WATER

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Elements

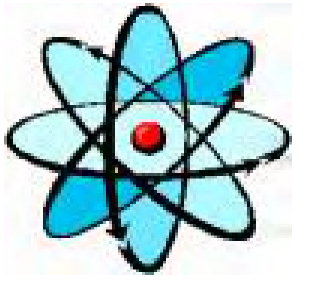
A. Chemical symbols: C H O P S N

C=carbon, H=hydrogen, O=oxygen, P=phosphorus, S=sulfur, N=nitrogen

B. Top 3

Earth's surface = O, Si, Al

Living things: C, H, O



C. Atoms: smallest particle of element

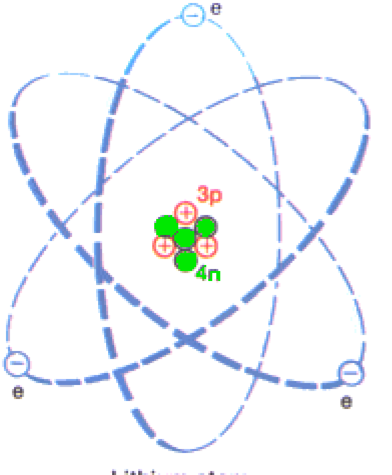
D. Parts of Atoms

1) protons (p+) = in nucleus; Atomic number; ID element

2) neutrons (n^o) = in nucleus

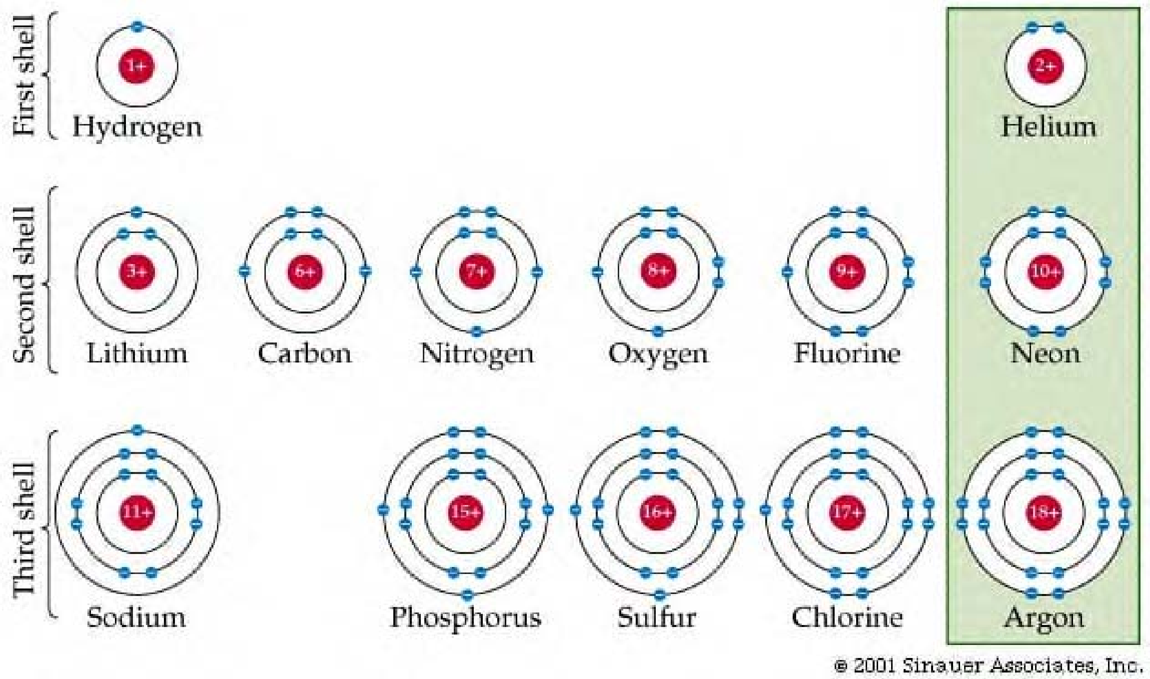
3) electrons (e^-) = orbit nucleus

*__*Neutral atoms : #p*$^+$ *= #e*$^-$__*



Electrons

1) Travel in energy shell or levels
2) **Valence** e-: outer level; affects reactivity



3) Maximum/level: 2 = 1st 8 = 2nd 18 = 3rd

4) Ions: atom lost or gained an e^-

H *atom* (1p,0n,1e): loses 1e → H^+ *ion*

Cl *atom* gains 1e → Cl^- *ion*

Chemical symbol
Atomic number
Atomic mass (average of all isotopes)

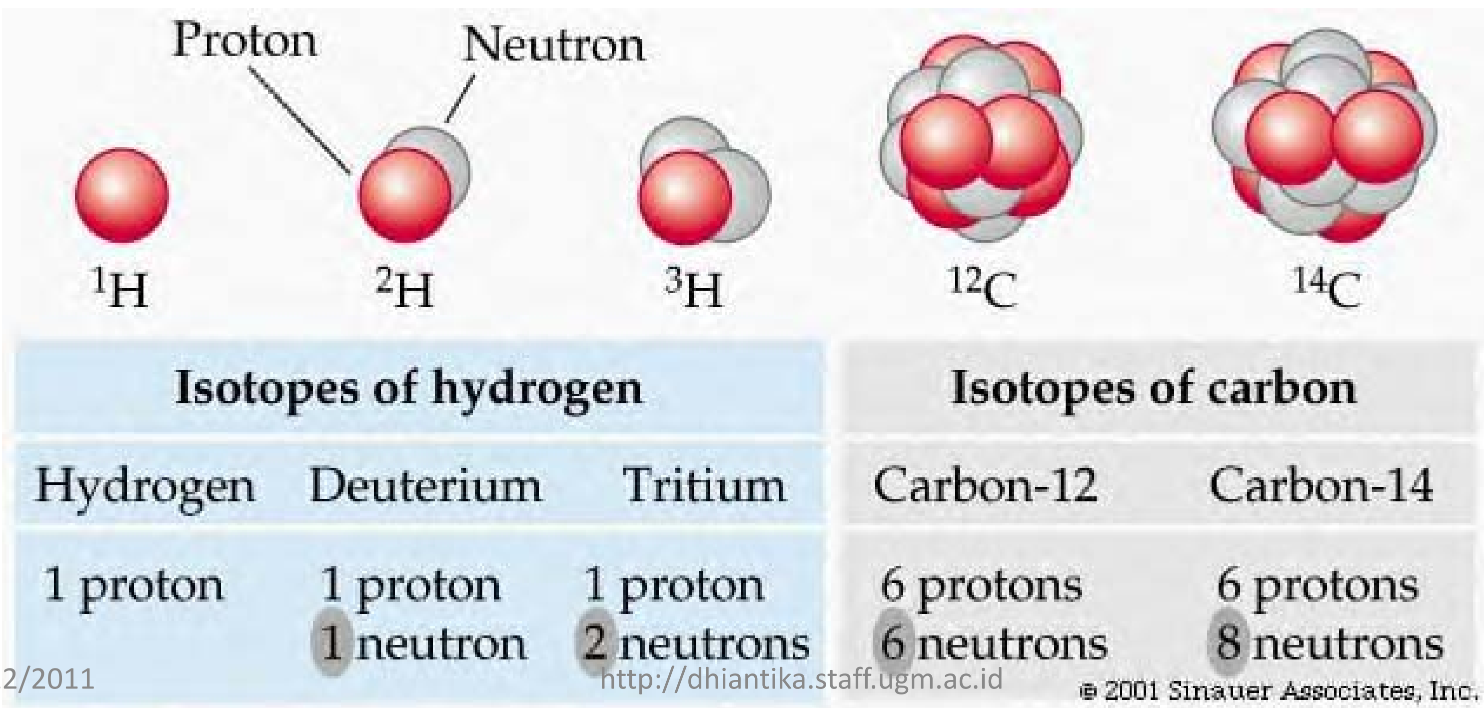
1 H 1.0079																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.4778	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.4	47 Ag 107.870	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	71 Lu 174.97	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.2	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	103 Lr (260)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (269)	109 Mt (268)	110 (269)	111 (272)	112 (277)	113	114 (285)	115 (289)	116	117	118 (293)

Lanthanide series	57 La 138.906	58 Ce 140.12	59 Pr 140.9077	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04
Actinide series	89 Ac 227.028	90 Th 232.038	91 Pa 231.0359	92 U 238.02	93 Np 237.0482	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)

Isotopes: atoms of same element that differ by # of neutrons

ex: C-12 and ^{14}C *mass # = #p⁺ + #nᵒ*

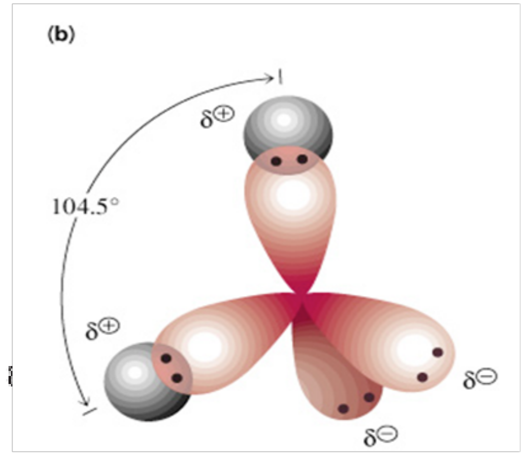
^{12}C	^{14}C
$p^+ = 6$	$p^+ = 6$
$e^- = 6$	$e^- = 6$
$n^o = 6$	$n^o = 8$



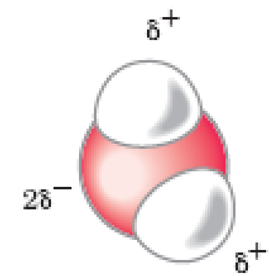
WATER

- Water plays a central role in the chemistry of all life
- Proteins, polysaccharides, nucleic acids and membranes all assume their characteristic shapes in response to water
- The chemical properties of water are related to the functions of biomolecules, entire cells,and organisms

Structure of the water molecule



(a)

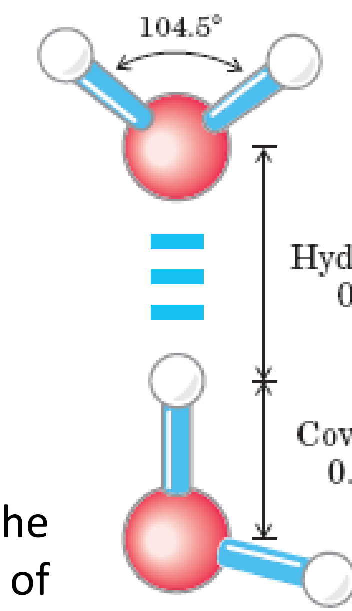


(b)

Properties of Water :

Water is a polar molecule
The sharing of electrons between H and O is unequal → two electric dipoles

Water is highly cohesive
Water molecules interact strongly with one another through hydrogen bonds

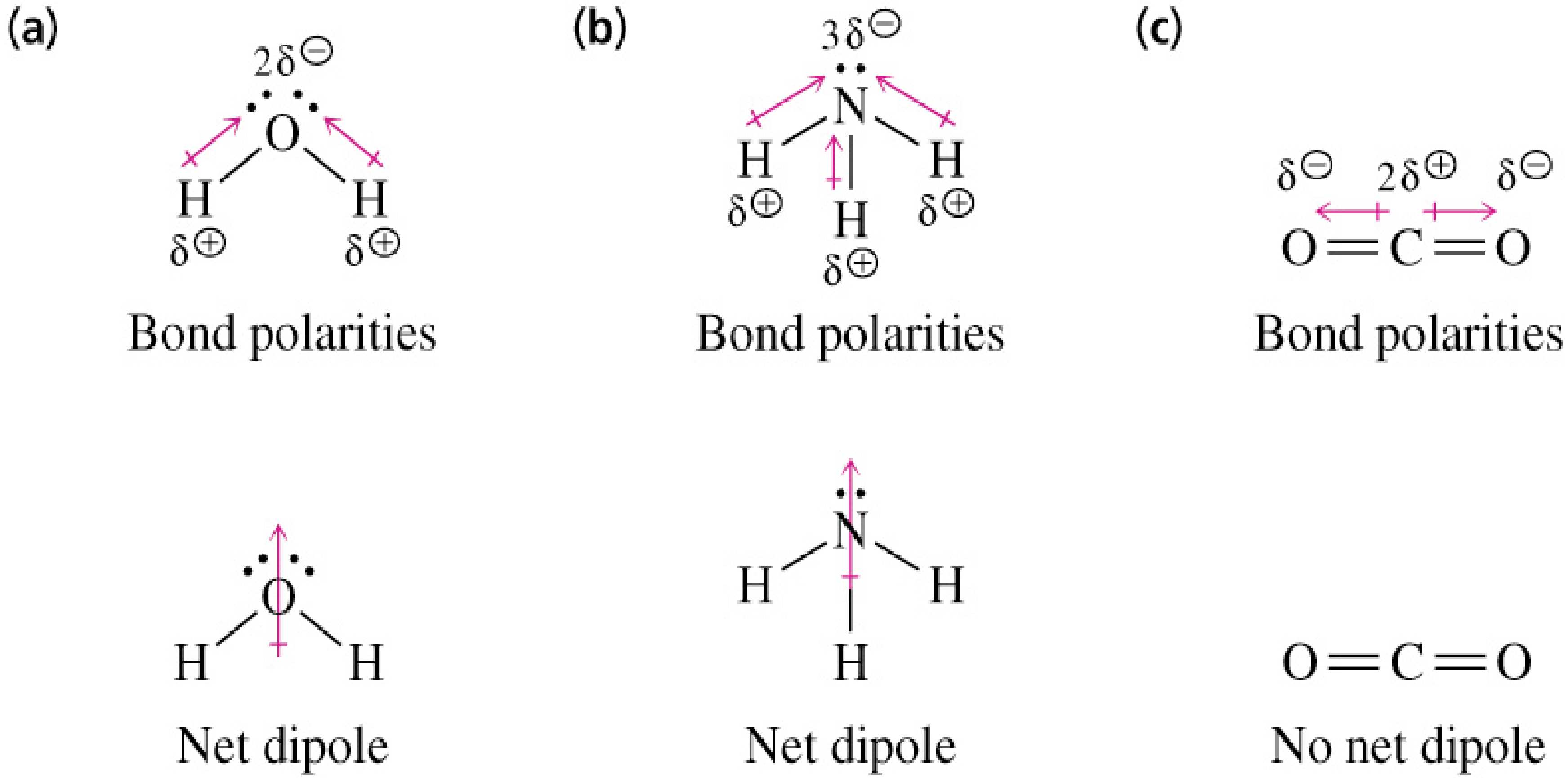


(c)

a **hydrogen bond =** an electrostatic attraction between the oxygen atom of one water molecule and the hydrogen of another .

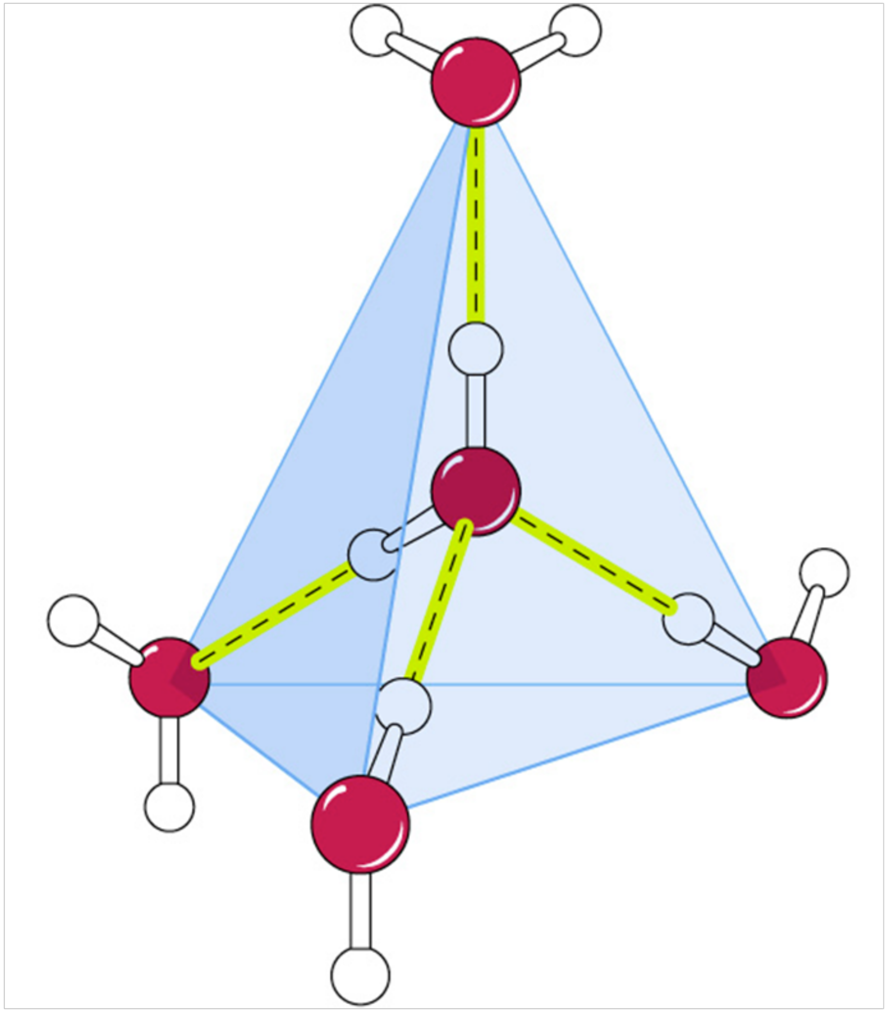
Polarity of Small Molecules

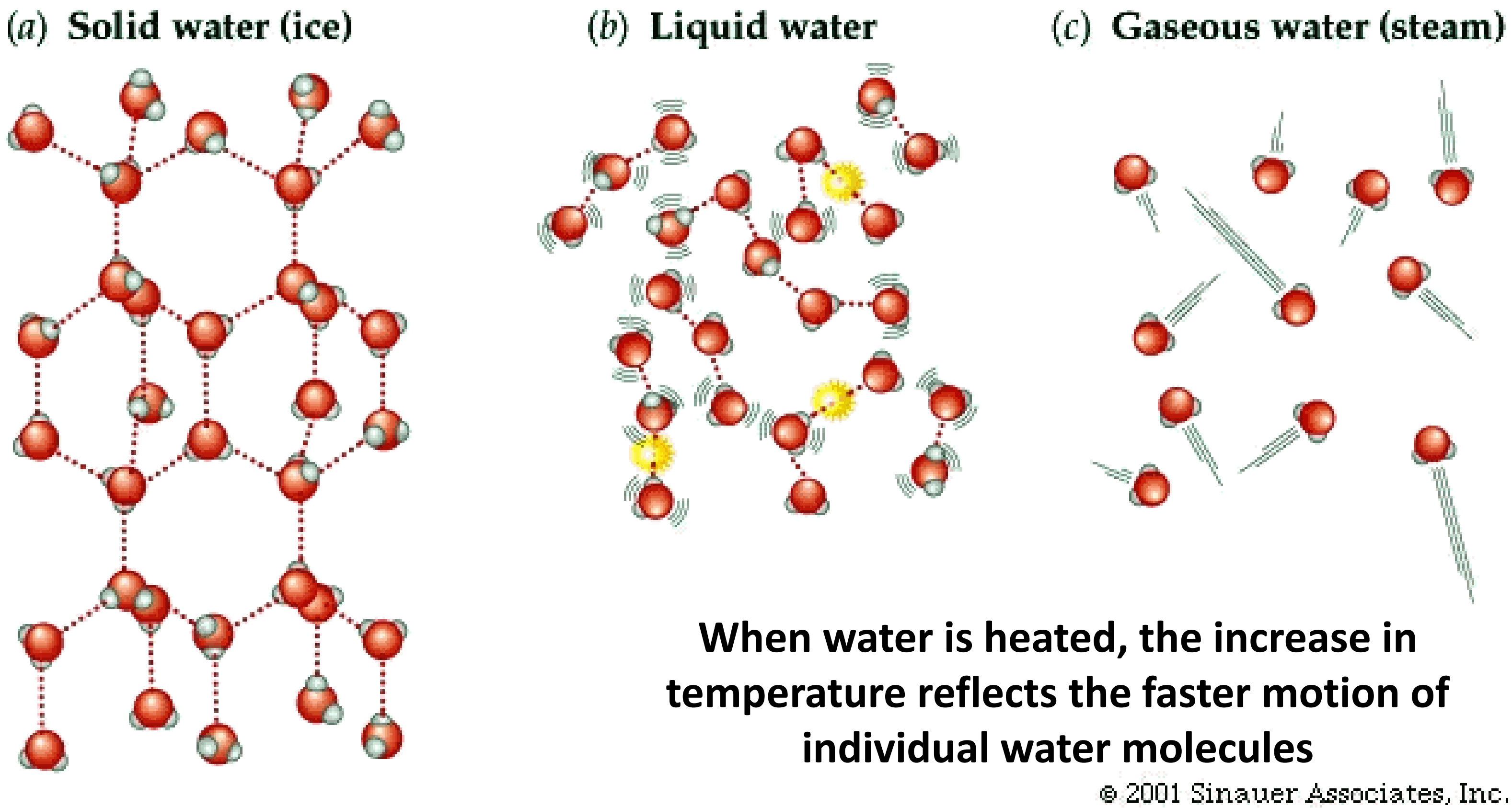
Water and ammonia each have a permanent dipole while CO_2 does not



Hydrogen bonding by a water molecule

- **A water molecule can form up to four hydrogen bonds**
- **Hydrogen bonds shown in yellow**

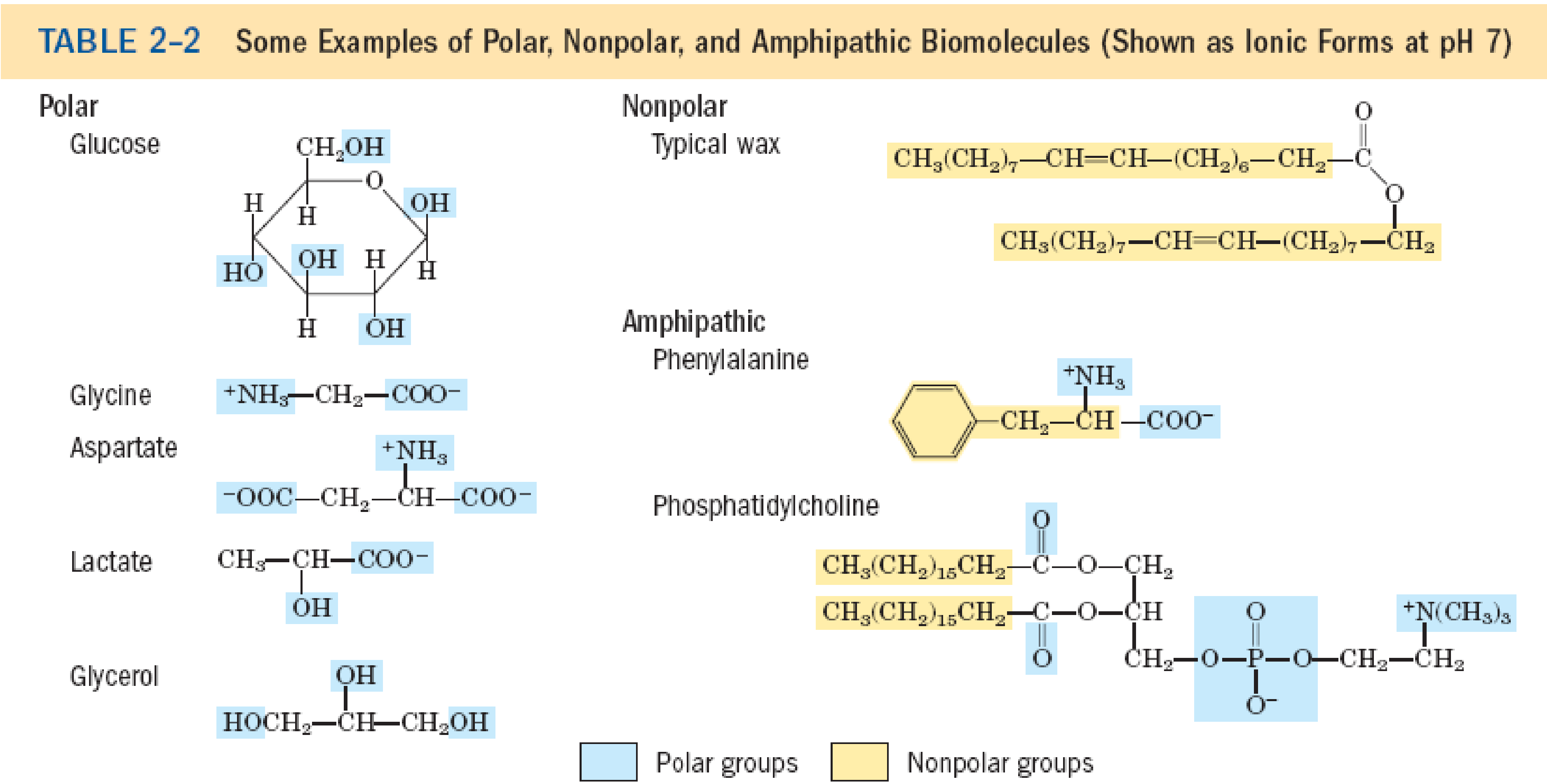




When water is heated, the increase in temperature reflects the faster motion of individual water molecules

The lifetime of each hydrogen bond in liquid water is just 1 to 20 picoseconds (1ps = 10^{-12} s); upon breakage of one hydrogen bond, another hydrogen bond forms, within 0.1 ps.

Biomolecules



Ionic and Polar Substances Dissolve in Water

- **Hydrophilic** (water-loving) substances [polar and ionic (**electrolytes**)] readily dissolve in H_2O
- Polar water molecules align themselves around ions or other polar molecules
- A molecule or ion surrounded by solvent, molecules is **solvated**
- When the solvent is water, the molecules or ions are **hydrated**

Water readily dissolves such compounds by :
replacing solute-solute hydrogen bonds with solute-water hydrogen bonds

Solubilities of molecules in water

- **Solubility in water depends upon the <u>ratio</u> of <u>polar</u> <u>to</u> <u>nonpolar</u> <u>groups</u> in a molecule**
- **The larger the portion of nonpolar groups the less soluble the molecule is in water**
- **The larger the portion of polar groups (e.g. hydroxyl groups (-OH)) the more soluble the molecule is in water.**

TABLE 2.1 Solubilities of short-chain alcohols in water

Alcohol	Structure	Solubility in water (mol/100 g 20°C)[a] H2O at
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

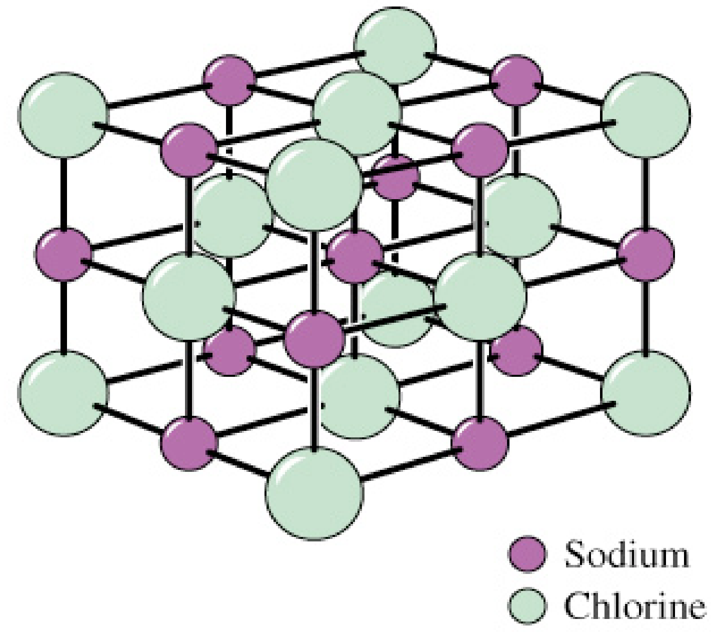
[a]Infinity (\`) indicates that there is no limit to the solubility of the alcohol in water.

Dissolution of NaCl in water

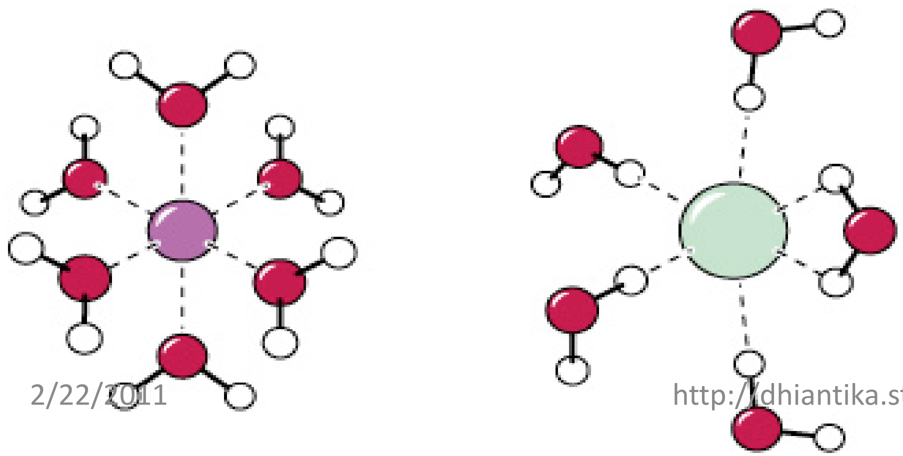
(a) Electrostatic forces hold ions together in crystalline sodium

(b) Water molecules form solvation spheres around Na^{+} and Cl^{-}

(a) NaCl crystal



(b)

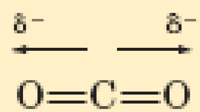
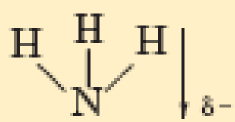
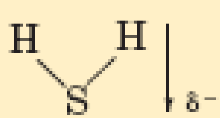


Nonpolar Substances Are Insoluble in Water

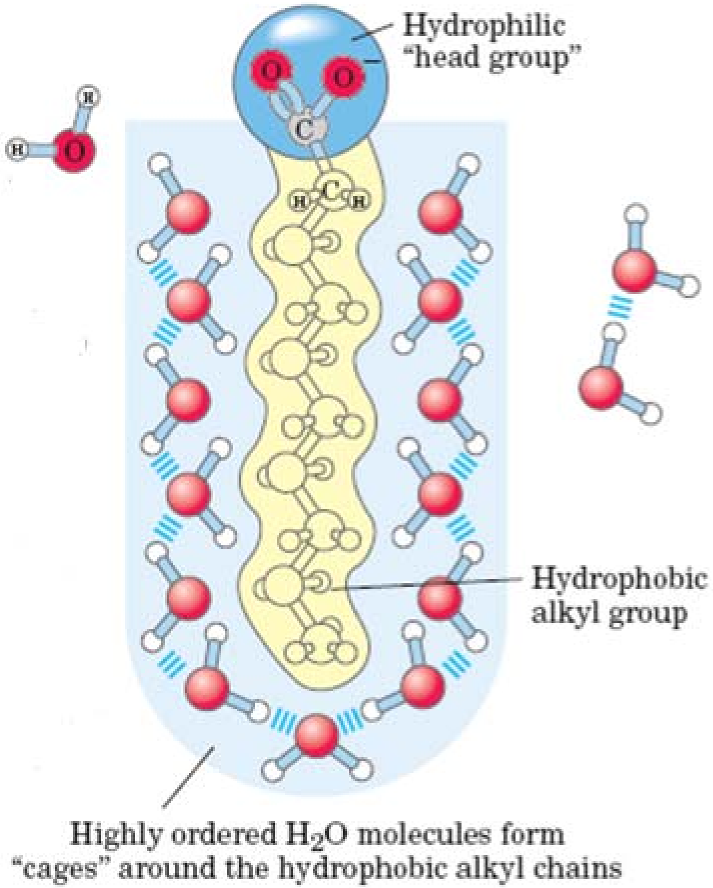
- **Hydrophobic** (water-fearing) molecules are nonpolar. Ex : lipids and waxes.
- **Hydrophobic effect** - the exclusion of nonpolar substances by water (critical for protein folding and self-assembly of biological membranes)
- **Amphipathic molecules** have hydrophobic chains and ionic or polar ends.
- **Biomolecules are amphipathic**; proteins, pigments, certain vitamins, and the sterols and phospholipids of membranes all have polar and nonpolar surface regions.

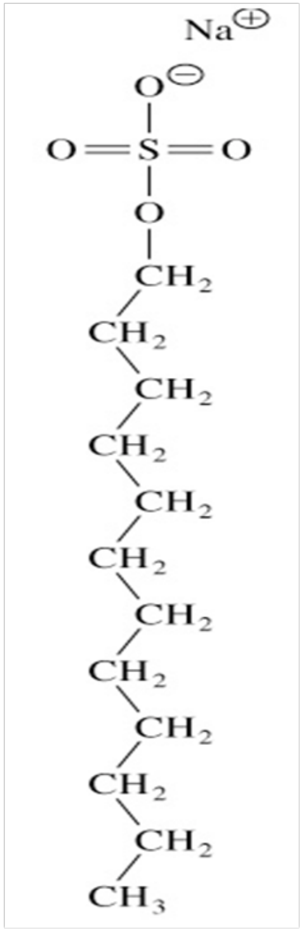
Nonpolar Gases Are Poorly Soluble in Water

TABLE 2–3 Solubilities of Some Gases in Water

Gas	*Structure**	*Polarity*	*Solubility in water (g/L)†*
Nitrogen	$N{\equiv}N$	Nonpolar	0.018 (40 °C)
Oxygen	$O{=}O$	Nonpolar	0.035 (50 °C)
Carbon dioxide		Nonpolar	0.97 (45 °C)
Ammonia		Polar	900 (10 °C)
Hydrogen sulfide		Polar	1,860 (40 °C)

Amphipathic molecules



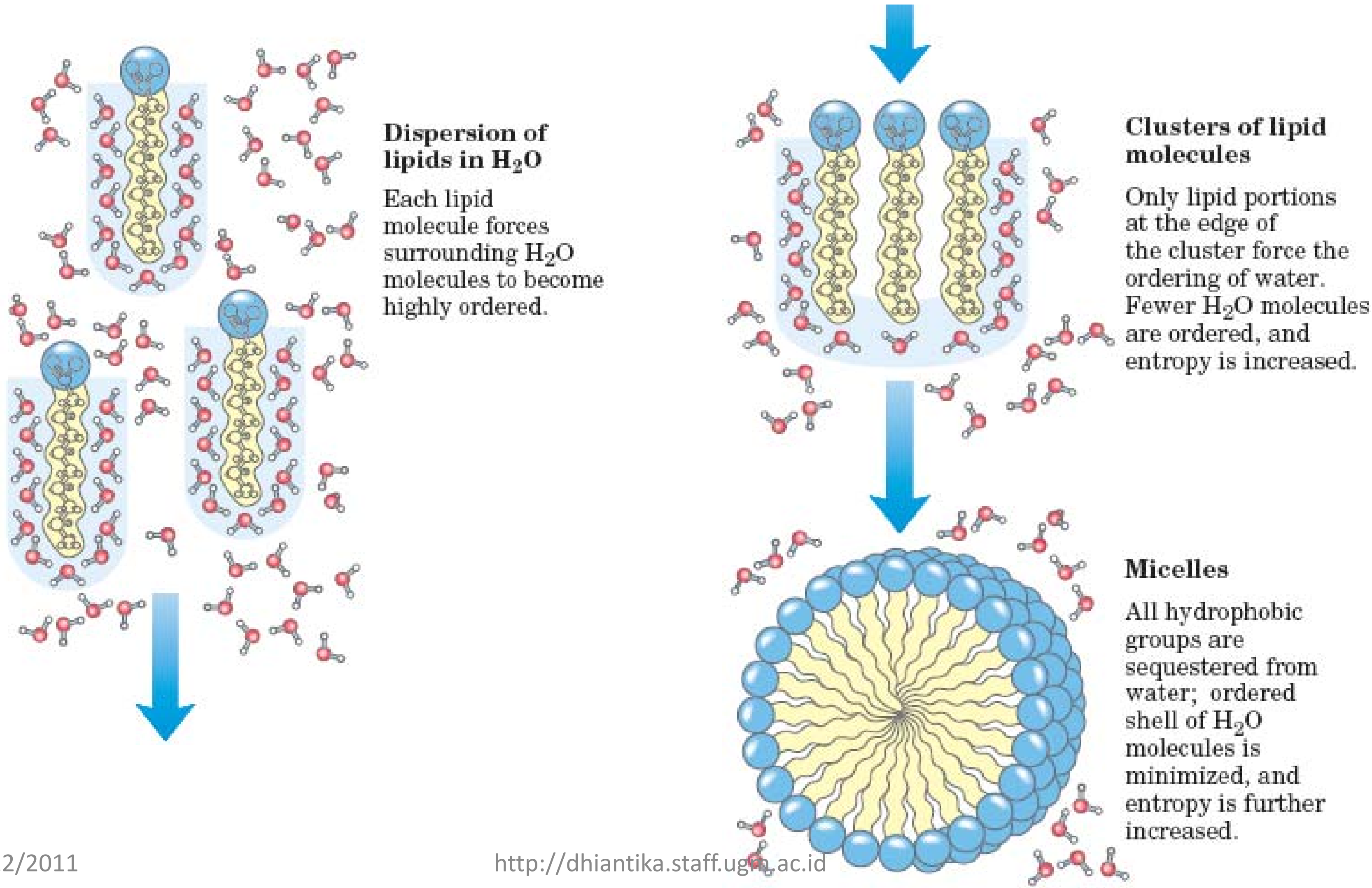


Longchain fatty acids have very hydrophobic alkyl chains

Sodium dodecyl sulfate (SDS), 12 carbon tail and polar sulfate group

Micelles

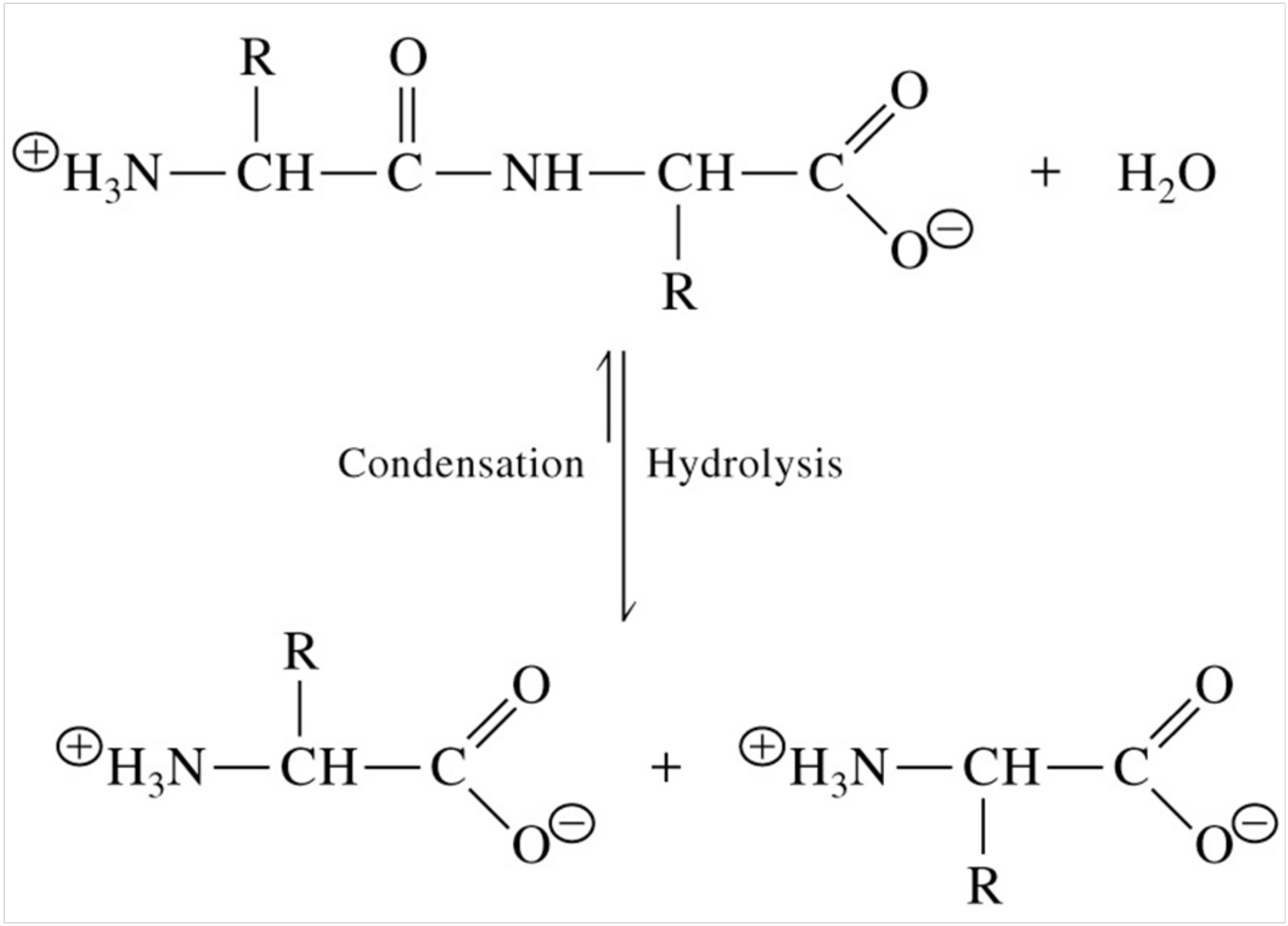
→ **stable structures of amphipathic compounds in water**



Water Is Nucleophilic

- **Nucleophiles - electron-rich atoms or groups**
- **Electrophiles - electron-deficient atoms or groups**
- **Water is a relatively weak nucleophile**
- **Due to its high cellular concentration, hydrolysis reactions in water are thermodynamically favored**

Hydrolysis of a peptide

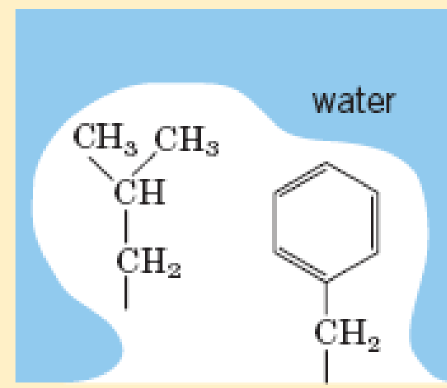


Noncovalent forces

Non-covalent interaction in biomolecules

1. The folding of a single polypeptide or polynucleotide chain into its three-dimensional shape
2. The binding of an antigen to a specific antibody
3. The binding of a hormone or a neurotransmitter to its cellular receptor protein

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

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

A. Charge-Charge Interactions (Ion Pairing)

- **<u>Electrostatic</u> <u>interactions</u> between two charged particles**
- **Can be the strongest type of noncovalent forces**
- **Can extend over greater distances than other forces**
- **<u>Charge</u> <u>repulsion</u> occurs between similarly charged groups**

Types of attractive charged interactions :

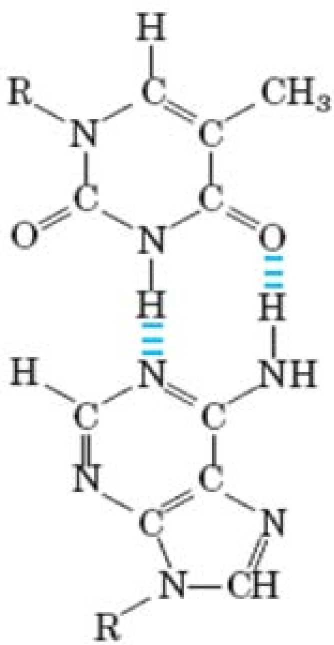
- **Salt bridges** - attractions between oppositely-charged functional groups in proteins
- **Ion pairing** - a salt bridge buried in the hydrophobic interior of a protein is stronger than one on the surface

B. Hydrogen Bonds

- **Among the strongest of noncovalent interactions**
- **H atom bonded to N, O, S can hydrogen bond to another electronegative atom (~0.2 nm distance)**
- **Total distance between the two electronegative atoms is ~0.27 to 0.30 nm**
- **In aqueous solution, water can H-bond to exposed functional groups on biological molecules**

Hydrogen Bonds

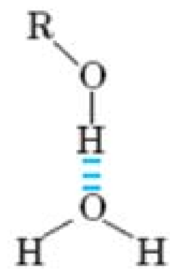
Between complementary bases of DNA



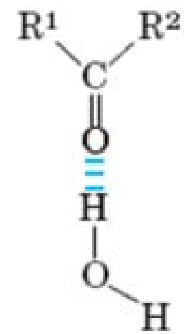
Thymine

Adenine

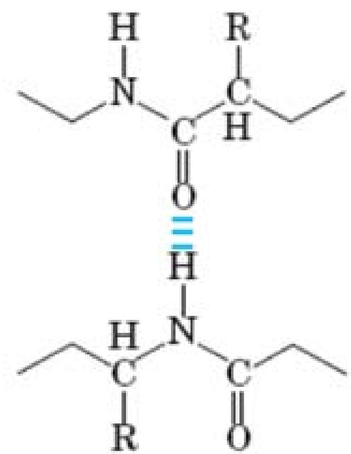
Between the hydroxyl group of an alcohol and water



Between the carbonyl group of a ketone and water



Between peptide groups in polypeptides



C. Van der Waals Forces

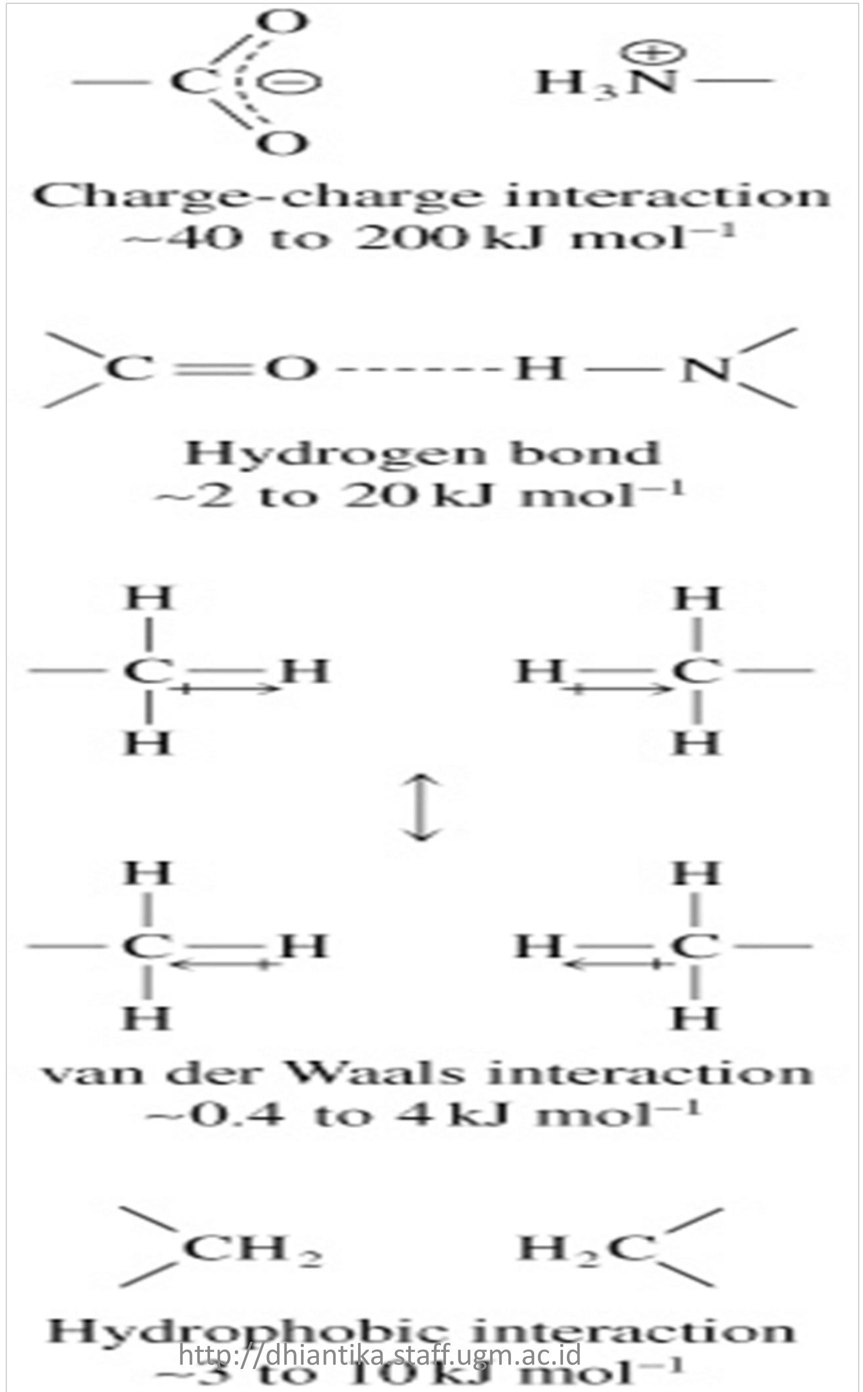
- <u>Weak</u> <u>short</u> <u>range</u> <u>forces</u> between:
  (a) Permanent dipoles of two uncharged molecules
  (b) Permanent dipole and an induced dipole in a neighboring molecule
- Although individually weak, many van der Waals interactions occur in biological macromolecules and participate in stabilizing molecular structures

TABLE 2.2 Van der Waals radii of several atoms

Atom	Radius (nm)
Hydrogen	0.12
Oxygen	0.14
Nitrogen	0.15
Carbon	0.17
Sulfur	0.18
Phosphorus	0.19

D. Hydrophobic Interactions

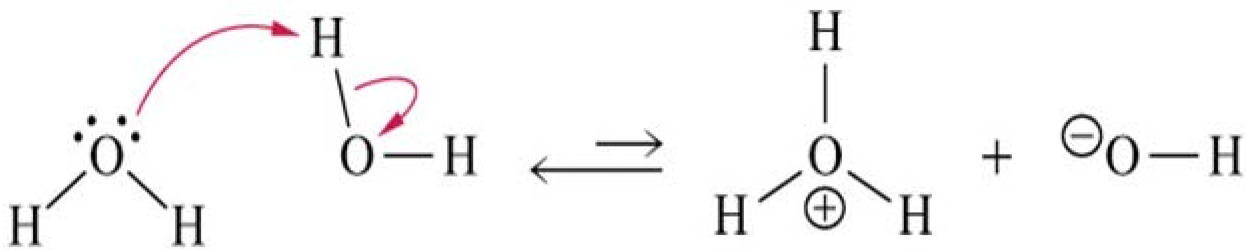
- **Association of a relatively nonpolar molecule or group with other nonpolar molecules**
- **Depends upon the increased entropy (+DS) which occurs when water molecules surrounding a nonpolar molecule are freed to interact with each other in solution**
- **The cumulative effects of many hydrophobic interactions can have a significant effect on the stability of a macromolecule**


Charge-charge interaction
~40 to 200 kJ mol^{-1}
Hydrogen bond
~2 to 20 kJ mol^{-1}
van der Waals interaction
~0.4 to 4 kJ mol^{-1}
Hydrophobic interaction
~3 to 10 kJ mol^{-1}

Ionization of Water, Weak Acids, and Weak Bases

Ionization of Water

- Pure water consists of a low concentration of **hydronium ions** (**H_3O^+**) and an equal concentration of **hydroxide ions** (**OH^-**)
- **Acids** are proton donors (e.g. H_3O^+) and **bases** are proton acceptors (e.g. OH^-)
- The ionization of water can be measured by its electrical conductivity; pure water carries electrical current as H migrates toward the cathode and OH toward the anode.



$$H_2O + H_2O \rightleftharpoons H_3O^{\oplus} + OH^{\ominus}$$

The pH Scale

- **pH** is defined as the negative logarithm of the concentration of $[H^+]$
- basis for the **pH scale → The ion product of water (Kw)**
- It is a convenient means of designating the concentration of H (and thus of OH) in any aqueous solution in the range between 1.0 M H^+ and 1.0 M OH-.

$$pH = -\log[H^{\oplus}] = \log\frac{1}{[H^{\oplus}]}$$

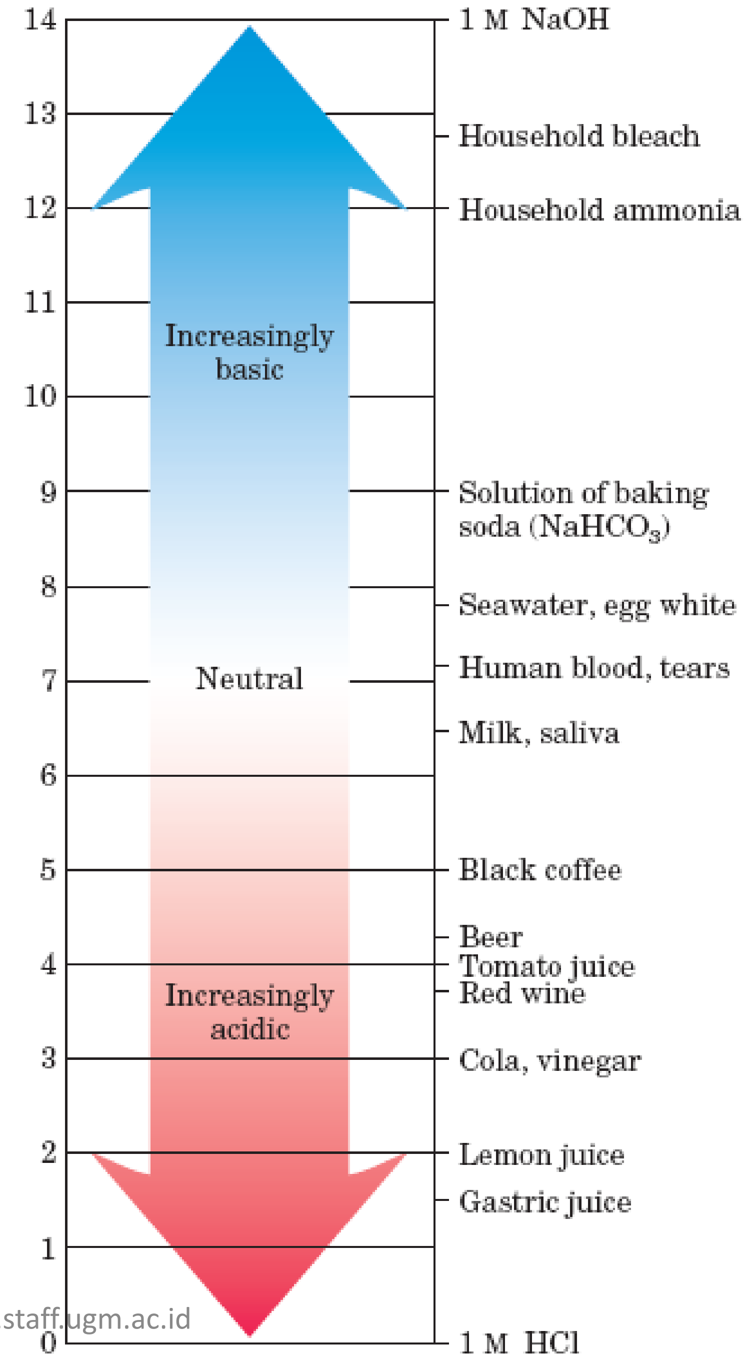
TABLE 2-6 The pH Scale

$[H^+]$ (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

*The expression pOH is sometimes used to describe the basicity, or OH^- concentration, of a solution; pOH is defined by the expression $pOH = -\log [OH^-]$, which is analogous to the expression for pH. Note that in *all* cases, pH + pOH = 14.

pH values for some fluids

- **Lower values are acidic fluids**
- **Higher values are basic fluids**



The pH affects
the structure and activity of biological macromolecules

- the catalytic activity of enzymes is strongly dependent on pH
- Measurements of the pH of blood and urine are commonly used in medical diagnoses.
- The pH of the blood plasma of people uncontrolled diabetes→ below the normal value of 7.4 → acidosis.
- disease states the pH of the blood is higher than normal → alkalosis

Strong Acids and Bases
vs
Weak Acids and Bases

Strong acids (such as: Hydrochloric, sulfuric, and nitric acids) and strong bases (such as: NaOH and KOH) dissociate completely in water :

$$HCl + H_2O \rightarrow Cl^- + H_3O^+$$

Note :

Cl^- is the **conjugate base** of HCl

H_3O^+ is the **conjugate acid** of H_2O

Weak acids and bases ???

- **Weak acids and bases → not completely ionized when dissolved in water**
- **These are common in biological systems and play important roles in metabolism and its regulation.**

Acetic acid is a weak acid

- Acids → proton donors
- Bases → proton acceptors
- A proton donor and its corresponding proton acceptor make up a **conjugate acid-base pair**

$$CH_3COOH \underset{}{\overset{K_a}{\rightleftharpoons}} H^{\oplus} + CH_3COO^{\ominus}$$

Acetic acid (weak acid) — Acetate anion (conjugate base)

Ka → dissociation constants → Equilibrium constants for ionization reactions

Conjugate acid-base pairs

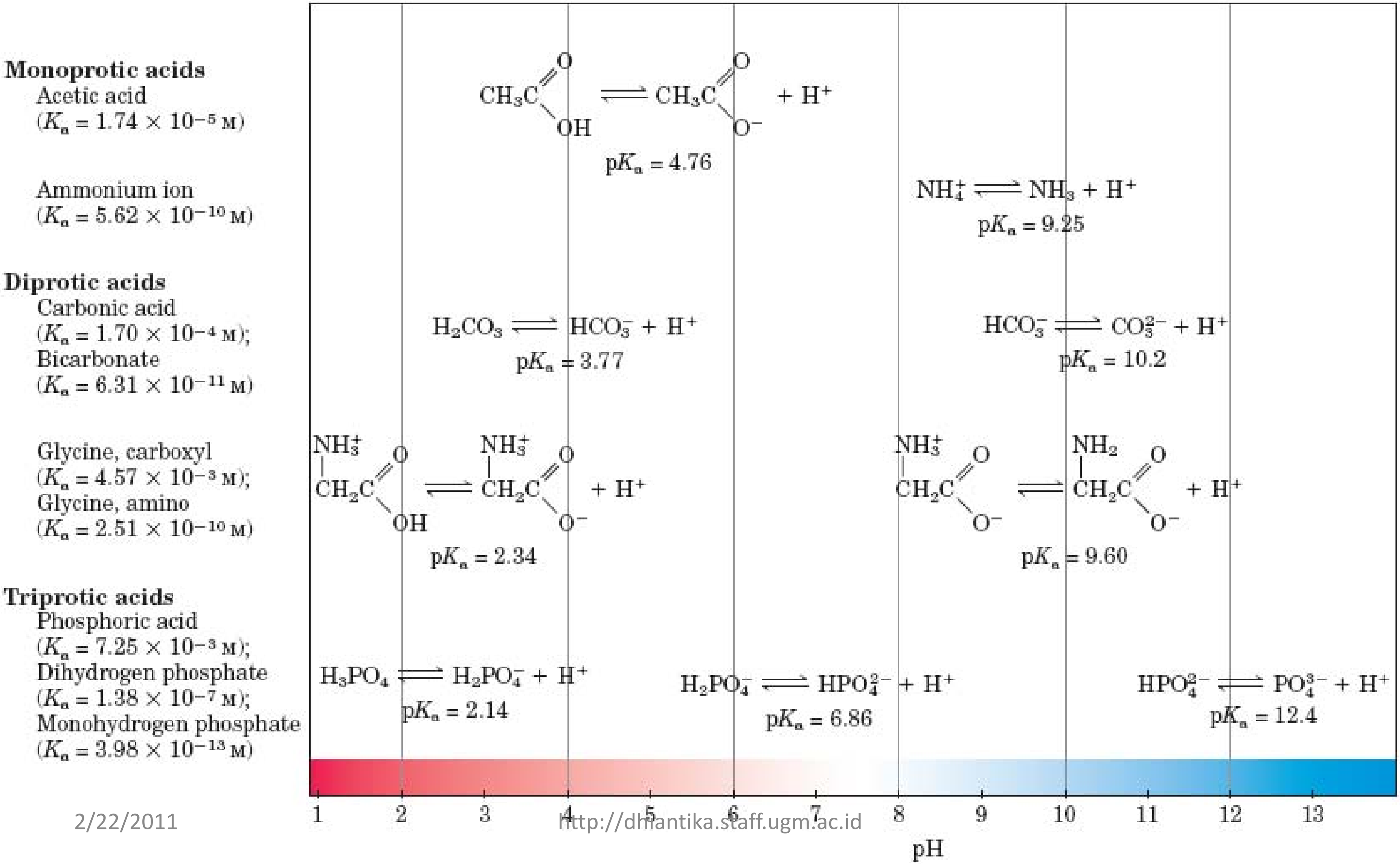


TABLE 2.4 Dissociation constants and pK_a values of weak acids in aqueous solutions at 25° C

Acid	K_a (M)	pK_a
HCOOH (Formic acid)	1.77×10^{-4}	3.8
CH_3COOH (Acetic acid)	1.76×10^{-5}	4.8
$CH_3CHOHCOOH$ (Lactic acid)	1.37×10^{-4}	3.9
H_3PO_4 (Phosphoric acid)	7.52×10^{-3}	2.2
$H_2PO_4^{\ominus}$ (Dihydrogen phosphate ion)	6.23×10^{-8}	7.2
HPO_4^{2-} (Monohydrogen phosphate ion)	2.20×10^{-13}	12.7
H_2CO_3 (Carbonic acid)	4.30×10^{-7}	6.4
$HCO_3^{\ominus}$ (Bicarbonate ion)	5.61×10^{-11}	10.2
$NH_4^{\oplus}$ (Ammonium ion)	5.62×10^{-10}	9.2
$CH_3NH_3^{\oplus}$ (Methylammonium ion)	2.70×10^{-11}	10.7

The Henderson-Hasselbalch Equation

Defines the pH of a solution in terms of:

(1) The pK_a of the weak acid

(2) Concentrations of the weak acid (HA) and conjugate base (A^-)

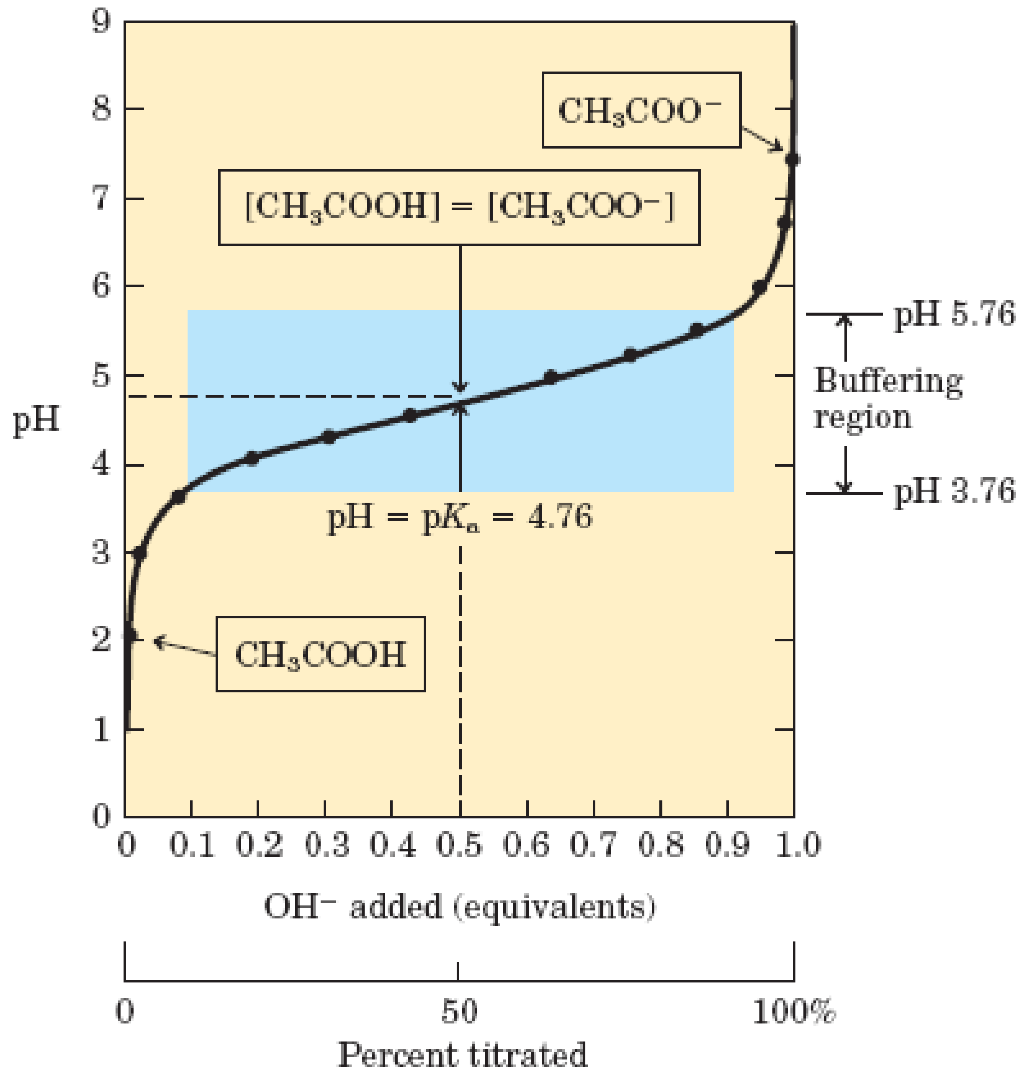
$$HA \rightleftharpoons H^+ + A^-,$$

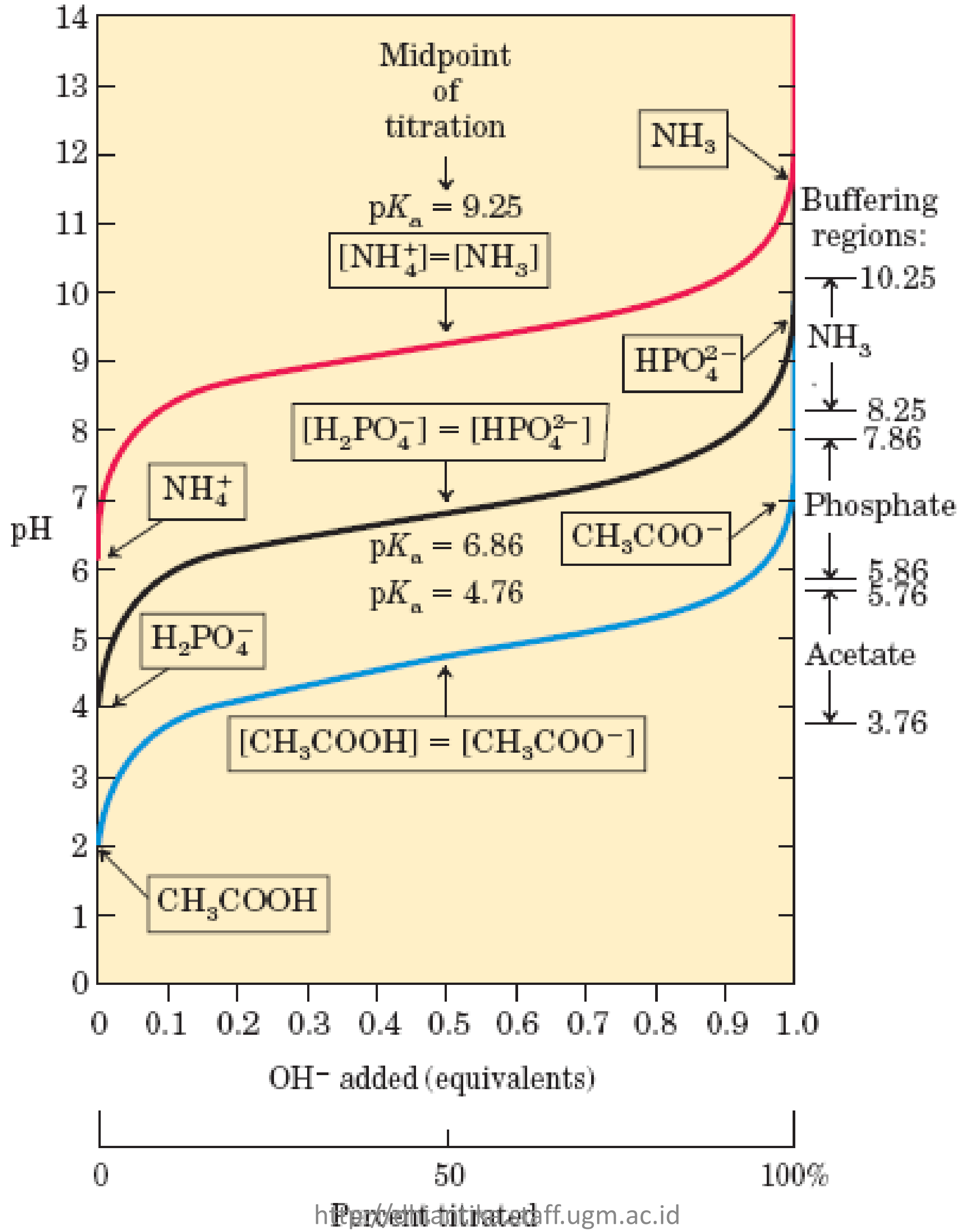
$$K_{eq} = \frac{[H^+][A^-]}{[HA]} = K_a$$

$$pH = pK_a + \log \frac{[A^{\ominus}]}{[HA]}$$

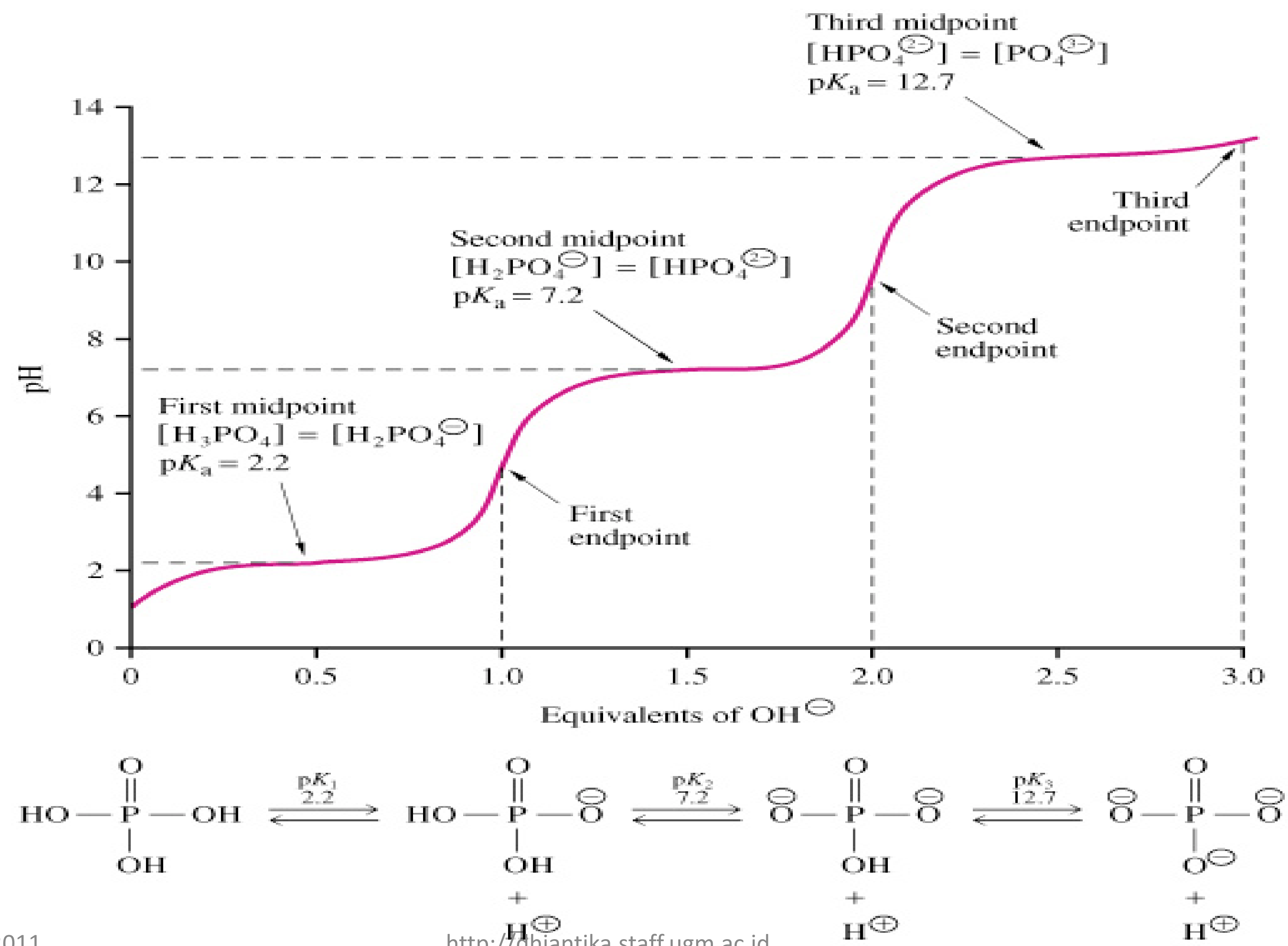
Titration curve of acetic acid (CH_3COOH)

- Titration is used to determine the amount of an acid in a given solution
- A measured volume of the acid is titrated with a solution of a strong base, usually sodium hydroxide (NaOH), of known concentration.
- Titration curves are used to determine pK_a values




Midpoint
of
titration
pK$_a$ = 9.25
[NH$_4^+$]=[NH$_3$]
NH$_3$
Buffering
regions:
10.25
NH$_3$
8.25
7.86
Phosphate
5.86
5.76
Acetate
3.76
HPO$_4^{2-}$
[H$_2$PO$_4^-$] = [HPO$_4^{2-}$]
NH$_4^+$
pK$_a$ = 6.86
pK$_a$ = 4.76
CH$_3$COO$^-$
H$_2$PO$_4^-$
[CH$_3$COOH] = [CH$_3$COO$^-$]
CH$_3$COOH
pH
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
OH$^-$ added (equivalents)
0
50
100%
Percent titrated

Titration curve for phosphoric acid (H_3PO_4)



(2.19)

Buffered Solutions Resist Changes in pH

- Buffer capacity is the ability of a solution to resist changes in pH
- Most effective buffering occurs where:

  solution pH = buffer pK_a
- At this point: [weak acid] = [conjugate base]
- Effective buffering range is usually at pH values equal to the pKa ± 1 pH unit

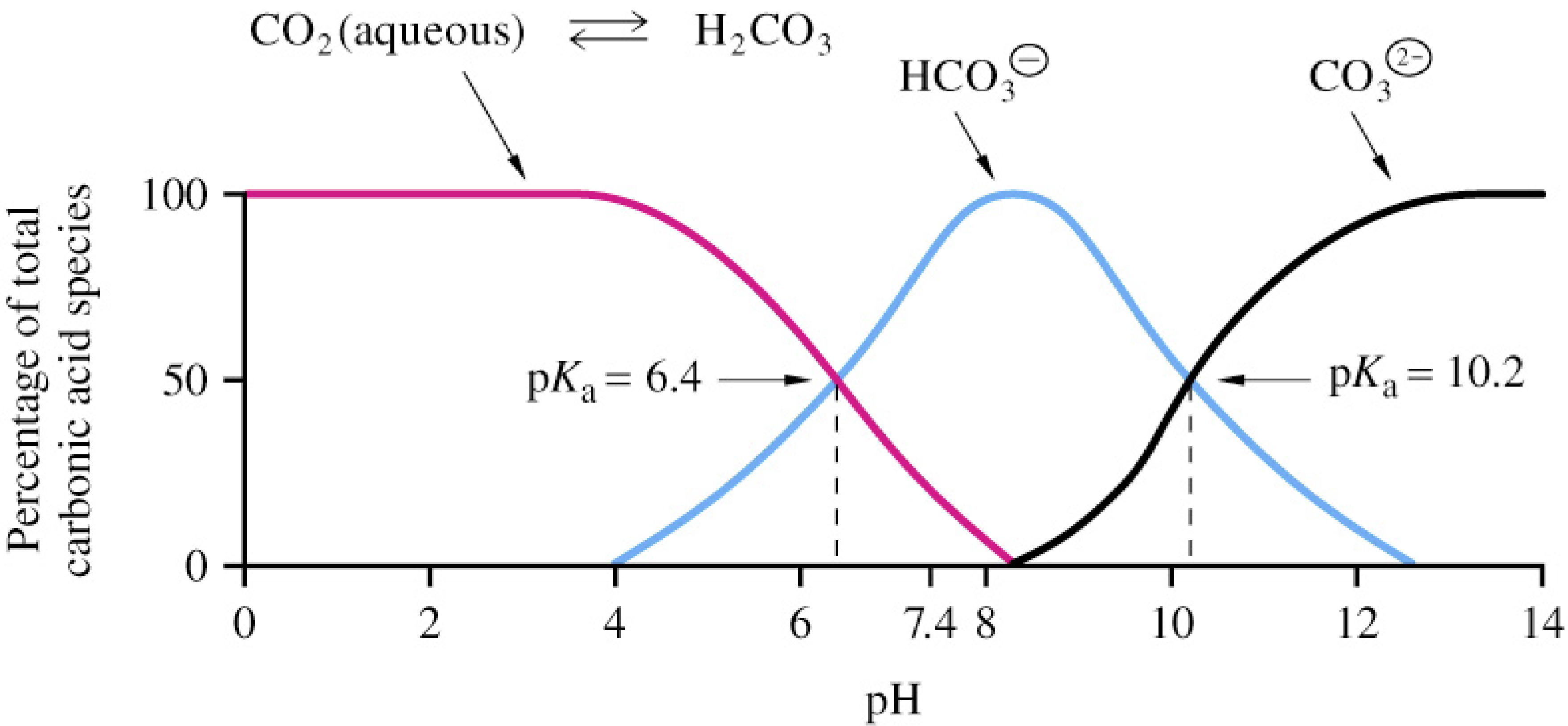
Carbonate buffering equilibria

$$H_2CO_3 \rightleftharpoons H^{\oplus} + HCO_3^{\ominus}$$

$$CO_2(\text{aqueous}) + H_2O \rightleftharpoons H_2CO_3$$

$$CO_2(\text{gaseous}) \rightleftharpoons CO_2(\text{aqueous})$$

Percentages of carbonic acid and its conjugate bases as a function of pH



Regulation of the pH of blood in mammals