Chapter 2 Water

2.1 Weak Interactions in Aqueous Systems
2.2 Ionization of Water, Weak Acids, and Weak Bases
2.3 Buffering against pH Changes in Biological Systems
2.4 Water as a Reactant
2.5 The Fitness of the Aqueous Environment for Living Organisms

2.1 Weak Interactions in Aqueous Systems

- Water is a polar molecules：unequal charge distribution
- Polar biomolecules dissolve readily in water
- H-bond between water molecules make water in condensed phase.
- Polar molecules replace water-water interactions with more energetically favorable water-solute interactions.
- Nonpolar molecules tend to cluster together.

Weak Interactions in Aqueous Systems

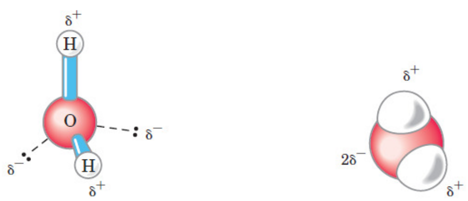
- Hydrogen bonds
- Ionic interactions
- Hydrophobic interactions
- Van der Waals interactions

} individually weak

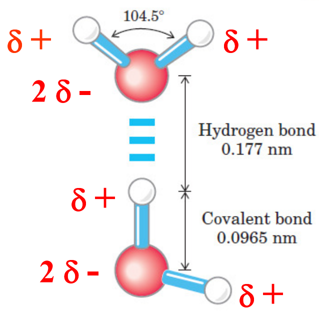
↓

collectively influence the 3-dimensional structures of proteins, nucleic acids, polysaccharides and membrane lipids!!

Hydrogen Bonding Gives Water Its Unusual Properties

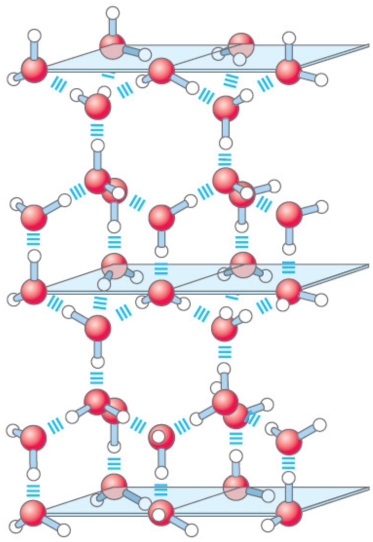


(a) (b)



Each water molecule

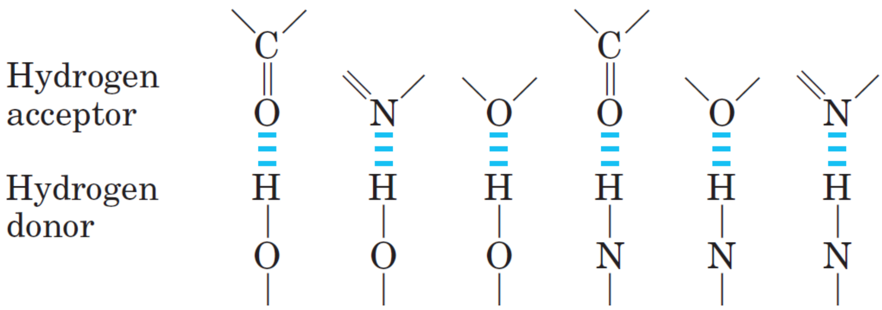
- **form 4 H-bonds in ice**
- **form average 3.4 H-bonds in liquid water**



Bond dissociation energy of H-bonds in liquid water about <u>23 kJ/mol</u>

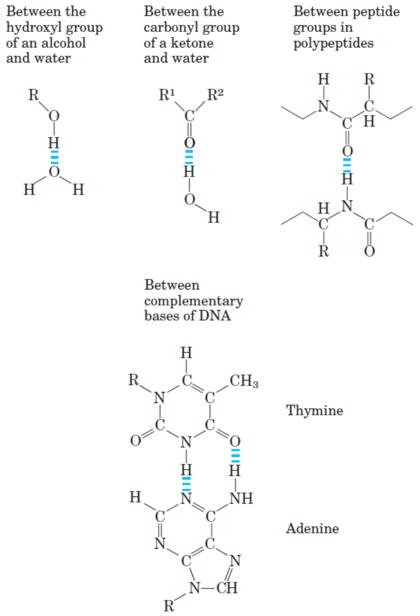
Compared to
C-C covalent bond, about <u>348 kJ/mol</u>
O-H covalent bond, about <u>470 kJ/mol</u>

Water Forms Hydrogen Bonds with Polar Solutes

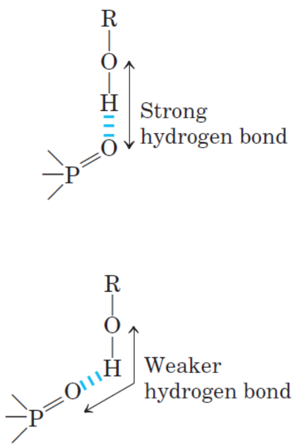


Common hydrogen bonds in biological systems

Biologically important H-bonds

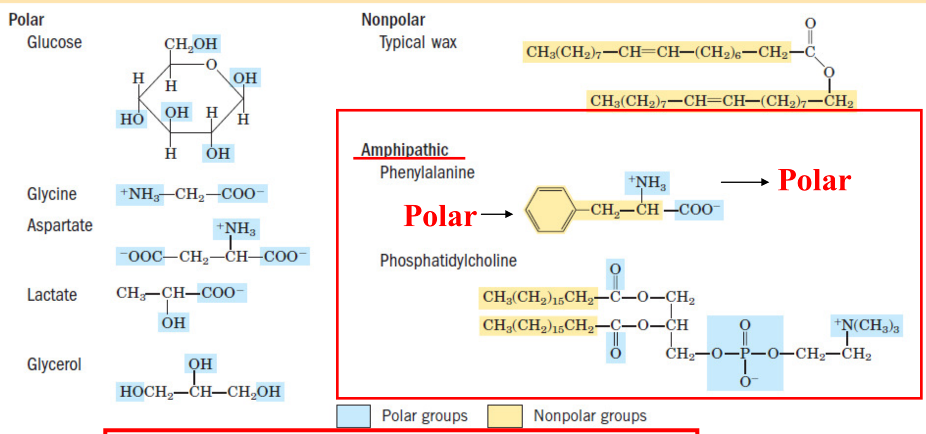


Directionality of the hydrogen bond



Water Interacts Electrostatically with Charged Solutes

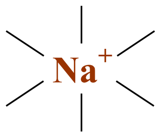
TABLE 2-2 Some Examples of Polar, Nonpolar, and Amphipathic Biomolecules (Shown as Ionic Forms at pH 7)



Hydrophilic (polar)
Hydrophobic (nonpolar)
Amphipathic (雙性)
} **molecules**

Water Interacts Electrostatically with Charged Solutes

Salts(e.g. NaCl)：dissolve in water due to "hydration" rx



6 H_2O molecules 包圍

$$F=\frac{Q_1 Q_2}{\varepsilon r^2}$$ **Ionic interaction**

ε ：**dielectric consts**

For water, ε=78.5
For benzene, ε=4.6

Ionic interaction in water is smaller than in benzene!!

Entropy Increases as Crystalline Substances Dissolve

Why NaCl dissolves in water?

$$NaCl_{(s)} \longrightarrow Na^+_{(g)} + Cl^-_{(g)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

lattice energy $\Delta H > 0$ hydration energy $\Delta H < 0$

$\Delta H_{total} > 0$ But $\Delta S_{total} \gg 0$

$$\Delta G = \Delta H - T\Delta S \begin{cases} \Delta H > 0 \\ \Delta S \gg 0 \end{cases} \Rightarrow \Delta G < 0$$

反應自發
NaCl 溶於水

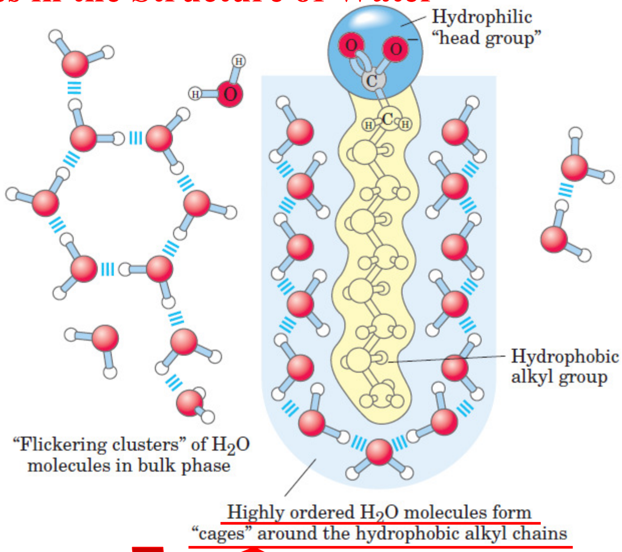
Nonpolar Gases Are Poorly Soluble in Water

TABLE 2-3 Solubilities of Some Gases in Water

Gas	*Structure**	*Polarity*	*Solubility in water (g/L)*†
Nitrogen	N≡N	Nonpolar	0.018 (40 °C)
Oxygen	O=O	Nonpolar	0.035 (50 °C)
Carbon dioxide	δ⁻ ← → δ⁻ O=C=O	Nonpolar	0.97 (45 °C)
Ammonia	H H H N (↓ δ⁻)	Polar	900 (10 °C)
Hydrogen sulfide	H H S (↓ δ⁻)	Polar	1,860 (40 °C)

The solubilities of polar gases (e.g. NH_3, H_2S) >> nonpolar gases (e.g. N_2, O_2, CO_2)

Nonpolar Compounds Force Energetically Unfavorable Changes in the Structure of Water



Clathrate (iceberg structure)!

$\Delta S << 0$

Nonpolar Compounds Force Energetically Unfavorable Changes in the Structure of Water

Clathrate (iceberg structure) :

Highly flexible H_2O molecules 被破壞
(after adding hydrophobic molecules)

⇩

Restrained in the solute molecule周圍

⇩

Cagelike shell

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta G > 0$$

$$\quad\quad + \quad\quad - $$

unfavorable！

Amphipathic compounds in aqueous solution

(Amphipathic compounds：
compounds contain regions that are polar (or charged) and regions that are nonpolar.)

Amphipathic compounds in aqueous solution

↓

形成micelles

Amphipathic compounds in aqueous solution – micelles formation

(1) Dispersion of lipids in H_2O

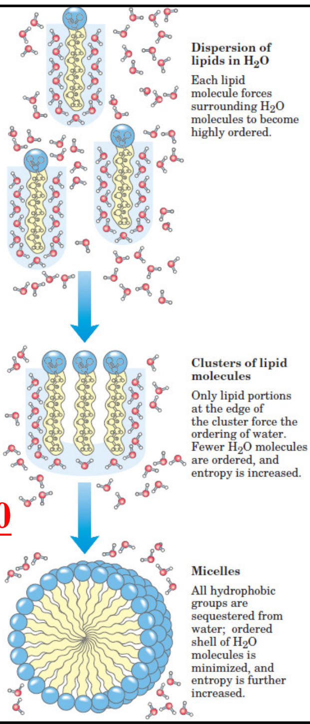
Each lipid molecule forces surrounding H_2O molecules to become highly ordered.

(2) Clusters of lipid molecules $\Delta S > 0$

Only lipid portions at the edge of the cluster force the ordering of water. (Fewer H_2O are ordered.)

(3) Micelles $\Delta S >> 0$

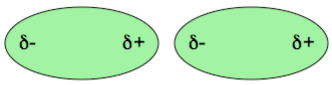
All hydrophobic groups are sequestered from water; ordered shell of H_2O is minimized.



London dispersion forces:

the attraction between nonploar molecules (吸引力)

$$\propto -\frac{B}{r^6}$$



instantaneous dipole **induced dipole**

Lennard Jones equation
(describes van der Waals interaction)

$$\frac{A}{r^{12}} - \frac{B}{r^6}$$

Nuclear repulsion

Hydrophobic interactions：

the forces that hold the nonpolar regions of the molecules together.

1. intrinsic attraction between nonpolar moieties

   $\Delta H < 0$ 親油吸引親油

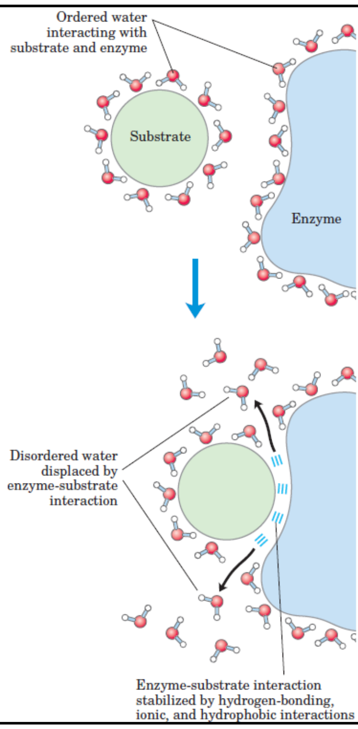
2. Minimiziny the number of ordered water molecules required to surround hydrophobic groups of solute molecule

   $\Delta S > 0$ Because Water molecules gain more freedom!

From 1 and 2 collectively:

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta G < 0$$

Enzyme-substrate interaction



van der Waals Interactions Are Weak Interatomic Attractions

TABLE 2-4 van der Waals Radii and Covalent (Single-Bond) Radii of Some Elements

Element	*van der Waals radius (nm)*	*Covalent radius for single bond (nm)*
H	0.11	0.030
O	0.15	0.066
N	0.15	0.070
C	0.17	0.077
S	0.18	0.104
P	0.19	0.110
I	0.21	0.133

Weak Interactions Are Crucial to Macromolecular Structure and Function

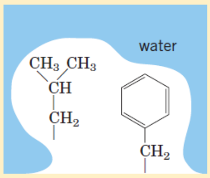
Four types on interactions
- **Hydrogen bonds**
- **Ionic interactions**
- **Hydrophobic interactions**
- **Van der Waals interactions**

The native structures of macromolecules

↓ **Determined by**

Weak-bonding possibilities are maximized!!

TABLE 2-5 Four Types of Noncovalent ("Weak") Interactions among Biomolecules in Aqueous Solvent

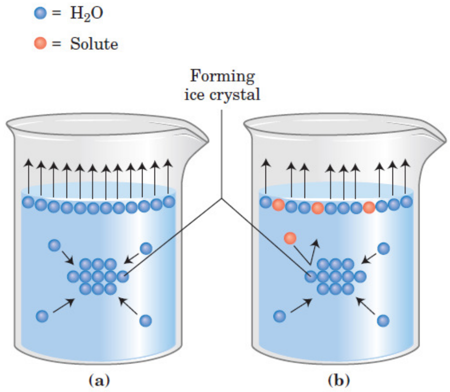
Hydrogen bonds	
Between neutral groups	>C=O···H—O—
Between peptide bonds	>C=O···H—N<
Ionic interactions	
Attraction	$—^{+}NH_3$ →← $^{-}O—C(=O)—$
Repulsion	$—^{+}NH_3$ ←→ H_3N^{+} —
Hydrophobic interactions	
van der Waals interactions	Any two atoms in close proximity

Solutes Affect the Colligative Properties of Aqueous Solutions (bulk properties)

van't Hoff equation

$\Pi = icRT$

Π : osmotic pressure
ic : the **osmolarity** of the solution
i : van't Hoff factor
c : solute's molar concentration



In **pure water,** every molecule at the surface is H_2O, and all contribute to the vapor pressure. Every molecule in the bulk solution is H_2O, and can contribute to formation of ice crystals.

In this **solution,** the effective concentration of H_2O is reduced; only 3 of every 4 molecules at the surface and in the bulk phase are H_2O. The vapor pressure of water and the tendency of liquid water to enter a crystal are reduced proportionately.

Solutes Affect the Colligative Properties of Aqueous Solutions

$\Pi = icRT$

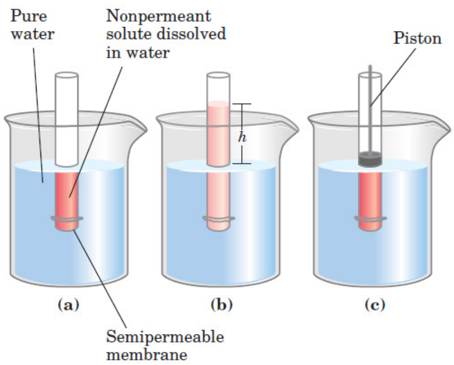
e.g. NaCl 在水中

Na^+ & Cl^-

i ≈2

但glucose在水中
仍然為glucose

i ≈1



Isotonic solutions(等滲壓溶液)：Solutions that have identical osmotic pressure

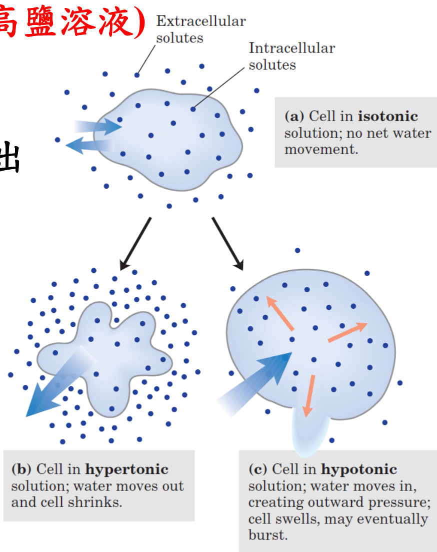
e.g. 靜脈注射液必須與血液是isotomic！

If ① hypertonic (高滲壓溶液,高鹽溶液)

osmotic pressure > blood

⟹ 紅血球內的solvent & small molecule 流出

⟹ 紅血球乾扁



(a) Cell in **isotonic** solution; no net water movement.

(b) Cell in **hypertonic** solution; water moves out and cell shrinks.

(c) Cell in **hypotonic** solution; water moves in, creating outward pressure; cell swells, may eventually burst.

② hypotonic (低滲壓溶液)

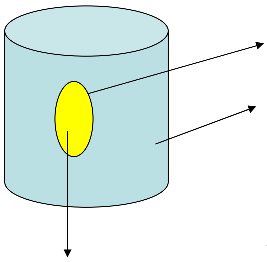
osmotic pressure < blood

⟹ 低滲壓溶液內solvent 流入紅血球

⟹ 紅血球漲破

e.g. 高鹽高糖保存食物，Why?

應用洗腎機及透析 (dialysis！) ←desalting



Dialysis membrane
(e.g. M.W.C.O 10kDa membrane)

M.W.C.O：
molecular weight cut-off
(粒子的分子量超過MWCO 將無法穿越membrane)

2.2 Ionization of Water, Weak Acids, and Weak Bases

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

at 25°C, $K_w=[H^+][OH^-]=10^{-14}$

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

$$K_w = K_{eq} \cdot [H_2O]$$
$$= K_{eq} \cdot 55.5M$$

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

The pH of some aqueous fluids

Human blood pH=7.4

Severely diabetic people：

pH of blood plasma <7.4

→ acidosis(酸中毒)

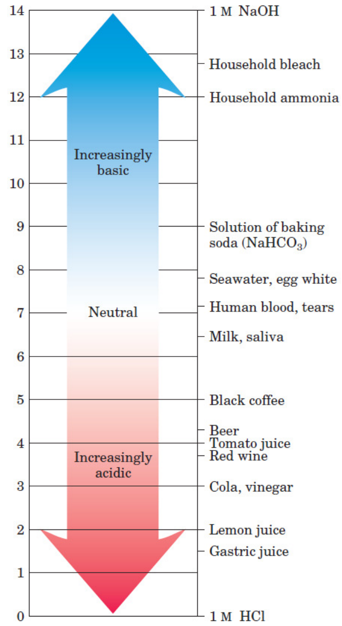


FIGURE 2–15 The pH of some aqueous fluids.

Henderson-Hasselbalch equation

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

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

$$-\log Ka + \log\frac{[A^-]}{[HA]} = -\log[H^+] \qquad pKa + \log\frac{[A^-]}{[HA]} = pH$$

$$pH = pKa + \log\frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

proton acceptor } conjugate
proton donor } acid-base pair

Henderson-Hasselbalch equation

$$pH = pKa + \log \frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

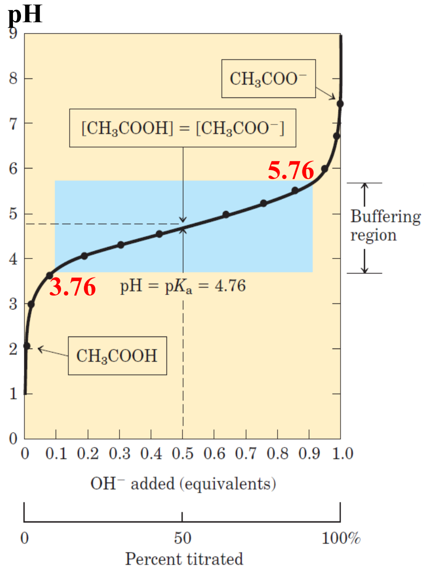
When $[CH_3COO^-] = [CH_3COOH]$
[proton acceptor] [proton donor]

$$pH = pKa + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

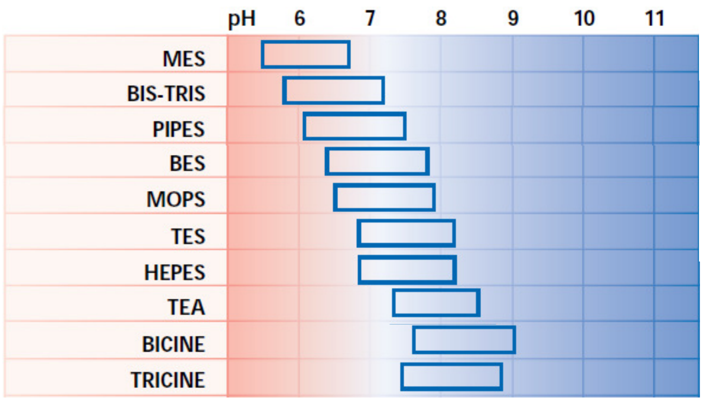
pH=pKa
when CH_3COOH half-dissociated

Buffering region: pKa ± 1

以CH_3COOH titrated with NaOH



常用的biological Buffers



*www.sigma-aldrich.com

Useful pH Ranges of Selected Biological Buffers (25° C, 0.1 M)