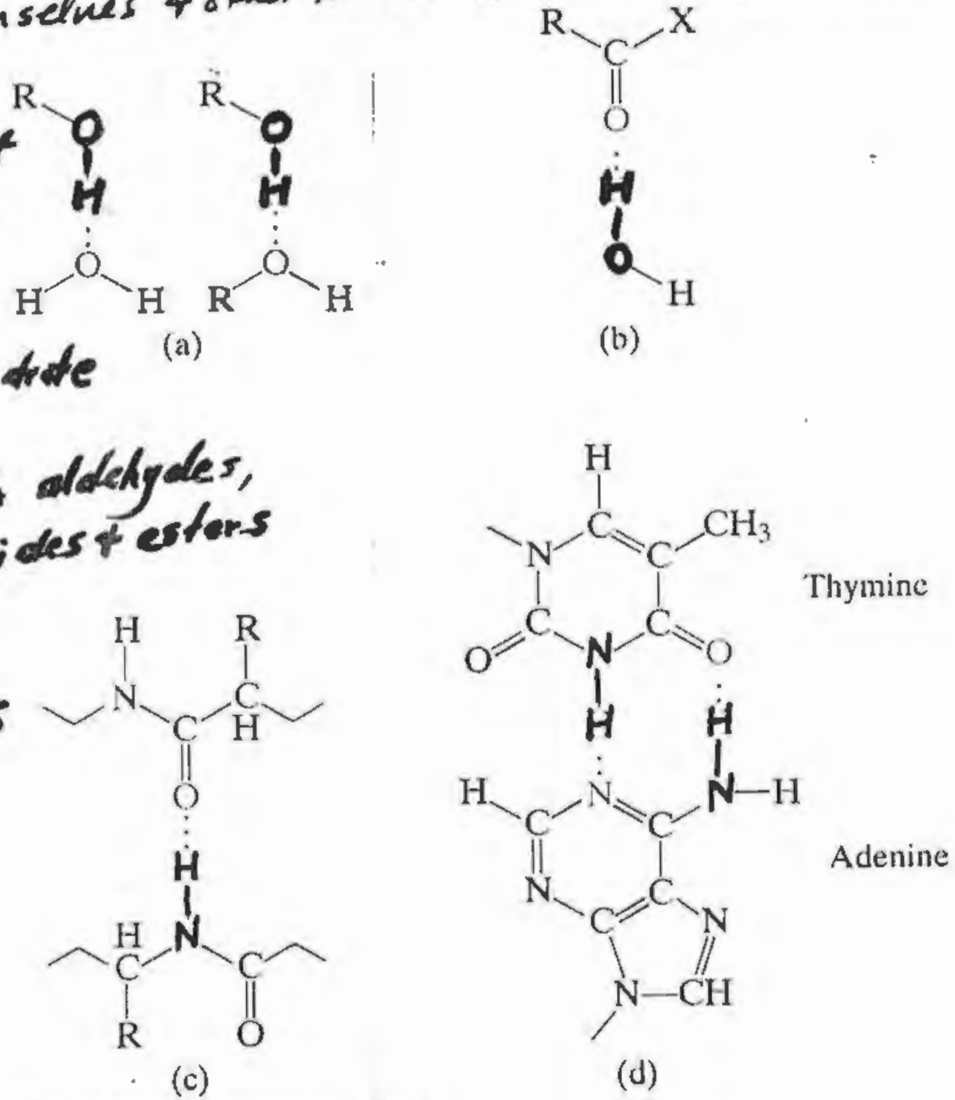


Figure 2-4 Concepts in Biochemistry, 3/e

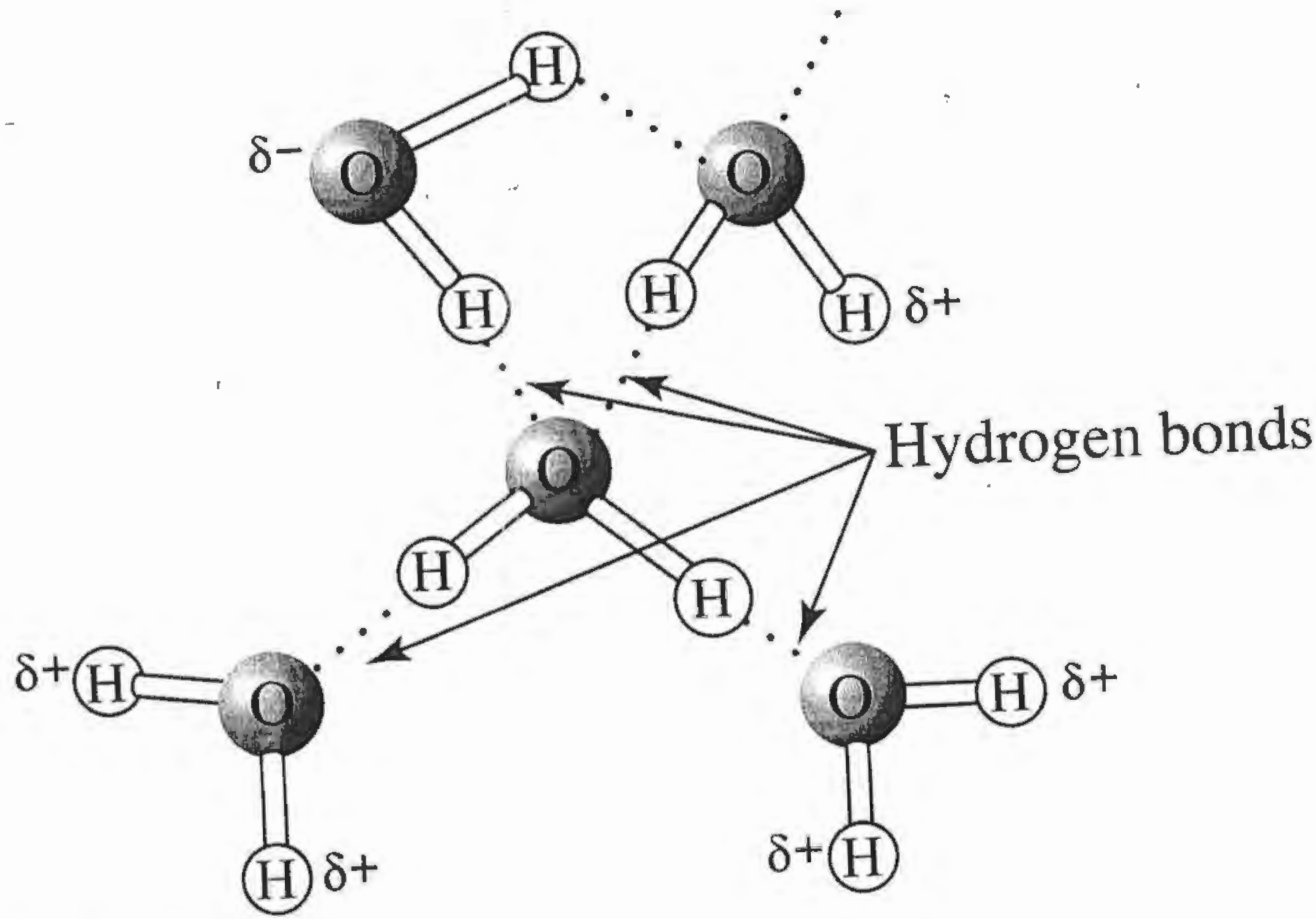
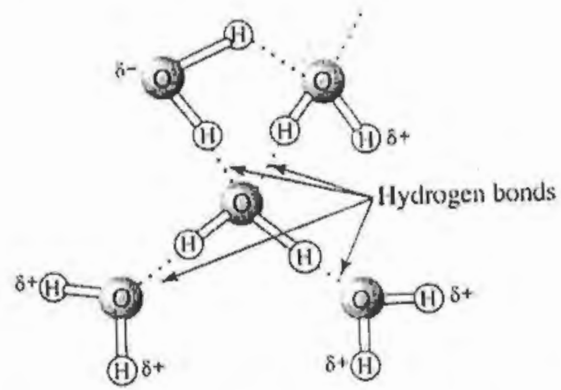


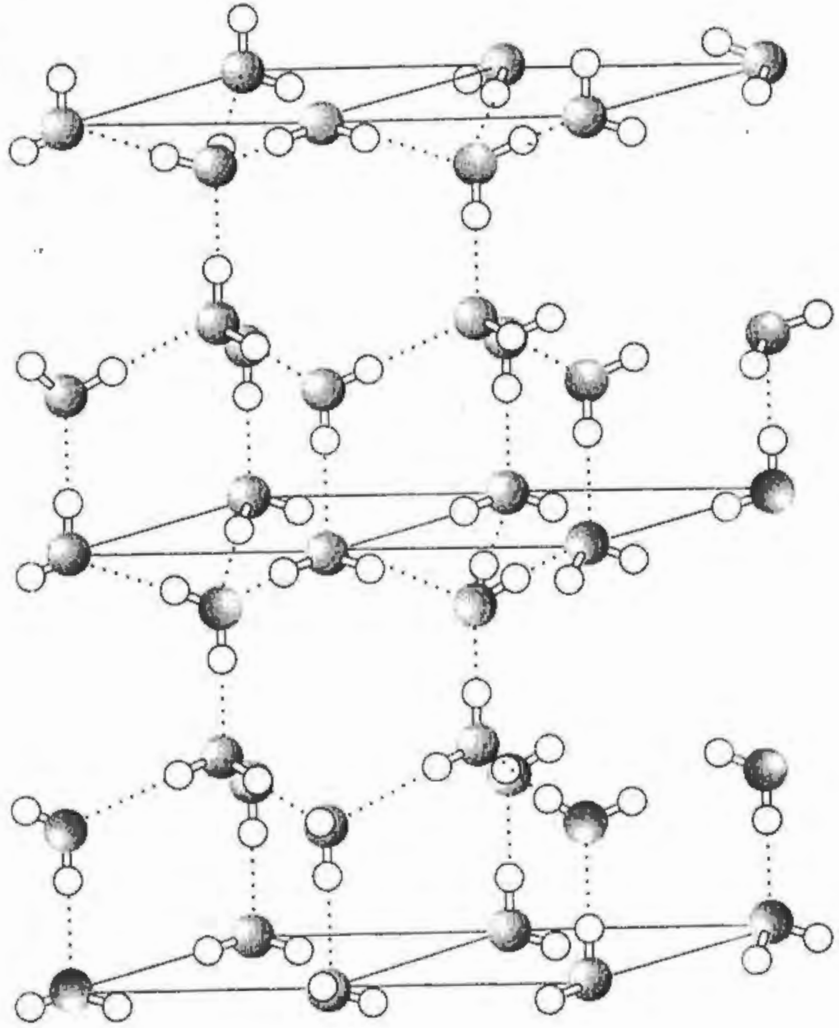
Figure 2-5a Concepts in Biochemistry, 3/e

The 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)

Figure 2-5 Concepts in Biochemistry, 3/e

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 — 4 H_2O molecules

∴ Larger vol. + less dense the ice-lattice

- Water forms Hydrogen bonds with solutes

H-bonds are not unique only to Water

- Hydrogen atoms covalently bonded to carbon atoms, which are not electronegative, 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

  $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$

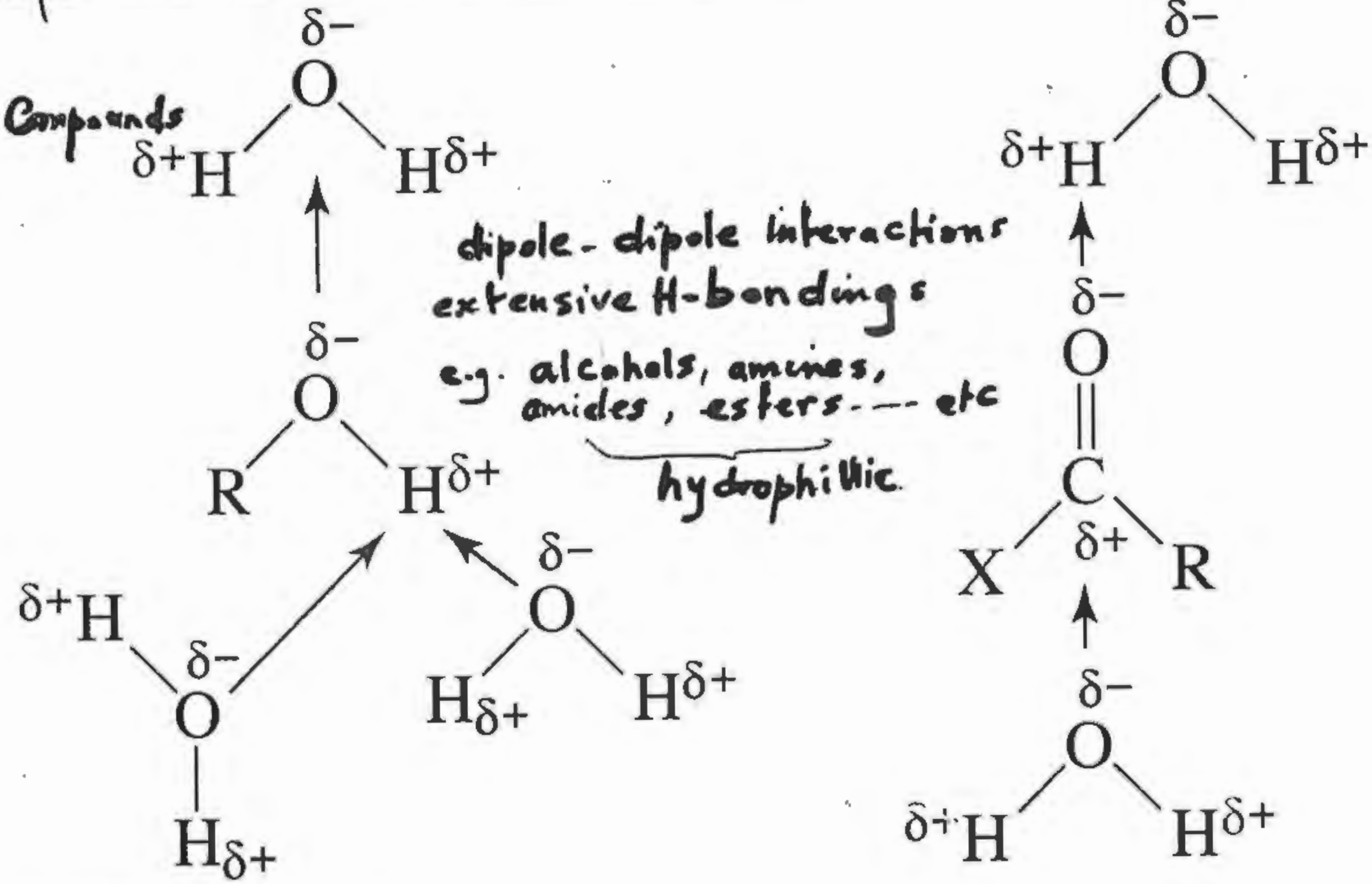
- B.P. for butane = -0.5 °C

  $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$

Water as a Solvent

Important solvent and transporter

1- Polar Compounds



dipole-dipole interactions
extensive H-bondings

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

$\underbrace{\text{amides, esters}}_{\text{hydrophilic}}$

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

2-Ionic Compounds

Individual ions are hydrated (solvated) by polar water molecules

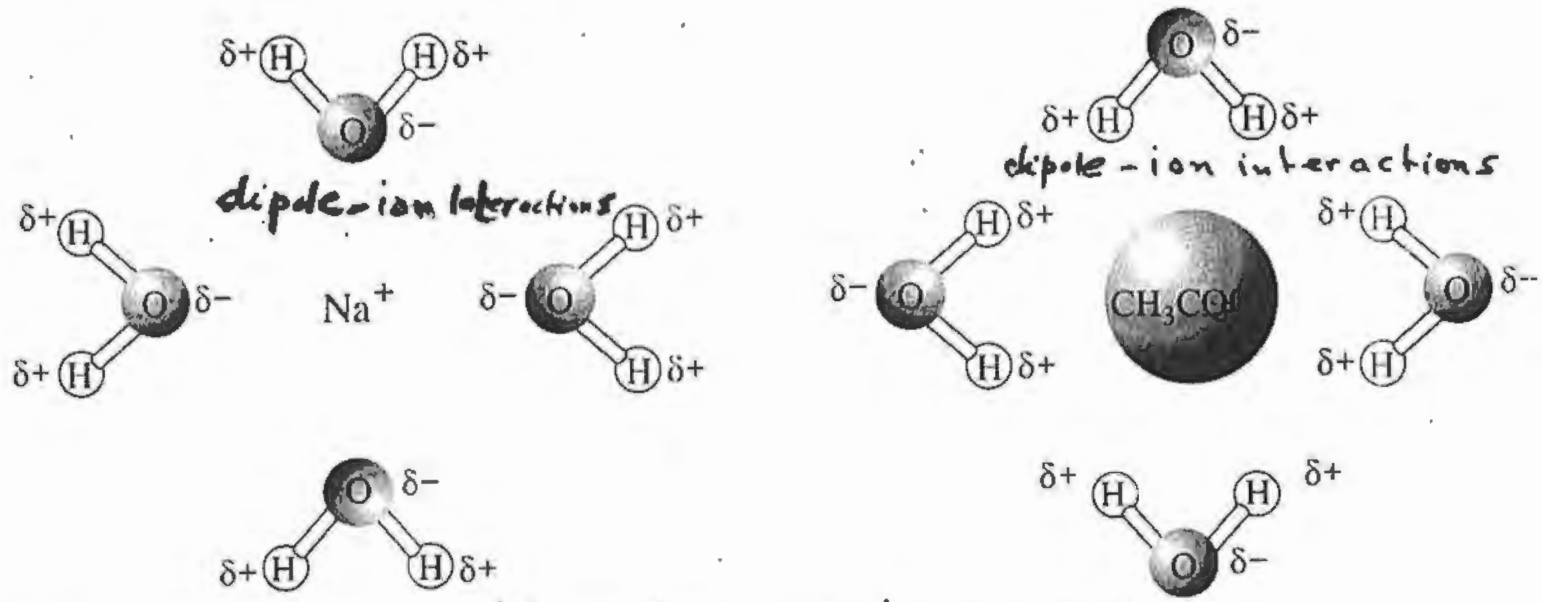


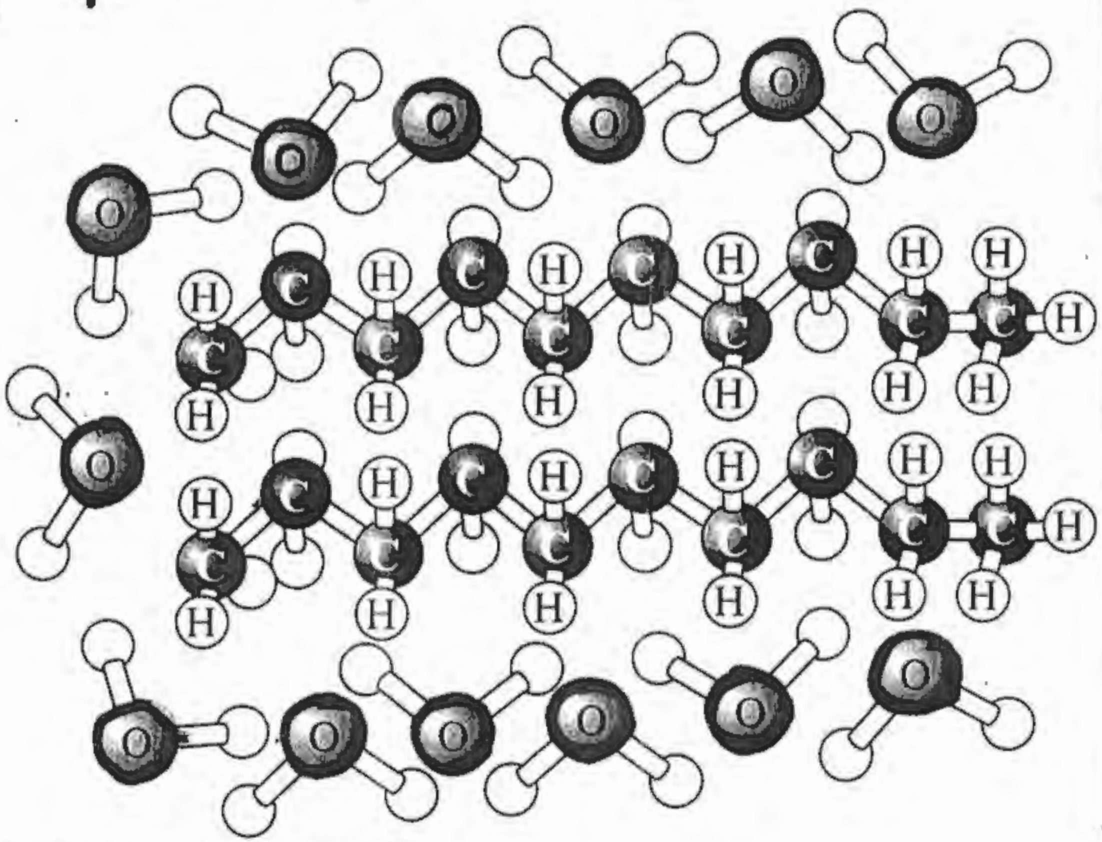
Figure 2-6b Concepts in Biochemistry, 3/e

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



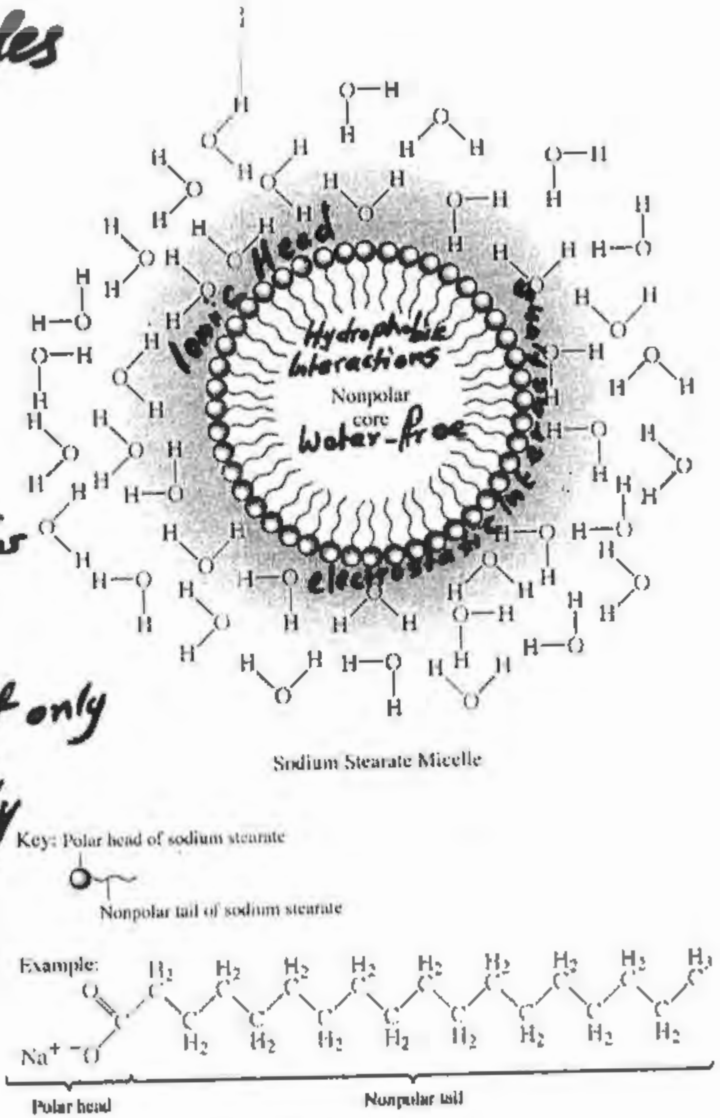
Water molecules in cage around hydrocarbon chain

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

Figure 2-7 Concepts in Biochemistry, 3/e

Amphiphilic Molecules

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



Amphiphilic Compound

Figure 2-8 Concepts in Biochemistry, 3/e