Water and Life (Slide 3)

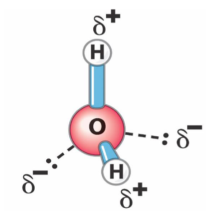
§1 Molecular Structure of Water

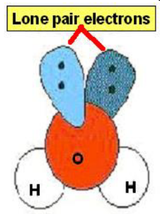
1. Structure

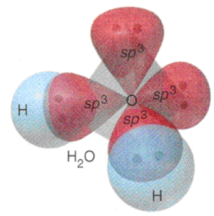
1° Composed of one oxygen atom and two hydrogen atoms.

2° Oxygen atom shares one electron with each hydrogen atom

3° Tetrahedral structure (sp^3 hybridization)







2. Bond

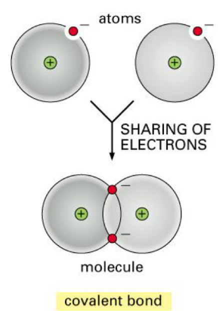
1° Covalent Bond

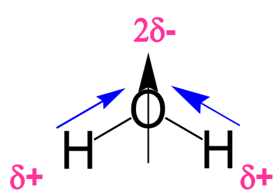
2° The sharing of electrons in a covalent bond is unequal (polarized bond)

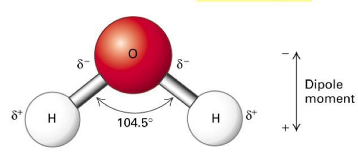
3° One end is partially positive and the other partially negative.

atomic number / electron shell

element	I	II	III	IV
1 Hydrogen	●			
2 Helium	●●			
6 Carbon	●●	●●●●		
7 Nitrogen	●●	●●●●●		
8 Oxygen	●●	●●●●●●		
10 Neon	●●	●●●●●●●●		
11 Sodium	●●	●●●●●●●●	●	
12 Magnesium	●●	●●●●●●●●	●●	
15 Phosphorus	●●	●●●●●●●●	●●●●●	
16 Sulfur	●●	●●●●●●●●	●●●●●●	
17 Chlorine	●●	●●●●●●●●	●●●●●●●	
18 Argon	●●	●●●●●●●●	●●●●●●●●	
19 Potassium	●●	●●●●●●●●	●●●●●●●●	●
20 Calcium	●●	●●●●●●●●	●●●●●●●●	●●





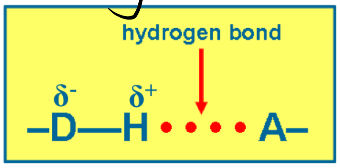


CO_2

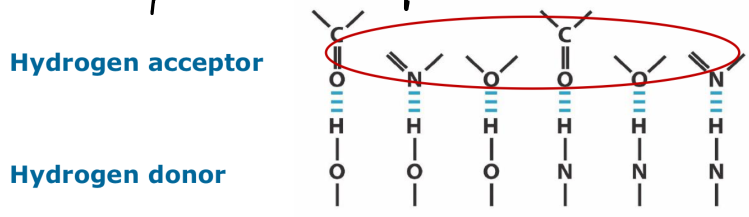
3. Hydrogen bonding

1° Special case of dipole interactions involved molecules having H bound to electronegative atoms.

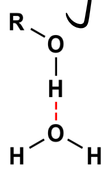
In biochemistry, that means N, O, S etc.



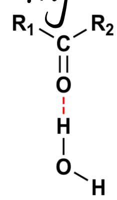
2° This attraction is directed along the donor-H axis and the lone pair of acceptor.



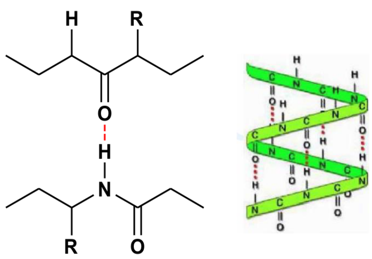
3° Some biologically important hydrogen bonds



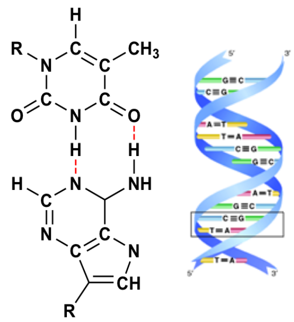
Between the hydroxyl group and water



Between the carbonyl group and water



Between amino acids in polypeptides



Between complementary bases of DNA

§2 Water — An Excellent Solvent

1. Noncovalent interaction

Water dissolves hydrophilic material.

{ many ionic compounds
polar organic compounds

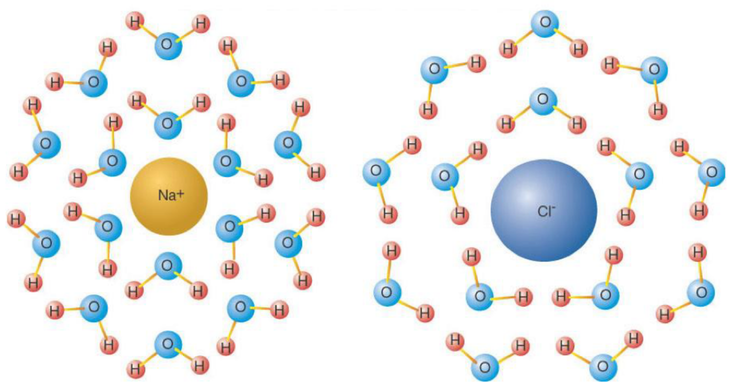
These compounds are soluble in water due to three kinds of noncovalent interactions:

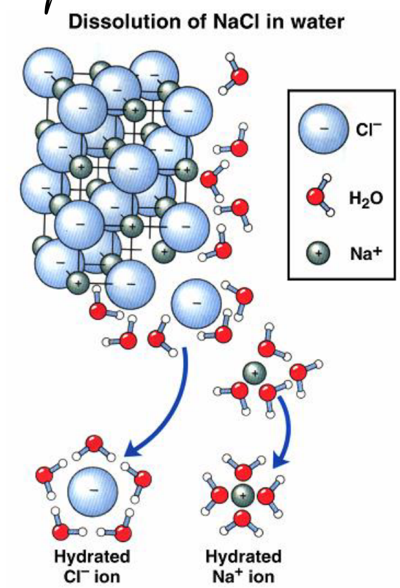
(ion dipole

dipole - dipole
hydrogen bonding

2. Ion-dipole

Ions are hydrated by water molecules. The water molecules orient so the opposite charge end points to the ion to partially neutralize charge.

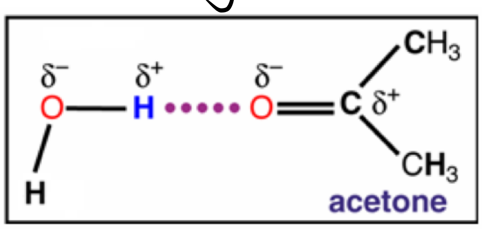


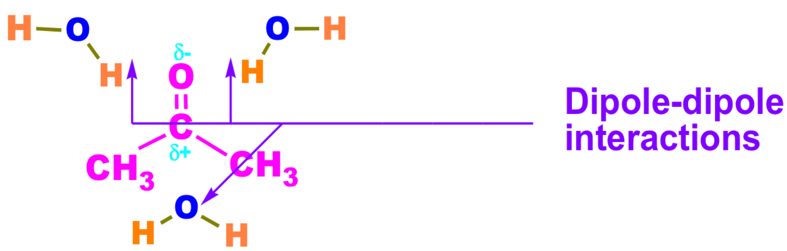


The shell of water molecule is a solvation sphere.

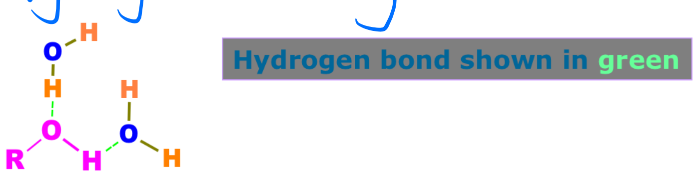
3. Dipole - dipole

The polar water molecule interacts with an O or N or an H on an O or N on an organic molecule.





4. Hydrogen-bonding



Alcohol	Structure	Solubility(mol/100g H_2O)
Methanol	CH_3OH	∞
Ethanol	CH_3CH_2OH	∞
Propanol	$CH_3(CH_2)_2OH$	∞
Butanol	$CH_3(CH_2)_3OH$	0.11
Pentanol	$CH_3(CH_2)_4OH$	0.030
Hexanol	$CH_3(CH_2)_5OH$	0.0058
Heptanol	$CH_3(CH_2)_6OH$	0.0008

5. Cellular concentration and diffusion

1° The viscosity of cytoplasm is higher than that of water.

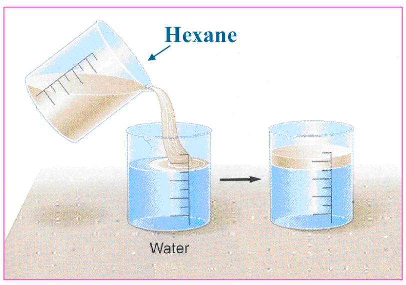
2° Charged molecules bind transiently to each other inside cells and this restricts their mobility.

3° Collision with other molecules inhibit diffusion due to an effect called molecular crowding.

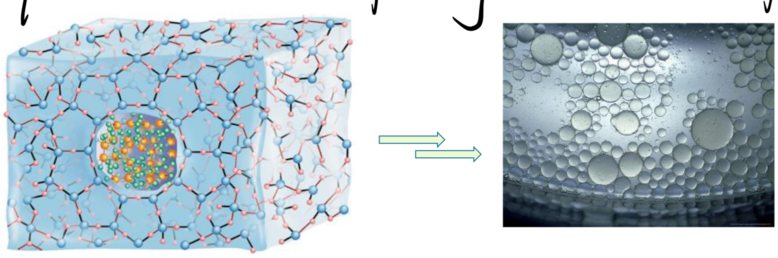
6. Nonpolar substances are insoluble in water.

They are said to be "hydrophobic".

CH_4, $CH_3CH_2CH_2CH_2CH_2CH_3$, hexane (petrol ether)



Water forms hydrogen-bonded cagelike structures around hydrophobic molecules, forcing them out of solution.



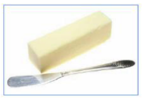
7. Amphipathic molecule

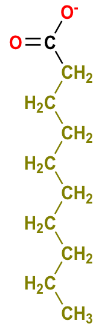
1° Amphipathic molecules contain both polar and nonpolar groups.

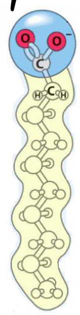
2° Ionized fatty acids are amphipathic. The carboxylate group is water soluble. But the long hydrocarbon chain is not water soluble.

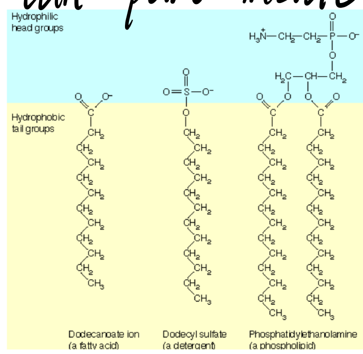
3° Amphipathic molecules tend to form micelles, colloidal aggregates with the charged "head" facing outward to the water and the nonpolar "tail" part inside.

Eg. Fatty acid etc

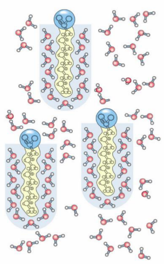




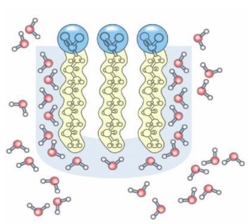




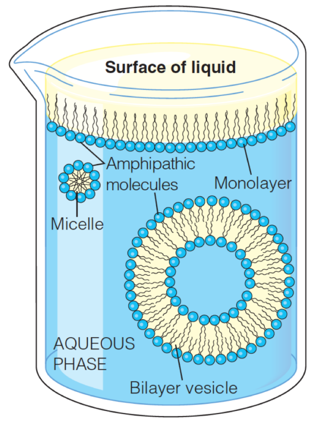
• **Amphipathic molecule**



Dispersion of lipids in water each lipid molecule forces surrounding water to become highly ordered.

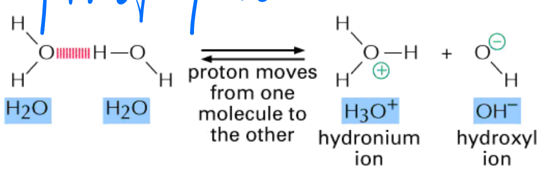


Cluster of lipid molecules. Water molecules are ordered only at the edge of the lipid cluster.



§3 Ionization of Water

1. The pH of pure water (At 25°C)



In pure water, the concentration of water is $\frac{1000}{18} = 55.5\,mol/L$. We can substitute 55.5 mol/L in the equilibrium constant expression.

$$K_{eq} = \frac{[H^+]\cdot[OH^-]}{55.5\,mol/L}$$

Keq, determined by electric-conductivity measurement of pure water, is $1.8 \times 10^{-16}\,mol/L$ at 25°C.

(55.5 mol/L) $K_{eq} = [H^+][OH^-] = K_w$

K_w: Ion product of water

$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} (mol/L)^2$

At natural pH,

$K_w = [H^+][OH^-] = [H^+]^2$

Solving for $[H^+]$ gives:

$[H^+] = [OH^-] = 1.0 \times 10^{-7}$ mol/L

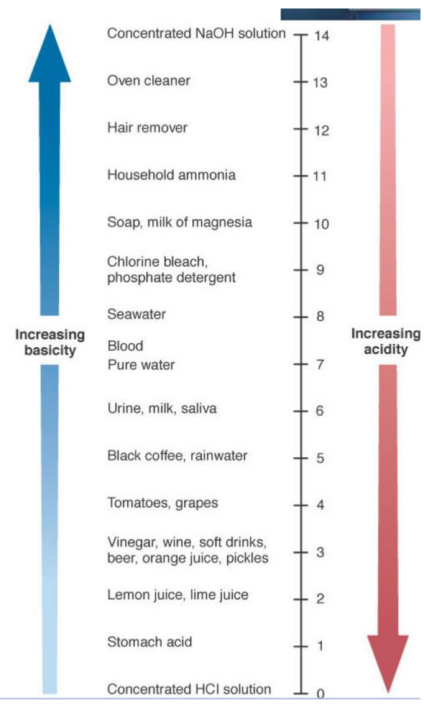
$pH = -\log[H^+] = 7$

* Organisms maintain their cytosolic pH very close to neutrality (typical pH = 7.4). The pH of certain intracellular compartments and extracellular fluids can vary.

2. pH scale

pH scale

$[H^+]$ (M)	pH	$[OH^-]$ (M)	pOH
10^0 (1)	0	10^{-14}	14
10^{-1}	1	10^{-13}	13
10^{-2}	2	10^{-12}	12
10^{-3}	3	10^{-11}	11
10^{-4}	4	10^{-10}	10
10^{-5}	5	10^{-9}	9
10^{-6}	6	10^{-8}	8
10^{-7}	7	10^{-7}	7
10^{-8}	8	10^{-6}	6
10^{-9}	9	10^{-5}	5
10^{-10}	10	10^{-4}	4
10^{-11}	11	10^{-3}	3
10^{-12}	12	10^{-2}	2
10^{-13}	13	10^{-1}	1
10^{-14}	14	10^0 (1)	0



3. Strong acids

Some compounds essentially completely ionize in aqueous solution and release free H^+.

$$HCl \longrightarrow H^+ + Cl^- \ (100\%)$$

e.g. What's the pH of a 1M HCl solution?

$$[H^+]_{total} = [H^+]_{HCl} + [H^+]_{H_2O}$$

$$[H^+]_{total} = 1.0M + 1.0\times10^{-7}M \approx 1.0$$

$$pH = -\log[1] = 0$$

What's the pH of a 10^{-8} M HCl solution?

$$[H^+]_{total} = [H^+]_{HCl} + [H^+]_{H_2O}$$

$$[H^+]_{total} = 10^{-8}M + 1.0\times10^{-7}M = 1.1\times10^{-7}$$

$$pH = 7 - \log[1.1] = 6.96$$

4. Weak acids

Some compounds capable of releasing protons do not completely ionize in aqueous solution.

$$HAc \longrightarrow H^+ + Ac^- \ (<100\%)$$

After approaching equilibrium, the dissociation constant given by:

$$K_a = \frac{[H^+][Ac^-]}{[HAc]}$$

For HAc, $K_a = 1.75\times10^{-5}M$; This indicated that only a small proportion of the acetic acid will dissociate.

5. pKa

pKa: An alternertive to Ka to describe acid strength.

$$HA \xrightleftharpoons{Keq} H^+ + A^-$$

$$Keq = \frac{[H^+][A^-]}{[HA]} = K_a \text{ (Dissociation constant)}$$

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

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

(Herderson Hasselbalch Equation)

pKa = pH when 50% of molecules are dissociated, the other 50% being neutral.

6. Strong bases

One type of base is any compound that will dissociate to release free OH^-.

$$NaOH \longrightarrow Na^+ + OH^-$$

pOH: rarely used. $pOH = 14 - pH$

Physiological systems rarely reach pH value above 8

7. Bronsted-Lowry Theory

1° Acid = Proton donor ; Base = Proton acceptor

+H⁺

共轭碱

Acid				Conjugate Base		
HA	+	B	⟶	A	+	BH
		Base				Conjugate Acid 共轭酸

-H⁺

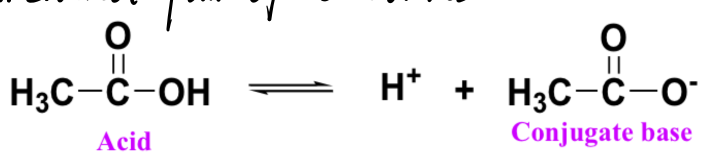
2° Conjugated acids

① The conjugated acid of a weak base will be a strong acid.

② The conjugated acid of a strong base will be a weak acid.

The strongest base usually carry a negative charge.

Weaker bases are usually neutral molecules with an unshared pair of electrons.



8. Evaluation of acid strength

1° All the acids form hydronium ion in water system.

The important difference is the conjugate base.

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

2° Some factors may influence the acid strength:

Electronegative

Resonanse

Inductive effects

Effects of electronegativity

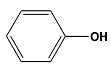
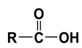
Increasing electronegativity →

	CH_4	NH_3	H_2O	HF
pka:	50	34	17	3.4

Acid strength →

	RCH_3	RNH_2	ROH	RCOOH
pka:	45	34.5	18	5

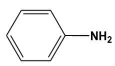
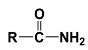
Resonance Effects

R-OH  

	R-OH	phenol	R-C(=O)-OH
pka	18	10	5

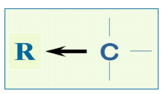
Ethanol has no resonance stabilization and is thus much less acidic.

Acid strength →

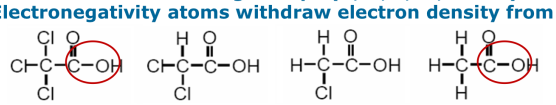
$R-NH_2$  

	$R-NH_2$	aniline	$R-C(=O)-NH_2$
pka	28	25	15

Inductive Effects



1: R - Electron Withdrawing Groups (N, O, F, Cl, Br etc)
Electronegativity atoms withdraw electron density from carbon.



← *Acid strength*

pka	0.52	1.25	2.85	4.74

2: R - Electron donatinging Groups (Alkyl groups etc)
Less Electronegativity atoms increase electron density on carbon

	H-COOH	CH_3-COOH	CH_3CH_2-COOH	$(CH_3)_3$-C-COOH
pka	3.75	4.75	4.87	5.01

9. pH in biochemistry

- Many important biomolecules contain weakly acidic and basic groups. Protein molecules have acidic (e.g., Carboxylate) and basic (e.g., Amino) groups on side groups of amino acids residues.
- Such groups respond to pH changes near physiological range (pH 6 - 8), affecting their structure and thus their function, in important ways.
- The catalytic efficiency of many enzymes critically depends on ionization state of the groups.
- Therefore, such enzymes are effective only at defined pH (or pH ranges).

Consequently, biochemical processes are sensitive to even small changes in pH, therefore:

1. Monitoring pH is essential in most biochemistry experiments .
2. Virtually all biochemistry experiments require pH buffers.
3. If buffer is not made correctly, the experiment may fail or, not represent what you think it does.

§4 Buffers

1. What's buffer?

Buffers are aqueous system that tends to resist change in pH when small amounts of acid (H^+) or base (OH^-) are added.

2. The importance of buffers

The chemical reactions of life constantly produces acids and bases within cells.

Most of catalysts in biological systems are extremely sensitive to pH

Biological buffers are important in maintaining cellular homogenous.