

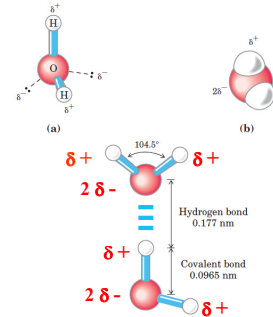
Chapter 2 Water

- 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

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Hydrogen Bonding Gives Water Its Unusual Properties



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2.1 Weak Interactions in Aqueous Systems

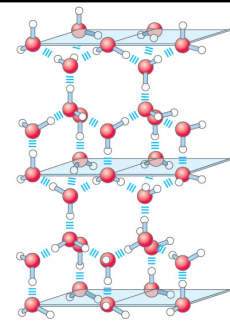
- Water is a polar molecules : unequal charge distribution
- Polar biomolecules dissolve readily in water
- H-bond between water molecules make water in condensed phase.
- Polar molecules replace water-water interactions with more energetically favorable water-solute interactions.
- Nonpolar molecules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

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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 23 kJ/mol

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

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Weak Interactions in Aqueous Systems

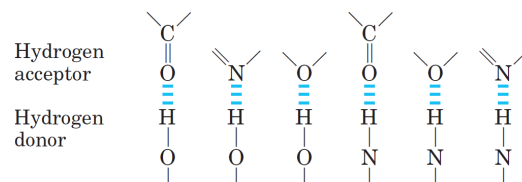
- Hydrogen bonds
 - Ionic interactions
 - Hydrophobic interactions
 - Van der Waals interactions
- } individually weak

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

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Water Forms Hydrogen Bonds with Polar Solutes



Common hydrogen bonds in biological systems

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Biologically important H-bonds

Between the hydroxyl group of an alcohol and water

Between the carbonyl group of a ketone and water

Between peptide groups in polypeptides

Between complementary bases of DNA

Thymine

Adenine

Directionality of the hydrogen bond

Strong hydrogen bond

Weaker hydrogen bond

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Entropy Increases as Crystalline Substances Dissolve

Why NaCl dissolves in water?

$$\text{NaCl}_{(s)} \rightarrow \text{Na}^+_{(g)} + \text{Cl}^-_{(g)} \rightarrow \text{Na}^+_{(aq)} + \text{Cl}^-_{(aq)}$$

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

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

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

反應自發
NaCl 溶於水

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Water Interacts Electrostatically with Charged Solutes

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

Polar

Glucose

Glycine

Aspartate

Lactate

Glycerol

Nonpolar

Typical wax

Amphipathic

Phenylalanine

Phosphatidylcholine

Polar groups

Nonpolar groups

Hydrophilic (polar)

Hydrophobic (nonpolar)

Amphipathic (雙性)

molecules

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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	O=C=O	Nonpolar	0.97 (45 °C)
Ammonia	H-N-H	Polar	900 (10 °C)
Hydrogen sulfide	H-S-H	Polar	1,860 (40 °C)

The solubilities of polar gases (e.g. NH₃, H₂S) >> nonpolar gases (e.g. N₂, O₂, CO₂)

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Water Interacts Electrostatically with Charged Solutes

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

Na^+

6 H₂O molecules 包圍

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

ϵ : dielectric consts For water, $\epsilon = 78.5$
For benzene, $\epsilon = 4.6$

Ionic interaction in water is smaller than in benzene!!

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Nonpolar Compounds Force Energetically Unfavorable Changes in the Structure of Water

Hydrophilic “head group”

Hydrophobic alkyl group

“Flickering clusters” of H₂O molecules in bulk phase

Highly ordered H₂O molecules form “cages” around the hydrophobic alkyl chains

Clathrate (iceberg structure)!

$\Delta S < 0$

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Nonpolar Compounds Force Energetically Unfavorable Changes in the Structure of Water

Clathrate (iceberg structure) :

Highly flexible H₂O molecules 被破壞
(after adding hydrophobic molecules)

↓
Restrained in the solute molecule 周圍

↓
Cagelike shell

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

+ -
unfavorable !

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London dispersion forces:

the attraction between nonpolar 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

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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

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Hydrophobic interactions :

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

1. intrinsic attraction between nonpolar moieties

$$\Delta H < 0 \quad \text{親油吸引親油}$$

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

$$\Delta S > 0 \quad \text{Because Water molecules gain more freedom!}$$

From 1 and 2 collectively:

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

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Amphipathic compounds in aqueous solution – micelles formation

(1) Dispersion of lipids in H₂O

Each lipid molecule forces surrounding
H₂O molecules to become highly
ordered.

$$\Delta S > 0$$

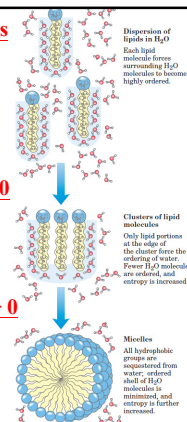
(2) Clusters of lipid molecules

Only lipid portions at the edge of the
cluster force the ordering of water.
(Fewer H₂O are ordered.)

$$\Delta S \gg 0$$

(3) Micelles

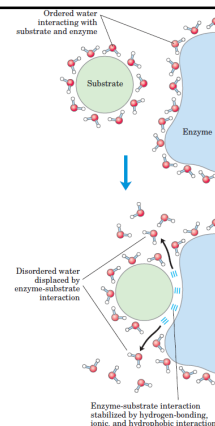
All hydrophobic groups are sequestered
from water; ordered shell of H₂O is
minimized.



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Enzyme-substrate interaction



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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

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Solutes Affect the Colligative Properties of Aqueous Solutions

$$\Pi = icRT$$

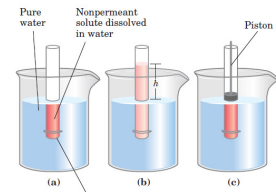
e.g. NaCl 在水中

$\text{Na}^+ \& \text{Cl}^-$

$$i \approx 2$$

但 glucose 在水中
仍然為 glucose

$$i \approx 1$$



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Weak Interactions Are Crucial to Macromolecular Structure and Function

Four types of interactions

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

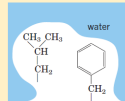
The native structures of macromolecules

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	$\text{C}=\text{O} \cdots \text{H}-\text{O}$
	Between peptide bonds	$\text{C}=\text{O} \cdots \text{H}-\text{N}$
Ionic interactions	Attraction	$-\text{NH}_3^+ \cdots \text{O}^-$
	Repulsion	$-\text{NH}_3^+ \cdots \text{H}_3\text{N}^+$
Hydrophobic interactions		Any two atoms in close proximity



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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 isotonic !

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

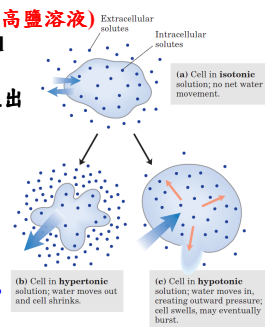
→ 紅血球乾扁

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?



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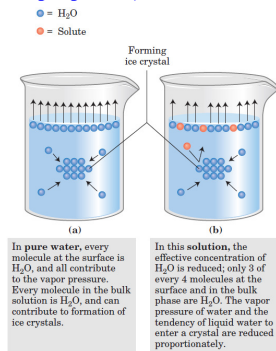
Solutes Affect the Colligative Properties of Aqueous Solutions (bulk properties)

van't Hoff equation

$$\Pi = icRT$$

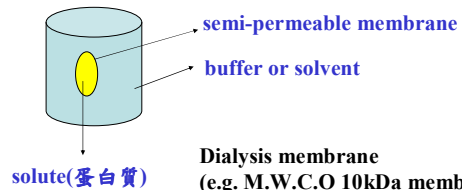
Π : osmotic pressure
 i : the osmolarity of the solution

c : solute's molar concentration



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應用洗腎機及透析 (dialysis !) ← desalting



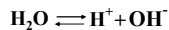
Dialysis membrane
(e.g. M.W.C.O 10kDa membrane)

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

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2.2 Ionization of Water, Weak Acids, and Weak Bases



at 25°C, $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$

$$K_{\text{eq}} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{K_w}{[\text{H}_2\text{O}]}$$

$$K_w = K_{\text{eq}} \cdot [\text{H}_2\text{O}]$$

$$= K_{\text{eq}} \cdot 55.5\text{M}$$

$$\text{pH} = -\log [\text{H}^+]$$

The pH of some aqueous fluids

Human blood pH=7.4

Severely diabetic people :

pH of blood plasma <7.4

acidosis(酸中毒)

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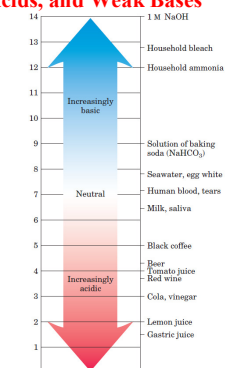
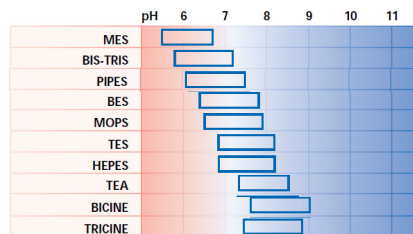


FIGURE 2-15 The pH of some aqueous fluids.

常用的生物 Buffers



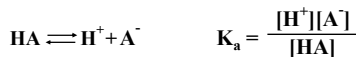
*www.sigma-aldrich.com

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

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Henderson-Hasselbalch equation



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

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

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

proton acceptor } conjugate
proton donor } acid-base pair

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Henderson-Hasselbalch equation

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

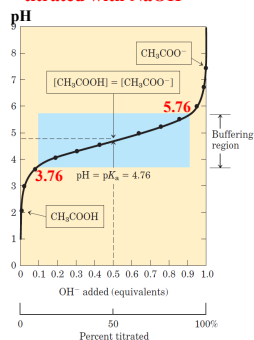
When $[\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COOH}]$
[proton acceptor] [proton donor]

$$\text{pH} = \text{pKa} + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

pH=pKa
when CH_3COOH half-dissociated

Buffering region: $\text{pKa} \pm 1$

$\alpha \text{CH}_3\text{COOH}$
titrated with NaOH



chap 2