Chapter 2: Water

Chapter 2 Opener Fundamentals of Biochemistry, 2/e

Water: excellent solvent for polar molecules

Polarity

H bond capability

Physical properties of water

Structure of water: non linear structure

The distance of closest approach between two nonbonded atoms

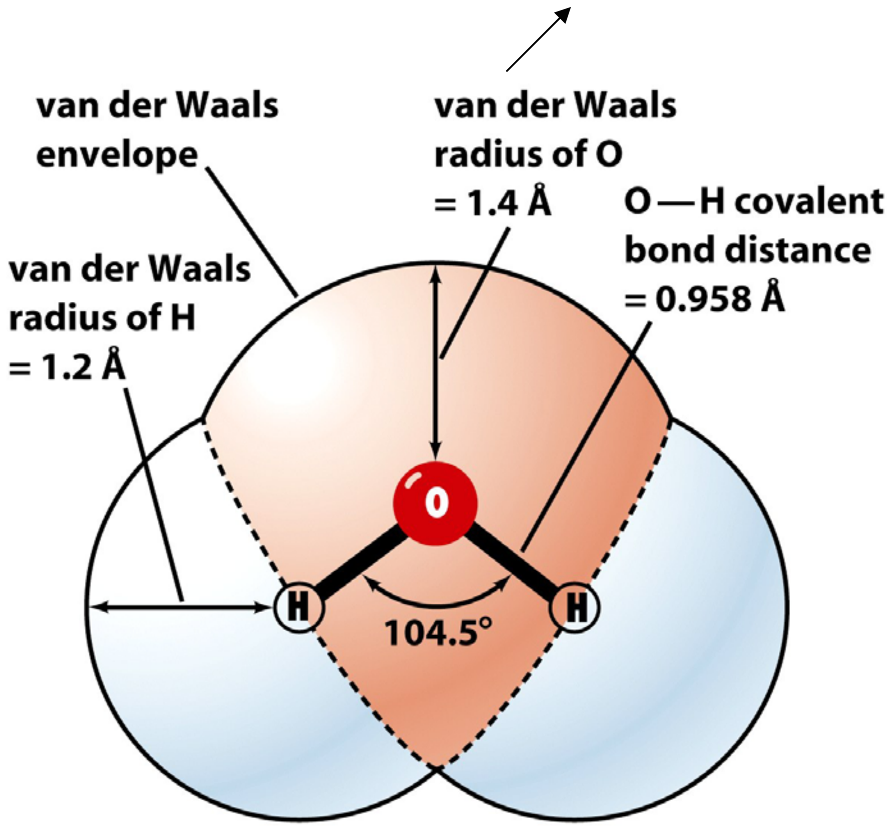


Figure 2-1a Fundamentals of Biochemistry, 2/e

Tetrahedral *sp*^{3} orbitals of the oxygen atoms

water is polar (dipole)

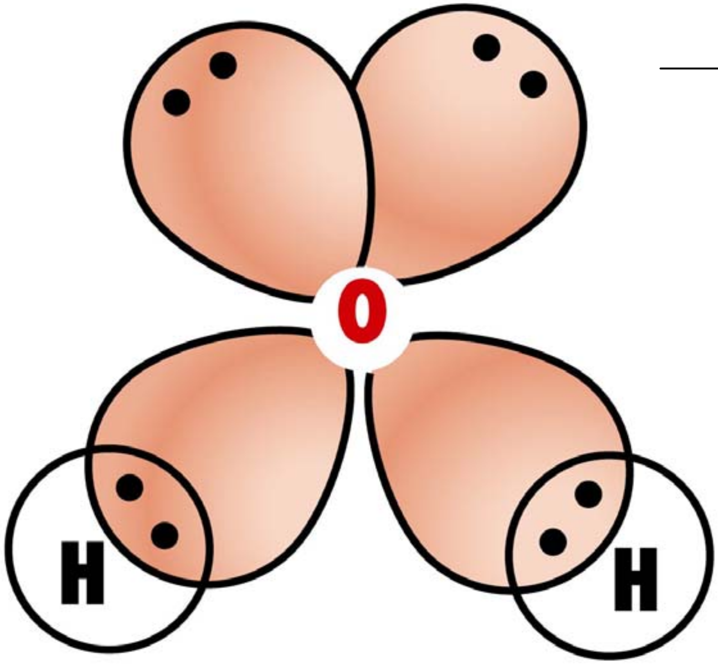


Figure 2-1b Fundamentals of Biochemistry, 2/e

→ Partial– charge (δ^-) of –0.66e

→ Partial + charge (δ^+) of +0.33e

Directional intermolecular association: H bond

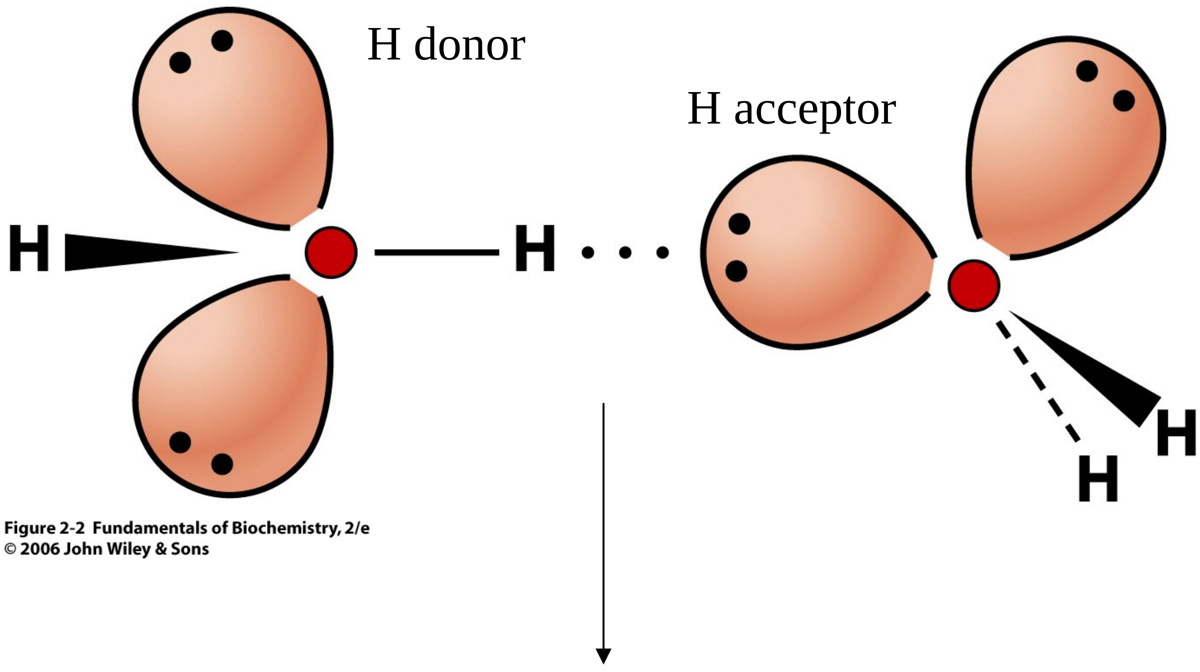


Figure 2-2 Fundamentals of Biochemistry, 2/e

$\sim 1.8 < (1.4 + 1.2)$

The structure of ice: six membered ring

each molecule interacts with four other molecules
(maximum possible interaction)

density
melting point

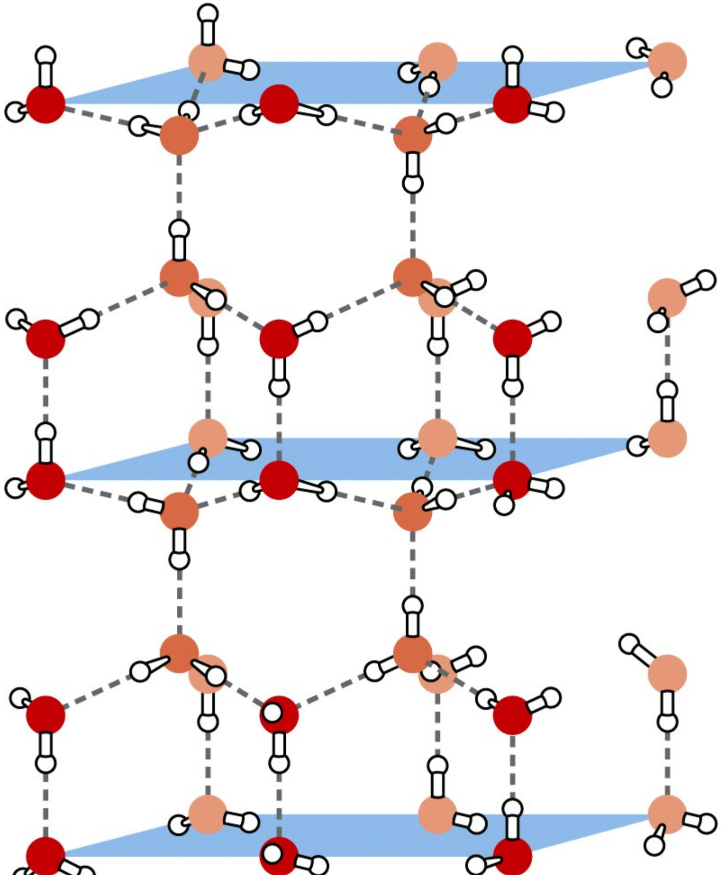


Figure 2-3 Fundamentals of Biochemistry, 2/e

The structure of liquid water is irregular

reorientation of each molecule: ~1/10^{-12} sec

Possible combination

Rapid fluctuation of H-bonds

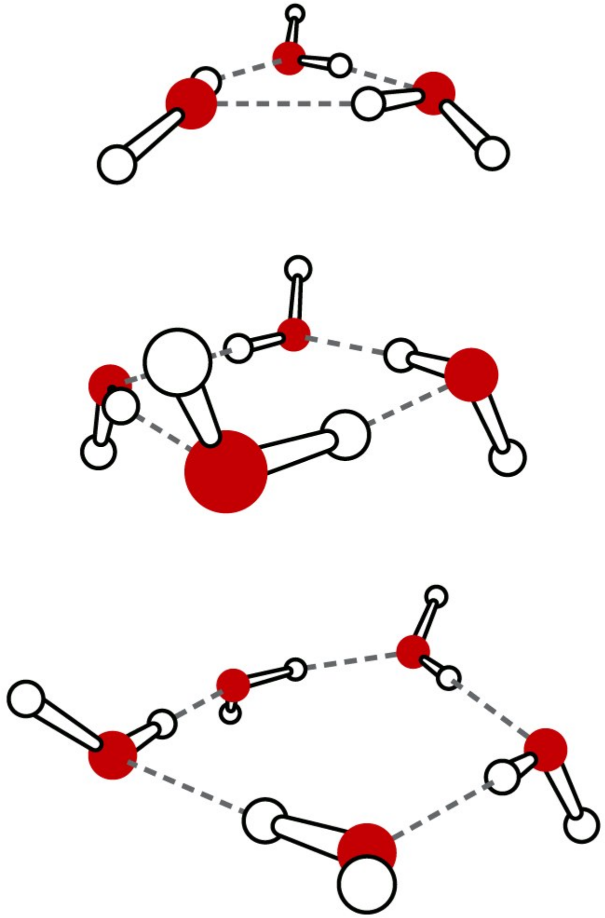


Figure 2-4 Fundamentals of Biochemistry, 2/e

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	$—O—H \cdots O<$	20
Dipole–dipole interaction	$>C{=}O \cdots >C{=}O$	9.3
London dispersion forces	$—CH_2—H \cdots H—CH_2—$	0.3

Table 2-1 Fundamentals of Biochemistry, 2/e

Ionic (fully charged): NaCl
Nonionic: covalent (most organic molecules)
polar (partially charged): oxygen
nonpolar: carbon

Dipole-dipole interactions

permanent

induced

momentary

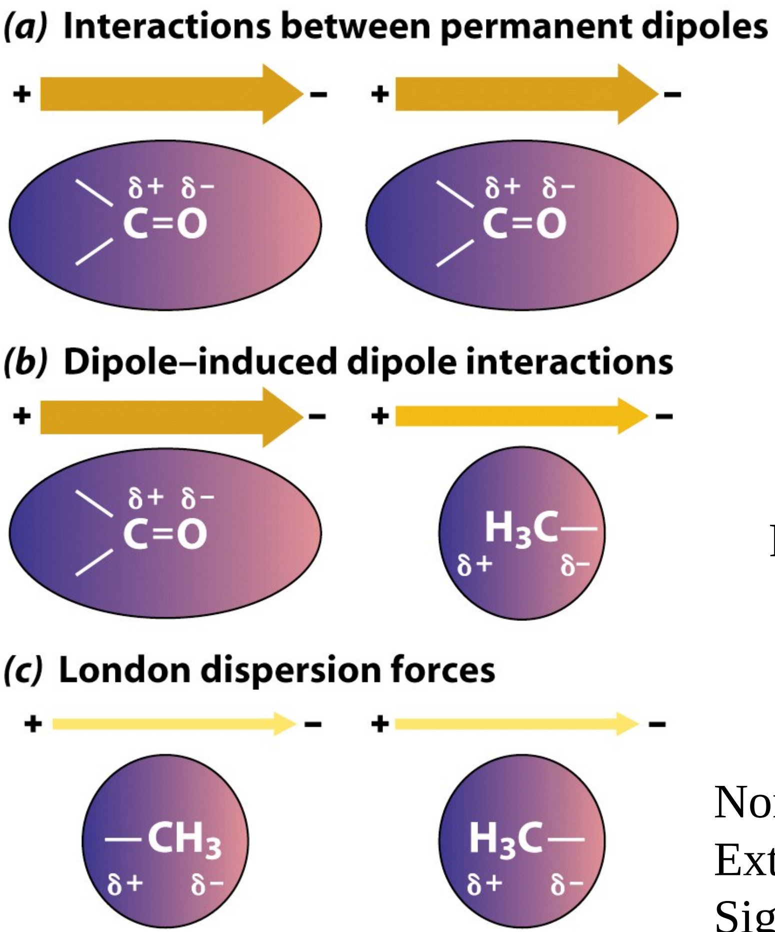


Figure 2-5 Fundamentals of Biochemistry, 2/e

Polar & polar interaction

Polar & nonpolar interaction

Nonpolar & nonpolar interaction
Extremely weak
Significant only in close contact
Extremely important for structure

Water as a solvent

hydrophilic

hydrophobic

(hydrated = solvated)

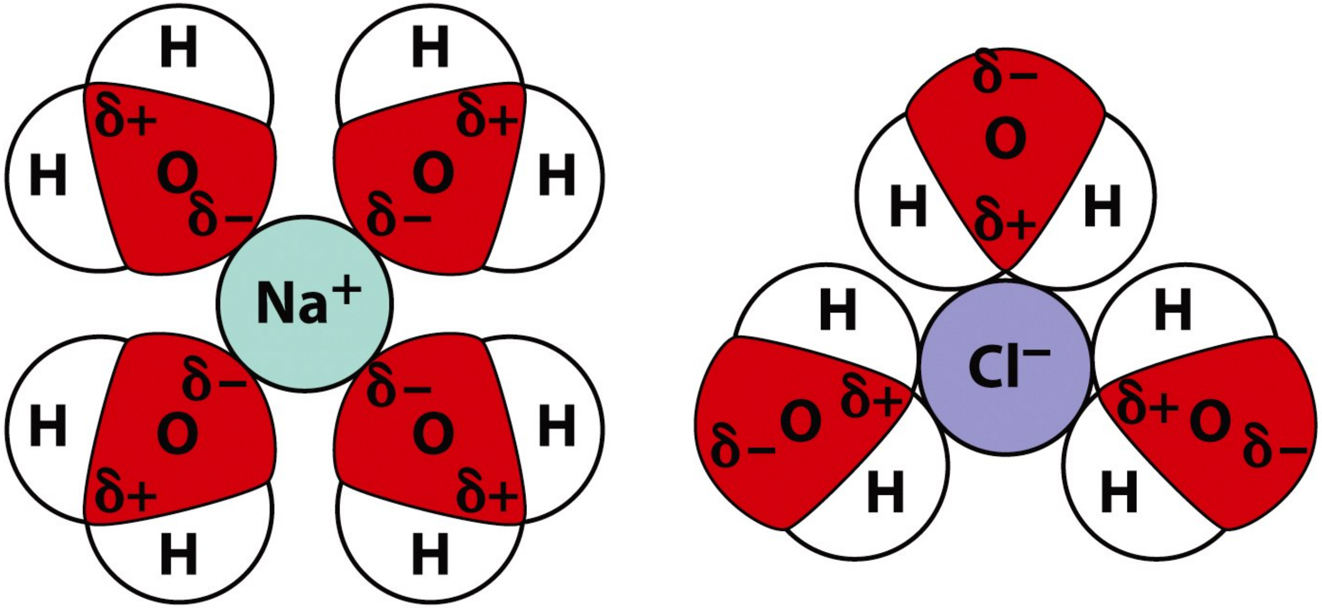


Figure 2-6 Fundamentals of Biochemistry, 2/e

H bonding by functional groups

functional groups as H donor or H acceptor

most biomolecules contain functional groups

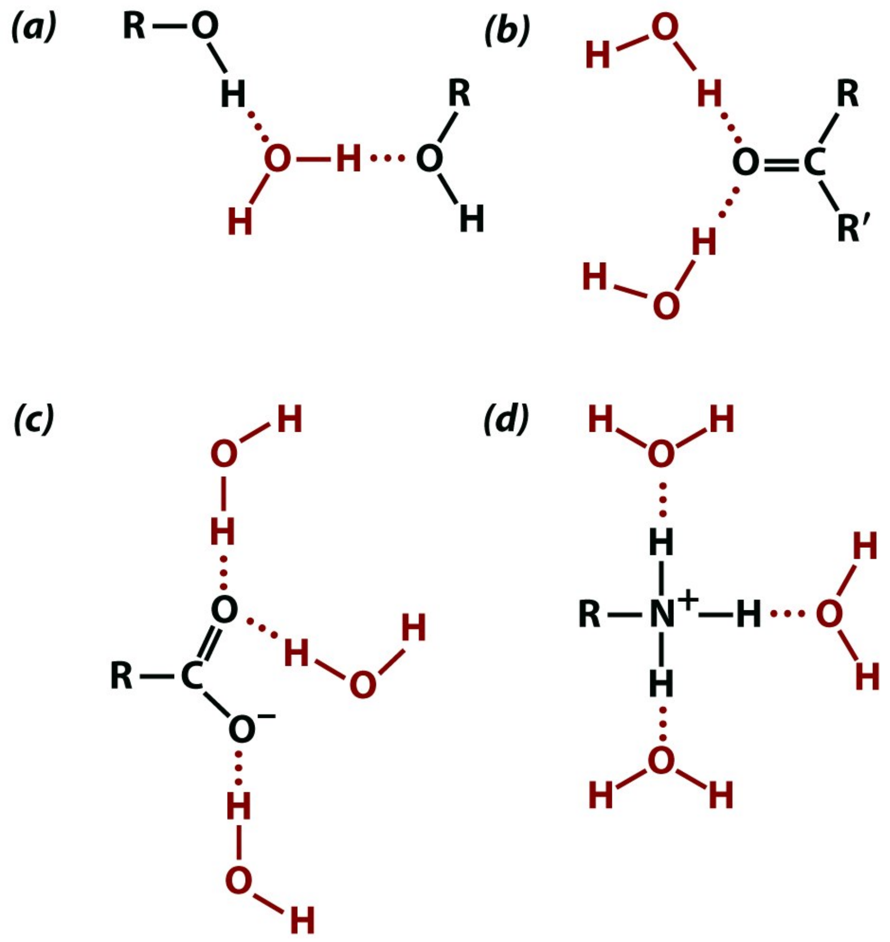


Figure 2-7 Fundamentals of Biochemistry, 2/e

The hydrophobic effect

the tendency of water to minimize its contacts with hydrophobic molecules

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

Process	ΔH ($kJ \cdot mol^{-1}$)	$-T\Delta S$ ($kJ \cdot mol^{-1}$)	ΔG ($kJ \cdot mol^{-1}$)
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

Entropically driven

Orientation of water molecules around a nonpolar solute

maximizing H bonds capacity
H bond network around the molecule
increase of order in water molecules

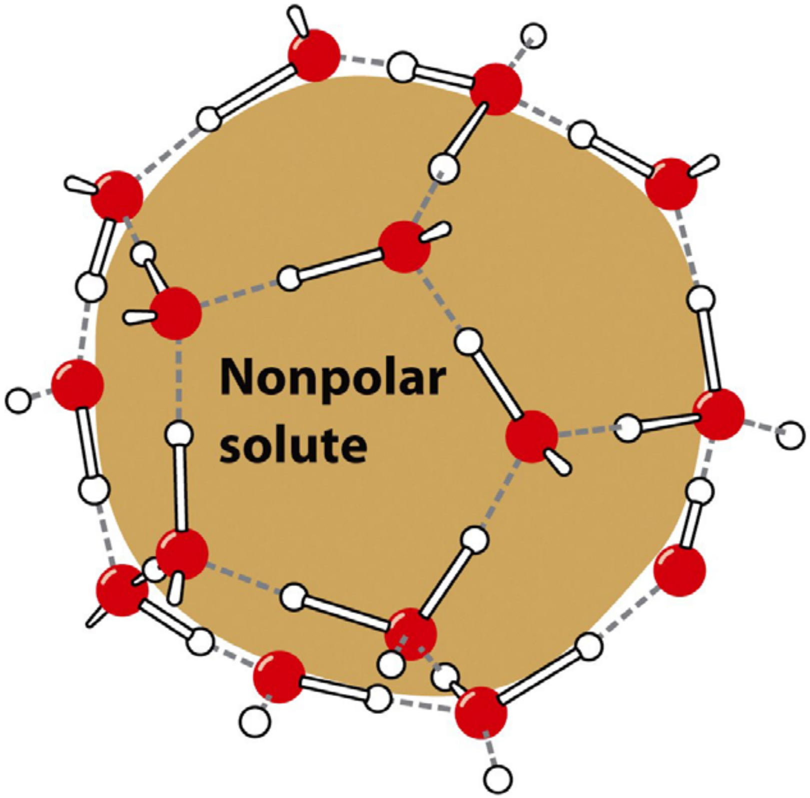


Figure 2-8 Fundamentals of Biochemistry, 2/e

Aggregation of nonpolar molecules in water

Hydrophobic molecules are not dispersed (not solvated)

Entropy is increased

(decrease in the molecule but increase in water)

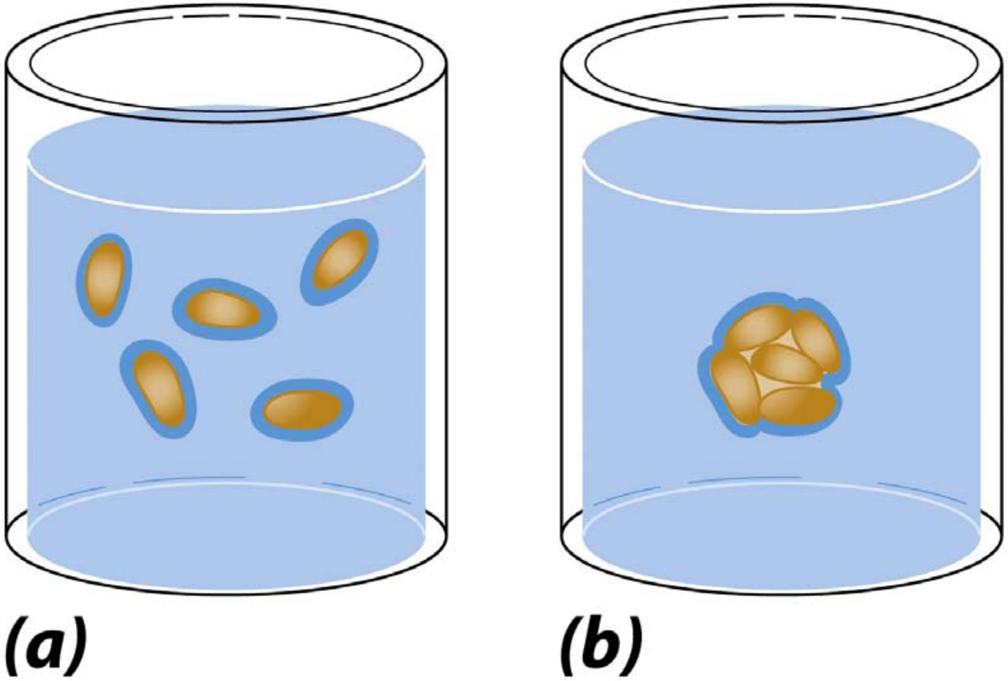
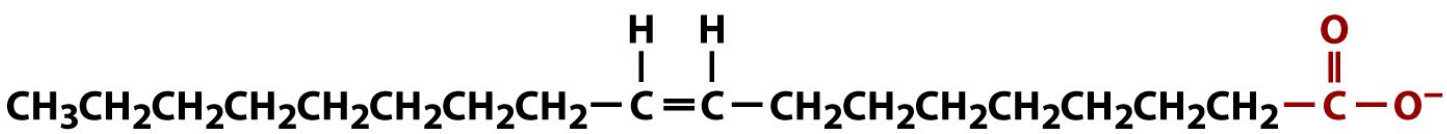


Figure 2-9 Fundamentals of Biochemistry, 2/e

Amphiphiles form micelles and bilayers

Amphiphiles: fatty acids

Palmitate ($C_{15}H_{31}COO^-$)



Oleate ($C_{17}H_{33}COO^-$)

Figure 2-10 Fundamentals of Biochemistry, 2/e

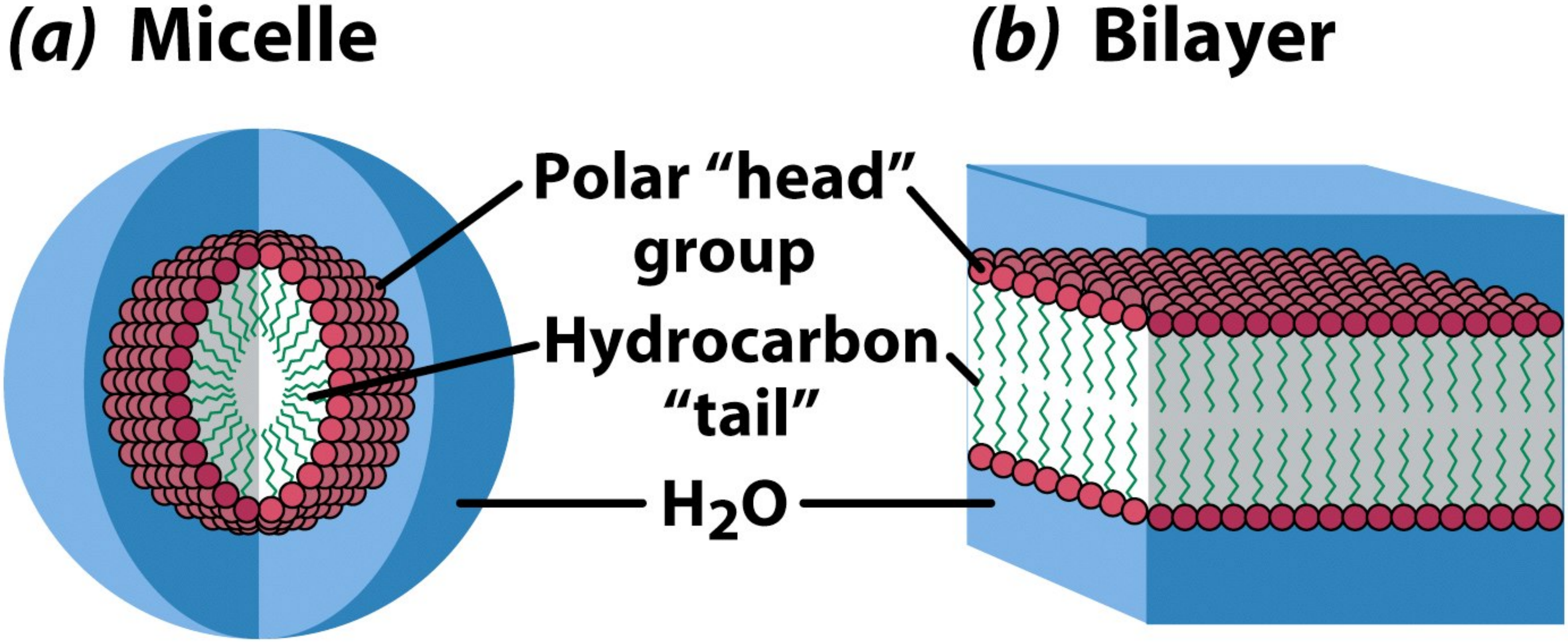


Figure 2-11 Fundamentals of Biochemistry, 2/e

Osmosis

movement of a solution to a lower conc

prevent the inward flow ⟶ osmotic pressure

implications of osmotic pressure for living organisms

animal, plant, bacteria, etc

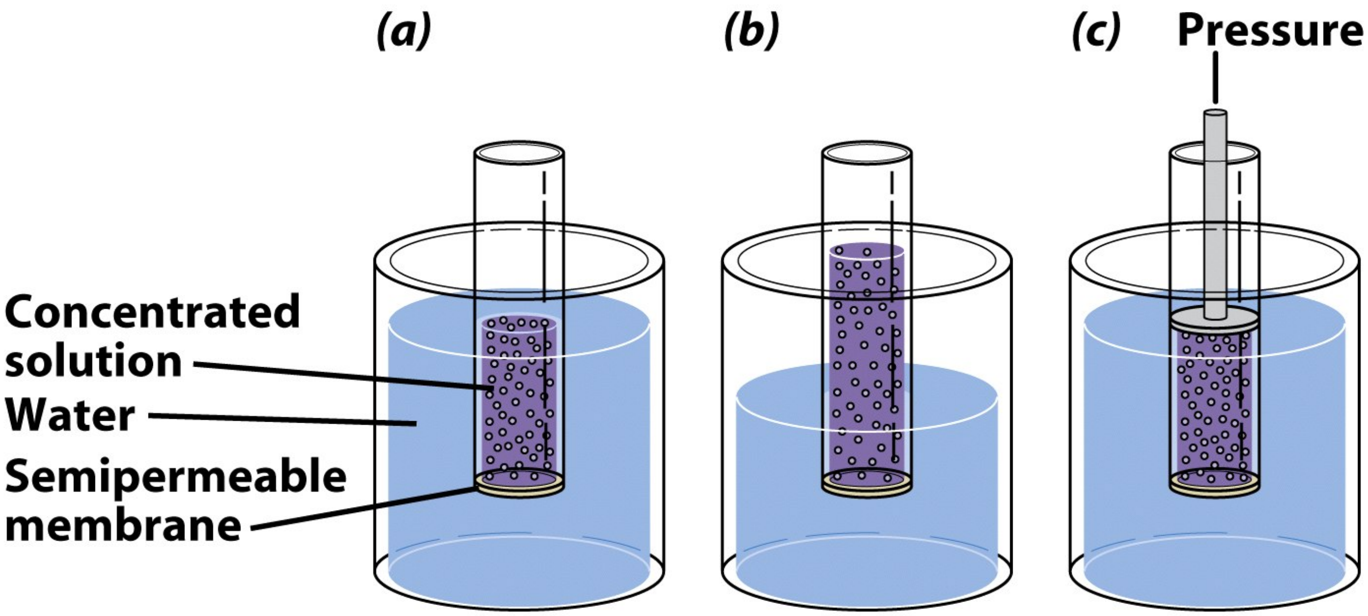


Figure 2-13 Fundamentals of Biochemistry, 2/e

Diffusion

random movement of molecules to a lower conc.

diffusion rate is proportional to $1/d^2$ (diffusion in all directions)

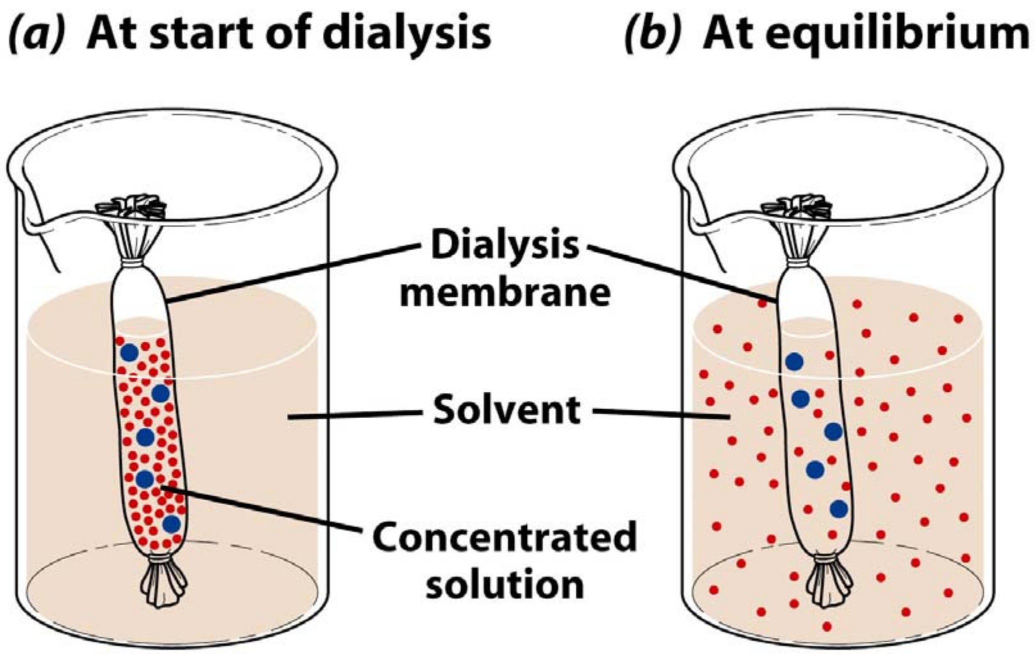
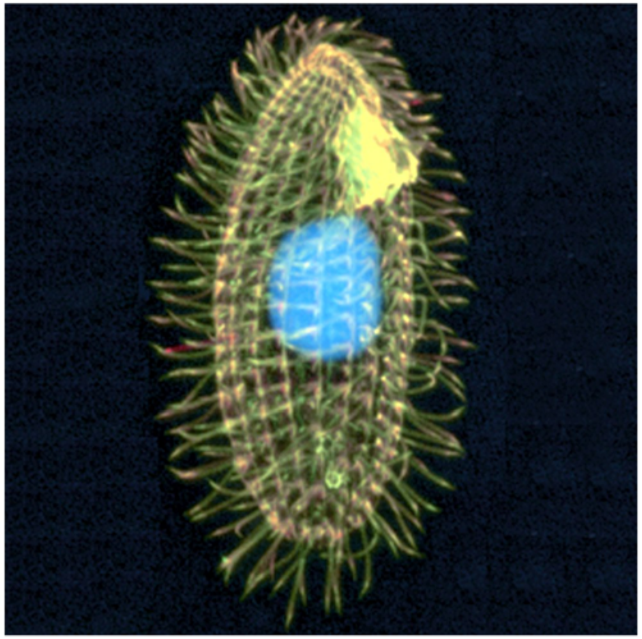


Figure 2-14 Fundamentals of Biochemistry, 2/e

Diffusion determines the cell suze

- diffusion is important for transportation of molecules
- surface to volume ratio: should be high or low?
- the larger the less surface area
  - limit in cell size
  - monocellular & multicellular

tetrahymena



Unnumbered Figure pg 31 Fundamentals of Biochemistry, 2/e

Chemical properties of water

Ionization of water

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

very slightly ionize

H^+ (proton) actually exists as H_2O^+ (hydronium ion)

Proton jumping

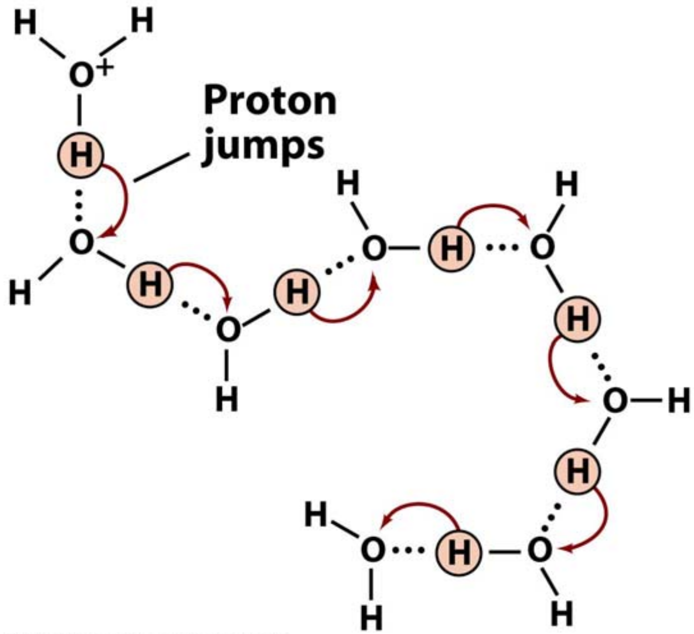


Figure 2-15 Fundamentals of Biochemistry, 2/e

Dissociation constant of water

$K = [H^+][OH^-]/[H_2O]$
$[H^+][OH^-] = [H_2O]\ K = K_w = 10^{-14}$

$pH = -\log [H^+] = \log (1/[H^+])$

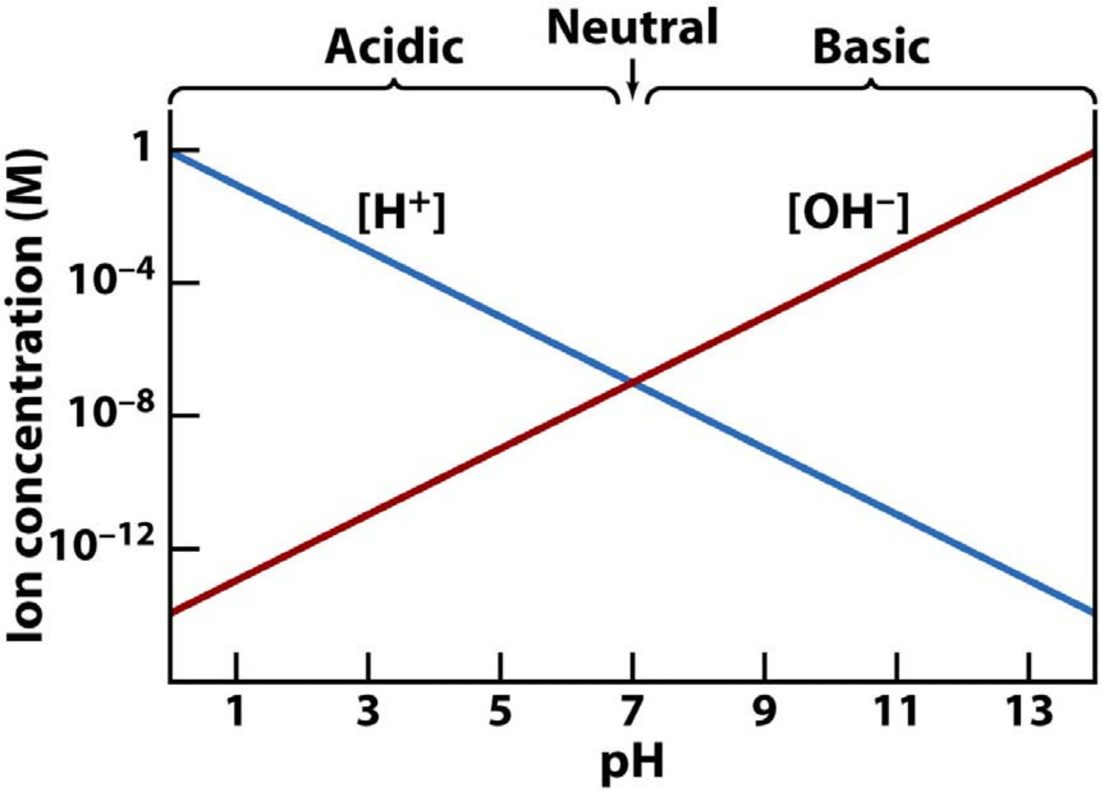


Figure 2-16 Fundamentals of Biochemistry, 2/e

Table 2-3 pH Values of Some Common Substances

Substance	pH
1 M NaOH	14
Household ammonia	12
Seawater	8
Blood	7.4
Milk	7
Saliva	6.6
Tomato juice	4.4
Vinegar	3
Gastric juice	1.5
1 M HCl	0

Table 2-3 Fundamentals of Biochemistry, 2/e

Acid-base chemistry

An acid can donate a proton and a base can accept a proton

$HA + H_2O \rightleftharpoons H_3O^+$ (conjugate acid) + A^- (conjugate base)

$HA \rightleftharpoons H^+ + A^-$ (acid reaction)

$HB^+ \rightleftharpoons H^+ + B^-$ (base reaction)

Dissociation of acid

$K = [H_3O^+][A^-]/[HA][H_2O]$

$K [H_2O] = Ka = [H^+][A^-]/[HA]$

$[H^+] = K ([HA]/[A^-])$

$-\log [H^+] = -\log K - \log ([HA]/[A^-])$

$pK = -\log K$

$pH = pK + \log ([A^-]/[HA])$: Henderson-Hasselbalch equation

It is useful for calculating pH changes of weak acid or base

not for strong acid or base

Table 2-4 Dissociation Constants and pK Values at 25°C of Some Acids

Acid	K	pK
Oxalic acid	5.37×10^{-2}	1.27 (pK_1)
H_3PO_4	7.08×10^{-3}	2.15 (pK_1)
Formic acid	1.78×10^{-4}	3.75
Succinic acid	6.17×10^{-5}	4.21 (pK_1)
Oxalate$^-$	5.37×10^{-5}	4.27 (pK_2)
Acetic acid	1.74×10^{-5}	4.76
Succinate$^-$	2.29×10^{-6}	5.64 (pK_2)
2-(*N*-Morpholino)ethanesulfonic acid (MES)	8.13×10^{-7}	6.09
H_2CO_3	4.47×10^{-7}	6.35 (pK_1)[a]
Piperazine-*N*,*N′*-bis(2-ethanesulfonic acid) (PIPES)	1.74×10^{-7}	6.76
$H_2PO_4^-$	1.51×10^{-7}	6.82 (pK_2)
3-(*N*-Morpholino)propanesulfonic acid (MOPS)	7.08×10^{-8}	7.15
N-2-Hydroxyethylpiperazine-*N′*-2-ethanesulfonic acid (HEPES)	3.39×10^{-8}	7.47
Tris(hydroxymethyl)aminomethane (Tris)	8.32×10^{-9}	8.08
NH_4^+	5.62×10^{-10}	9.25
Glycine (amino group)	1.66×10^{-10}	9.78
HCO_3^-	4.68×10^{-11}	10.33 (pK_2)
Piperidine	7.58×10^{-12}	11.12
HPO_4^{2-}	4.17×10^{-13}	12.38 (pK_3)

Source: Dawson, R.M.C., Elliott, D.C., Elliott, W.H., and Jones, K.M., *Data for Biochemical Research* (3rd ed.), pp. 424–425, Oxford Science Publications (1986); *and* Good, N.E., Winget, G.D., Winter, W., Connolly, T.N., Izawa, S., and Singh, R.M.M., *Biochemistry* **5,** 467 (1966).

[a]The pK for the overall reaction $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$; see Box 2-2.

Table 2-4 Fundamentals of Biochemistry, 2/e

Titration curve

$HA \rightleftharpoons H^+ + A^-$

At initial stage

$$K = [H^+][A^-]/[HA]$$
$$= [H^+]^2/[HA]$$
$$K[HA] = [H^+]^2$$
$$pH = (pK + p[HA])/2$$

During titration with acid or base

$$pH = pK + \log([A^-]/[HA])$$

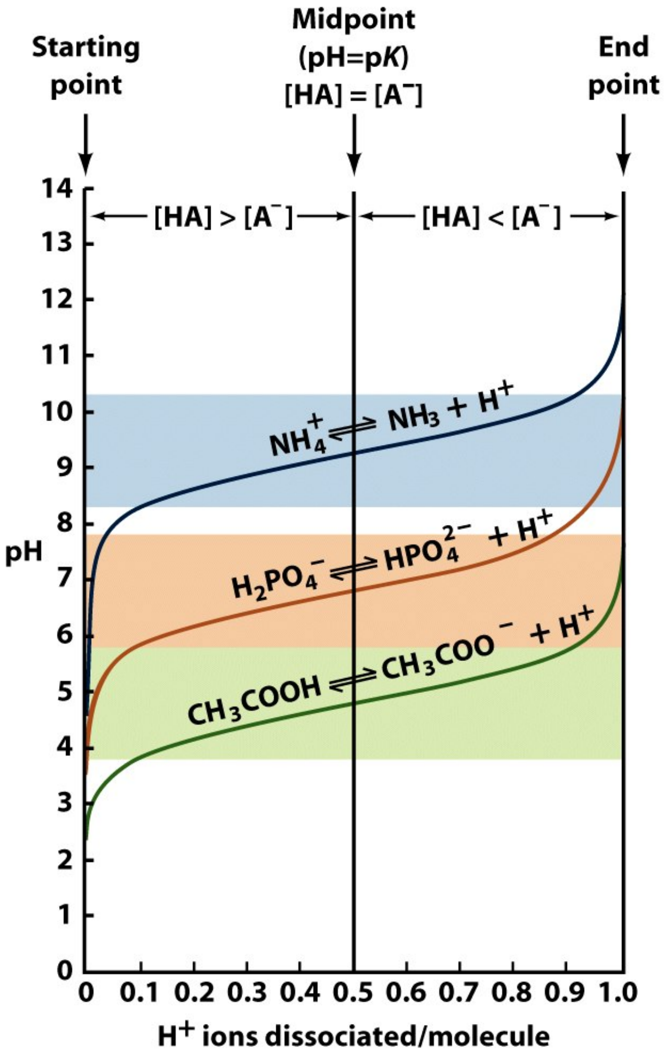


Figure 2-17 Fundamentals of Biochemistry, 2/e

0.1M acetic acid 500 ml을 0.1 M KOH로 적정할 때의 적정곡선은
다음과 같은 계산을 통해 얻어진 곡선과 일치한다. 초산의 Ka 값은 10^{-5} (pKa= 5)

1. at the start: 아무것도 첨가하지 않았을 때 (이온화된 것들이 너무 적으므로 무시)
   $Ka = [H^+][A]/[HA] = [H^+]^2/[HA]$
   pH = (pKa + p[HA])/2 = (5+ 1)/2 = 3

2. at any point: H-H 식 사용
   0.1 M KOH 100 ml 첨가하였을 때
   $HA \leftrightarrow H^+ + A^-$
   0.1 x 0.5
   -0.1 x 0.1 0.1 x 0.1

   $pH = 5 + \log([A^-]/[HA]) = 5 + \log(0.01/0.04) = 4.4$

   0.1 M KOH 250 ml 첨가하였을 때
   $pH = 5 + \log([A^-]/[HA]) = 5 + \log(0.025/0.025) = 5$

   0.1 M KOH 350 ml 첨가하였을 때
   $pH = 5 + \log([A^-]/[HA]) = 5 + \log(0.0350/0.0150) = 5.48$

3. at the end point: 0.1 M KOH 500 ml 첨가하였을 때
   이론적으로 pH = 7, 그러나 $A^- + HOH \leftrightarrow HA + OH^-$
   Kb로 계산하면 $Kb = 10^{-14} - Ka = 10^{-9} = [HA][OH^-]/[A^-] = [OH^-]^2/[A^-]$
   그러므로 $pOH = (pKb + \log(1/[A^-]))/2$
   $= (9 + \log(1/0.05))/2 = 5.15$
   그러므로 pH = 8.85

Buffer

Buffering range

Buffering capacity

Polyprotic acid

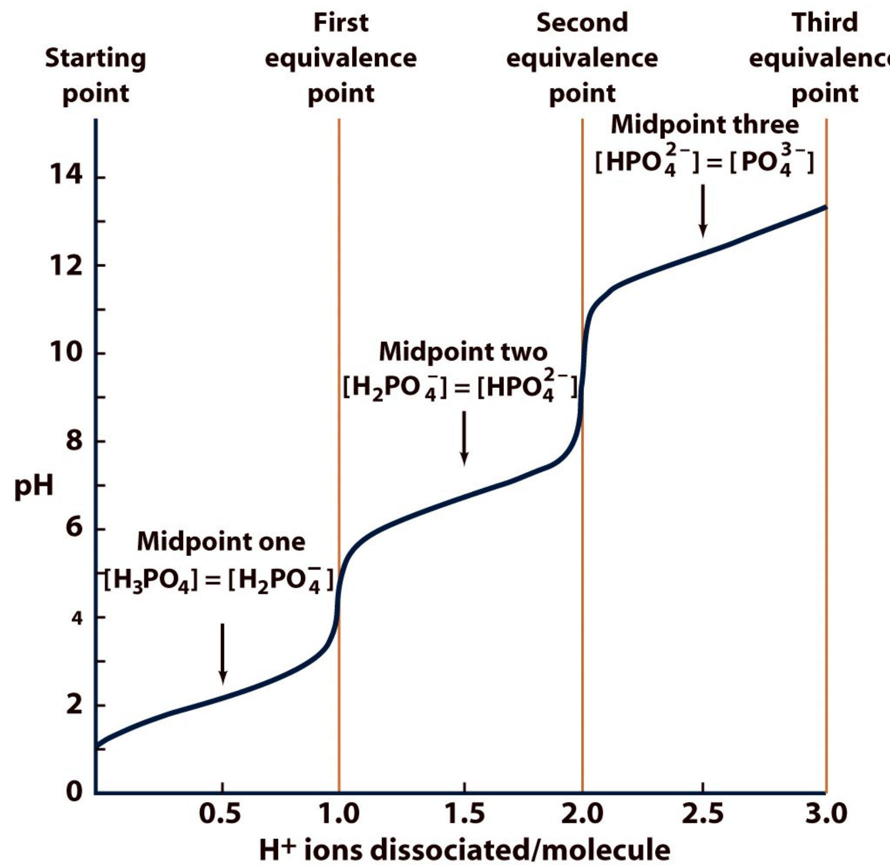


Figure 2-18 Fundamentals of Biochemistry, 2/e