Equilibria, Molecules and Water

- Lecture 3 9/01/09
- Chapter 2 Voet, Voet and Pratt

Summary

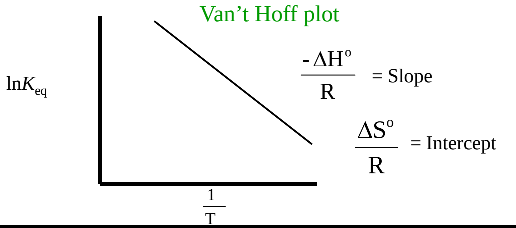
Chapter 1 - Introduction to the Chemistry of Life

1. What can Biochemistry say about possible Origin of Life?
2. What are the possible advantages of Compartmentation of Cells?
3. How do Prokaryotes and Eukaryotes differ in levels of Organization?
4. How do we classify organisms?
5. Is there common ground for all cells?
6. How do the principles of *Thermodynamics* apply to living organisms?

Equilibrium Constant K_{eq}

$$\ln K_{eq} = \frac{-\Delta H^o}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^o}{R}$$

R = gas constant for a 1M solution
Plot $\ln K_{eq}$ vs. 1/T (remember T is in absolute degrees Kelvin)



Standard State for Biochemistry

Unit Activity

25 °C

pH = 7.0 (not 0, as used in chemistry)

$[H_2O]$ is taken as 1, however, if water is in the Keq equation then $[H_2O]$ = 55.5

The prime indicates Biochemical standard state

K'_{eq} $\Delta G'^o$ $\Delta G'$

For the reaction $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$, calculate ΔG° and ΔG°' (i.e. T = 25 °C or 298K). The ionization constant for acetic acid is 1.8 x 10^{-5}. Is this reaction spontaneous?

1. ΔG° = -RT lnKeq = - (8.314J/mol/K) x (298K) ln(1.8 x 10^{-5})
   = 27069 J/mol = 27kJ/mol

2. For ΔG°'(the standard free energy change at pH7)

$$\Delta G = \Delta G^o + RT\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$\Delta G^{o\prime} = \Delta G^o + RT\ln [CH_3COO^-][H^+]/[CH_3COOH]$
= 27069 + (8.314J/mol/K) x (298K) ln [10^{-7}]
= 27069 - 39933 = -12864 J/mol

Covalent bond

The force holding two atoms together by the sharing of a pair of electrons.

H + H → H:H or H-H

The force: Attraction between two positively charged nuclei and a pair of negatively charged electrons.

Orbital: a space where electrons move around.

Electron can act as a wave, with a frequency, and putting a standing wave around a sphere yields only discrete areas by which the wave will be in phase all around. i.e different orbitals *S* and *P*

Valence orbitals: outermost orbital that is filled or partially filled with electrons. These can overlap and form covalent bonds.

Each orbital can have two electrons. Orbitals are designated by quantum numbers which define shells, orbital types spin etc

Element	electron or proton #	Val orbital #	Max # 0f electrons	own val electrons	Bond #	Lone pairs
H	1	1	2	1	1	0
C	6	4	8	4	4	0
N	7	4	8	5	3	1
O	8	4	8	6	2	2

Nitrogen N

•Nitrogen has five valence electrons
• Repulsion between the lone pair and the other orbital electrons make the N-N bond less stable (171 kJ/mole) than the C-C bond (348 kJ/mole).
• However, N-N triple bond is very stable 946 kJ/mole

Boron B

• Boron has only three valence electrons-this limits the stability and types of compounds it can make.

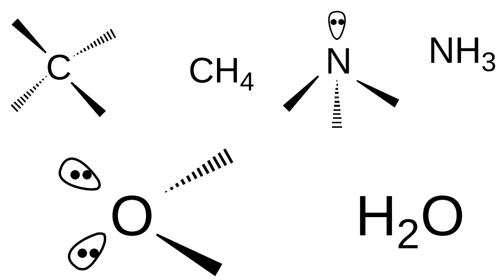
Silicon Si and Phosphate P

• Si-Si bonds are relatively weaker at 177 kJ/mole
• This makes longer Si-Si chains are unstable
• Si-O bonds are very stable 369 kJ/mole
•Poly phosphates are even less stable

Carbon

- Carbon forms the basis of life
- Carbon has a tremendous chemical diversity
- can make 4 covalent bonds
- can link together in C-C bonds in all sorts of flavors:
  - sp^1, sp^2 and sp^3 hybridized
- Readily forms stable hetronuclear bonds
- These bonds are less stable than C-C bonds and C-O-C and C-N bonds are places where cleavage sites are found

Molecular Shape: Tetrahedron sp^3



Chapter 2 Water

1. How is the molecular structure of water related to physical and chemical behavior?

2. What is a Hydrogen Bond?

3. What are Acids and Bases?

4. What is pH, and what does it have to do with the properties of Water?

5. What are Titration Curves?

6. What are buffers, and why they are important?

Table 2-1 Bond Energies in Biomolecules

Type of Bond	Example	Bond Strength ($kJ \cdot mol^{-1}$)
Covalent	O—H	460
	C—H	414
	C—C	348
Noncovalent		
Ionic interaction	$—COO^- \cdots {}^+H_3N—$	86
van der Waals forces		
Hydrogen bond	—O—H···O<	20
Dipole–dipole interaction	>C=O···>C=O	9.3
London dispersion forces	H–C(H)(—)—H···H—C(H)(—)—	0.3

Table 2-1 Fundamentals of Biochemistry, 2/e
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Non-covalent Bonding

1) **Electrostatic interactions**

by coulombs law $F = kq_1q_2 / r^2D$ q are charges r is radius

D = dielectric of the media, a shielding of charge.
And $k = 8.99 \times 10^9 Jm/C^2$
D = 1 in a vacuum
D = 2-3 in grease
D = 80 in water

Responsible for ionic bonds, salt linkages or ion pairs, optimal electrostatic attraction is 2.8Å

Dielectric effect	D
hexane	1.9
benzene	2.3
diethyl ether	4.3
$CHCl_3$	5.1
acetone	21.4
Ethanol	24
methanol	33
H_2O	80
HCN	116

H_2O is an excellent solvent and dissolves a large array of polar molecules.

However, it also weakens ionic and hydrogen bonds
Therefore, biological systems sometimes exclude H_2O to form maximal strength bonds!!

2) **Hydrogen bonds**

O-H·······N 2.88 Å N-H·······O 3.04 Å

H bond donor or an H bond acceptor

N—H O=C

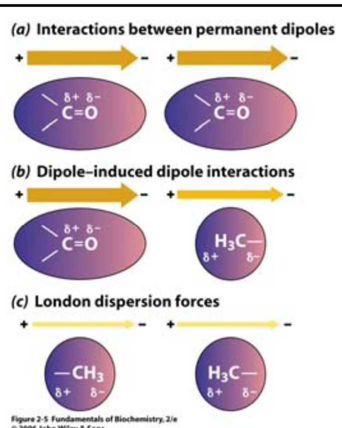
3-7 kcal/mol or 12-28 kJ/mol
very strong angle dependence

3) **van der Waals attraction**

Non-specific attractions 3-4 Å in distance (dipole-dipole attractions)

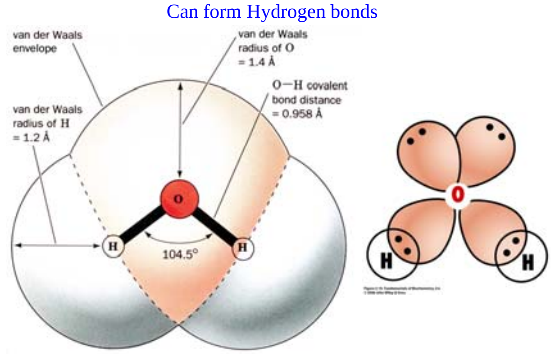
	Contact Distance Å	
H	1.2	1.0 kcal/mol
C	2.0	4.1 kJ/mol
N	1.5	weak interactions
O	1.4	important when many atoms
S	1.85	come in contact
P	1.9	

Can only happen if shapes of molecules match



Structure & Properties of Water

Bent geometry, O-H bond length of 0.958Å
Can form Hydrogen bonds



Hydrogen Bonds

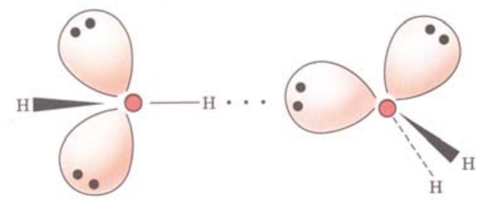
Physical properties of ice and water are a result of intermolecular hydrogen bonding

Heat of sublimation at 0^{o}C is 46 kJ/mol yet only 6 kJ/mol is gaseous kinetic energy and the heat of fusion of ice is 6 kJ/mol which is only 15% of the energy needed to melt ice.

<u>Liquid water is only 15% less hydrogen bonded than ice</u>

CH_4 boils at -164 ^{o}C but water is much higher.

A hydrogen bond between two water molecules



The structure of ice

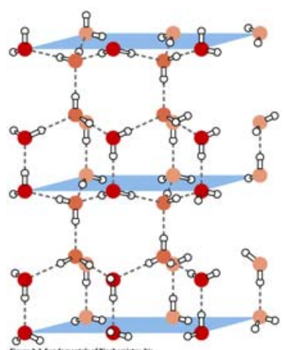


Figure 2-3 Fundamentals of Biochemistry, 2/e
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The structure of water is irregular

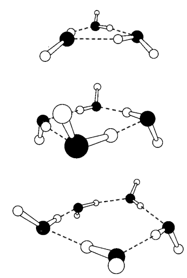


Figure 2-4. **Structure of a water trimer, tetramer, and pentamer.** These models are based on theoretical predictions and spectroscopic data. [After Liu, K., Cruzan, J.D., and Saykally, R.J., *Science* 271, 929 (1996).]

•Heat of sublimation of ice is 46.9 kJ/mol

•41 kJ/mol from hydrogen bonds.

•Only 15% of the hydrogen bonds are disrupted by melting

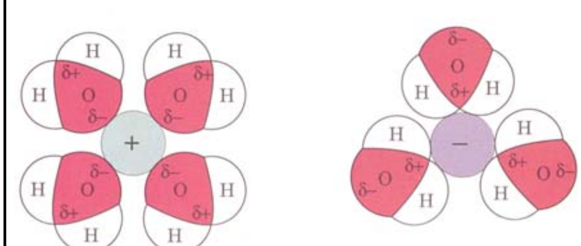
•Short term interactions are tetrahydral in nature

•Water reorients once in 10^{-12} sec that is a pico second

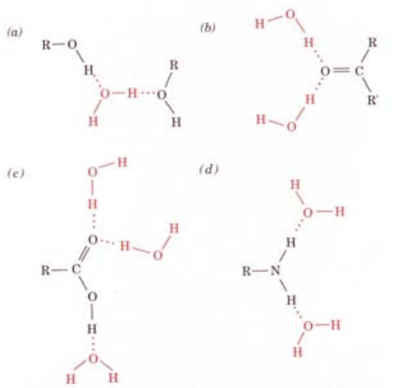
Water of Hydration

- Hydration - to be surrounded by H_2O
- A polar molecule is hydrated by the partial charge interaction of the water molecule
- Multiple H bonds increase solubility

Solvation of ions



Forms Hydrogen bonds with Functional Groups



The Hydrophobic effect

Free energy of transfer for hydrocarbons from water to organic solvent

Table 2-2 Thermodynamic Changes for Transferring Hydrocarbons from Water to Nonpolar Solvents at 25°C

Process	ΔH (kJ · mol^{-1})	$-T\Delta S$ (kJ · mol^{-1})	ΔG (kJ · mol^{-1})
CH_4 in $H_2O \rightleftharpoons CH_4$ in C_6H_6	11.7	−22.6	−10.9
CH_4 in $H_2O \rightleftharpoons CH_4$ in CCl_4	10.5	−22.6	−12.1
C_2H_6 in $H_2O \rightleftharpoons C_2H_6$ in benzene	9.2	−25.1	−15.9
C_2H_4 in $H_2O \rightleftharpoons C_2H_4$ in benzene	6.7	−18.8	−12.1
C_2H_2 in $H_2O \rightleftharpoons C_2H_2$ in benzene	0.8	−8.8	−8.0
Benzene in $H_2O \rightleftharpoons$ liquid benzene[a]	0.0	−17.2	−17.2
Toluene in $H_2O \rightleftharpoons$ liquid toluene[a]	0.0	−20.0	−20.0

[a]Data measured at 18°C.

Source: Kauzmann, W., *Adv. Protein Chem.* **14**, 39 (1959).

Table 2-2 Fundamentals of Biochemistry, 2/e
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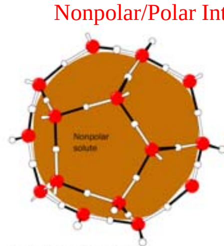
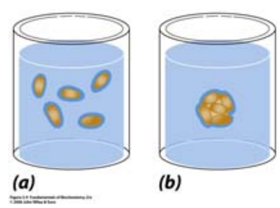
Nonpolar/Polar Interactions and Structured Water



A cage of water molecules (calatherate) surrounding the non-polar molecule. This cage has more structure than the surrounding bulk media.

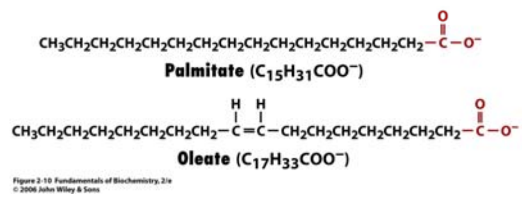
$\Delta G = \Delta H - T\Delta S$

To minimize the structure of water the hydrophobic molecules cluster together minimizing the surface area.



Amphiphiles

- Most biological molecules contain both polar and non-polar segments
- They are at the same time hydrophobic and hydrophilic



Amphiphiles: both polar and non-polar

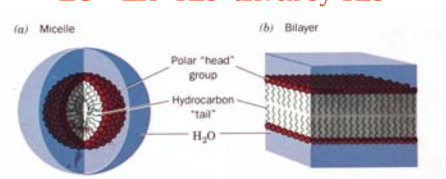
Detergents, Fatty acids, lipid molecules

- polar head; non-polar tail.
- Water is more concentrated than the molecules it surrounds so the shear numbers of ordered molecules is much greater. The greatest entropy is a function of both the dissolved molecule and the solvent.
- Proteins are also amphipathic and hydrophobic interactions are the greatest contributor the the three dimensional shape of proteins.

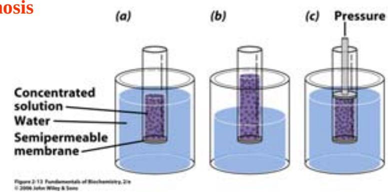
Amphiphiles form micelles, membrane bilayes and vesicles

- A single amphiphile is surrounded by water, which forms structured "cage" water. To minimize the highly ordered state of water the amphiphile is forced into a structure to maximize entropy

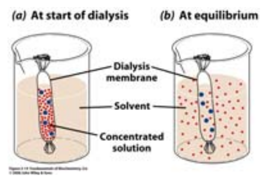
$\Delta G = \Delta H - T\Delta S$ driven by $T\Delta S$



Osmosis



Diffusion



Key Concepts:

Noncovalent bonds play important roles in determining the physical and chemical properties of water. They also have a significant effects on the structure and function of biomolecules.

H-bonding is responsible for water's high freezing and boiling points. Because water has a high heat capacity, it can absorb and release heat slowly. Water plays an important role in regulating heat in living organisms.

Lecture 4
Thursday 9/03/09
Acids and Bases

4) Hydrophobic interactions

Non-polar groups cluster together

$$\Delta G = \Delta H - T\Delta S$$

The most important parameter for determining a biomolecule's shape.

Entropy order-disorder. Nature prefers to maximize entropy "maximum disorder".

B. Consider the following reaction:

Glucose-1-phosphate ⟶ glucose-6-phosphate
$\Delta G°$ = -1.7 kcal/mole.

What is the equilibrium constant for this reaction at pH 7 and 25°C?

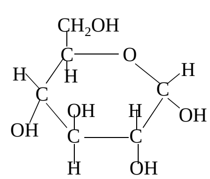
$$K_{eq} = e^{\frac{-\Delta G^o}{RT}}$$

$e^{-\{(-1700cal/mol)(4.184J/cal)\}/\{(8.3145J/K/mol)(298K)\}} = 17.6$

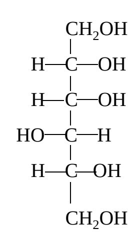
C. Consider the reaction with ΔH = 10 kJ and ΔS = 45 J•K^{-1}.
Is the reaction spontaneous (1) 10°C, (2) at 90°C ?

$\Delta G = \Delta H - T\Delta S$

How many water molecules could hydrogen-bond directly to glucose? To sorbitol?



Glucose



Sorbitol

Chemical Evolution

Life developed from “carbon-based” Self Replicating RNA molecules “RNA World” Catalytic RNA.

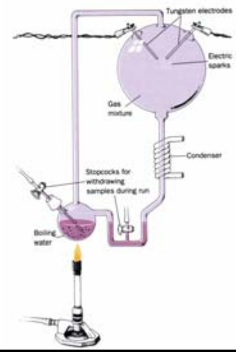
Chemical Evolution.

From HCN, NH_3, H_2O give rise to adenine or carbohydrates.

By sparking CH_4, NH_3, H_2O and H_2 these are formed:

PRODUCTS

Glycine
glycolic acid
Sarcosine
Alanine
Lactic acid
N-Methalanine
α-Amino-*n*-butyric acid
α - Aminoisobutyric acid
β- Alanine
Succinic Acid
Glutamic acid
and more



Covalent Polymerization in Life Processes

- C, H, O, N, P, and S all readily form covalent bonds.
- Only 35 naturally occurring elements are found in life processes.
- Earth’s Crust 47% O2, 28% Si, 7.9% Al, 4.5% Fe, and 3.5% Ca.
- B, C, N, Si and P can form three or more bonds and can link together.