# Water: molecular basis for life

Solvent for the molecules of life

Water is both a solvent and a reactant

- Water makes up 70% or more of the weight of most organisms

- Water is a "**universal solvent**" because it dissolves more substances than any other liquid.

- Its the solvent in which all metabolic reactions occur

- As a reactant water participates in biochemical processes including

  - hydrolysis

  - condensation

  - oxidation-reduction reactions
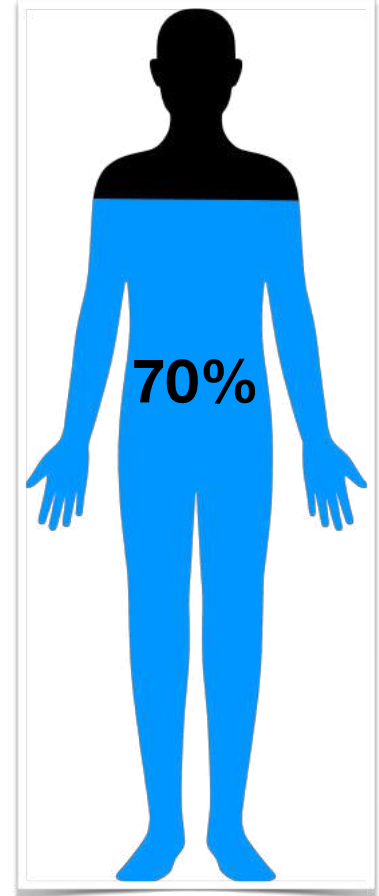
Water affects structure and function

- At the cellular level: properties of water affect the structure and function of all other cellular constituents

- The fundamental non-covalent bonds –

  - van Der Waal's interactions

  - ionic interactions and H-bonds

  - hydrophobic

  individually weak

  Collectively, have a very significant influence on the three-dimensional structures of biomolecules

- These fundamental noncovalent bonds differ in geometry, strength, and specificity and are greatly affected in different ways by the presence of water

Properties of water affect bonding abilities

- The strength and specificity of weak interactions are highly dependent on the medium in which they take place, and the majority of biological interactions take place in water.

- Biologically two properties are especially important:

  - Water is a **polar** molecule

  - Water is **highly cohesive**

# Properties of water affect bonding abilities
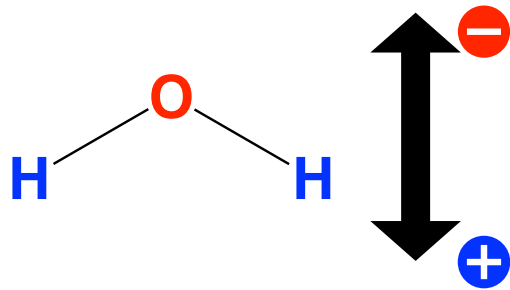
Water is a dipole
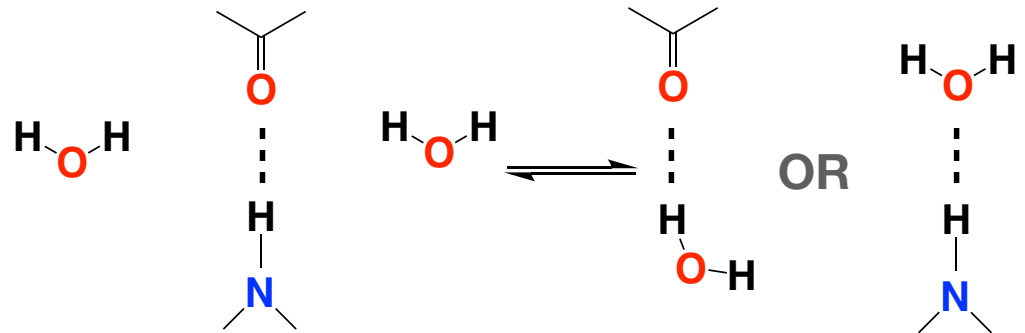
- **Water is a polar molecule.** The distribution of charge in a molecule of water is asymmetric owing to its bent structure.

- Oxygen draws electrons away from the hydrogen nuclei, creating a net positive charge in the region around the hydrogen nuclei. The result is an electrically polar structure.

Properties of water affect bonding abilities

- **Water is highly cohesive.** Water molecules interact strongly with one another through H-bonds. For eg. in ice networks of H-bonds hold the structure together.

  - In liquid water similar interactions link molecules and account for the cohesion of liquid water

  - In its liquid state, some H-bonds are broken. The highly cohesive nature of water dramatically affects the interactions between molecules in aqueous solution.
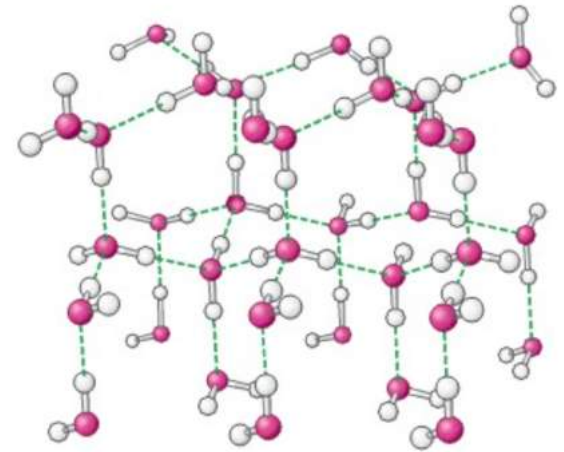
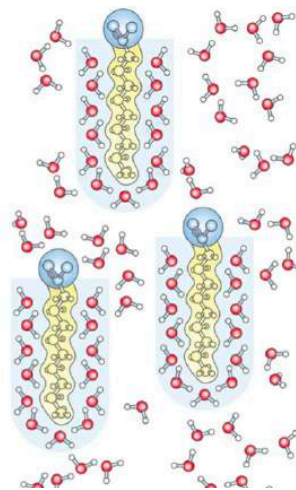# van der Waal's interactions: London dispersion forces

- Weak intermolecular forces between molecules as a result of each inducing polarization in the other

- Occurs between all molecules

- The **transient asymmetry** in the electronic charge around an atom acts through electrostatic interactions to induce a complementary asymmetry in the electron distribution around its neighboring atoms.

- The resulting attraction between two atoms increases as they come closer to each other, until they are separated by the **van der Waals contact distance**

- At a shorter distance, very strong repulsive forces become dominant because the outer electron clouds overlap.
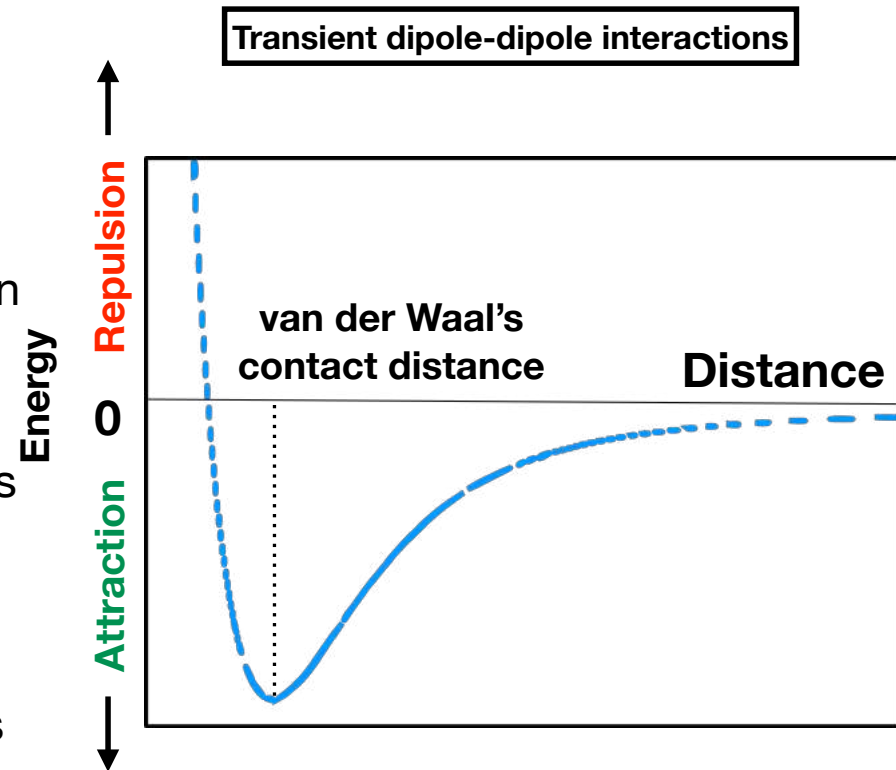
Electrostatic interactions

- Are attractive or repulsive interaction between objects having electric charges

- Both ionic interactions and hydrogen bonds are electrostatic interactions

- Governed by Coulomb's law: $F = (Q_1 Q_2)/\varepsilon r^2$

- Ionic interactions between dissolved ions are much stronger in less polar environments.

- The dependence on r^2 is such that ionic attractions or repulsions operate only over short distances—in the range of 10 to 40 nm (depending on the electrolyte concentration) when the solvent is water.

Hydrophobic interactions

Hydrophilic "head group"

Hydrophobic alkyl group

"Flickering clusters" of H_2O molecules in bulk phase

Highly ordered H_2O molecules form "cages" around the hydrophobic alkyl chains.
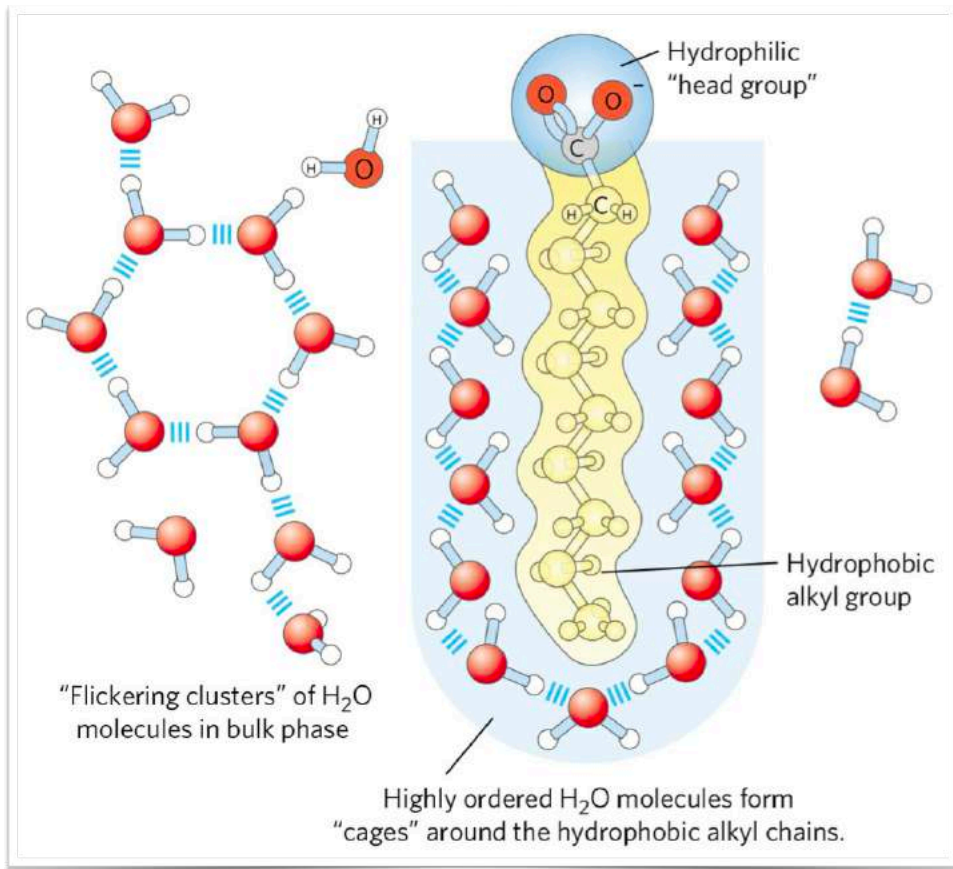
Dispersion of lipids in H_2O
Each lipid molecule forces surrounding H_2O molecules to become highly ordered.
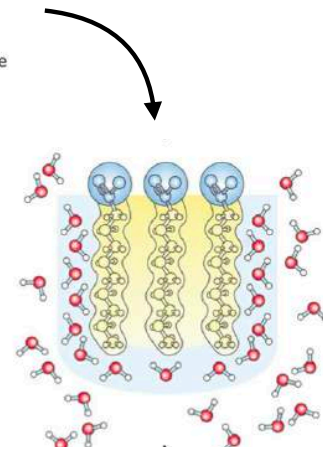
Clusters of lipid molecules
Only lipid portions at the edge of the cluster force the ordering of water. Fewer H_2O molecules are ordered, and entropy is increased.
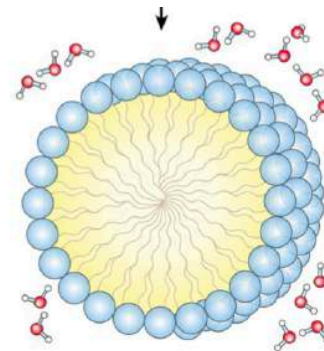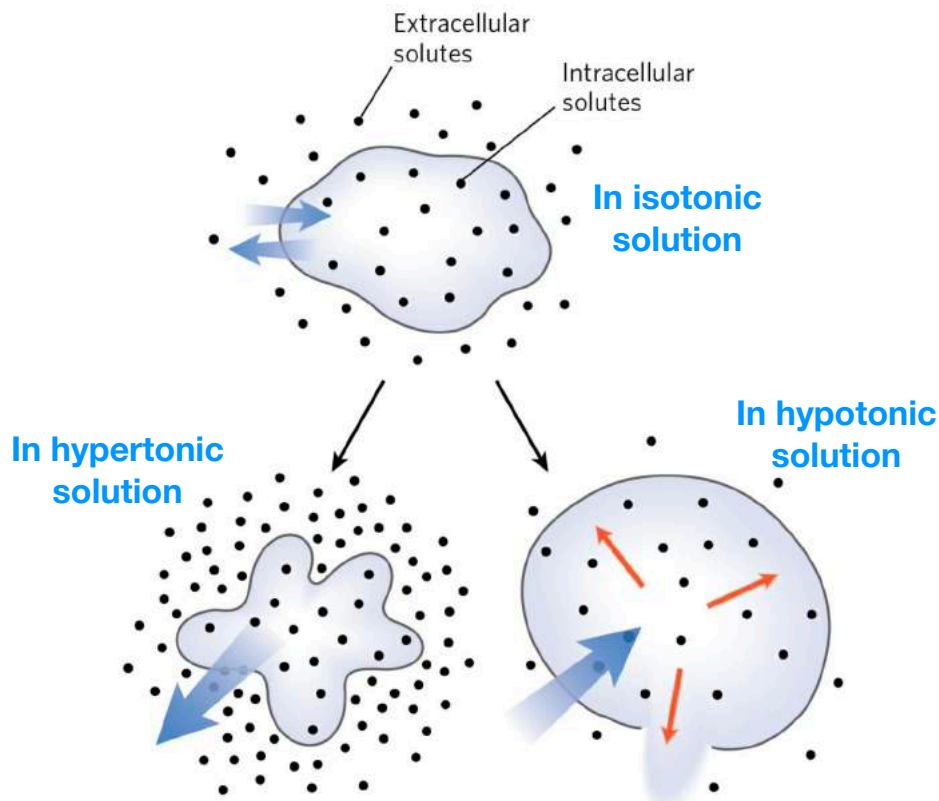
Micelles
All hydrophobic groups are sequestered from water; ordered shell of H_2O molecules is minimized, and entropy is further increased.

Courtesy: Nelson and Cox

Osmolarity

Physical properties of aqueous solutions are strongly influenced by the concentrations of solutes

Extracellular solutes

Intracellular solutes

In isotonic solution

In hypotonic solution

In hypertonic solution

- When two aqueous compartments are separated by a semipermeable membrane (such as the plasma membrane separating a cell from its surroundings), **water moves across that membrane to equalize the osmolarity** in the two compartments.

- This tendency of water to move across a semipermeable membrane produces the **osmotic pressure**.

In multicellular animals, blood plasma and interstitial fluid (the extracellular fluid of tissues) are maintained at an osmolarity close to that of the cytosol.

Osmolarity

Dependence on number of molecules and NOT mass of molecule

- Osmolarity depends on the number of dissolved molecules, not their mass

- Macromolecules (proteins, nucleic acids, polysaccharides) have much lesser effect on the osmolarity of a solution than would an equal mass of their monomeric components.

- Storing fuel as polysaccharides (starch or glycogen) rather than as glucose or other simple sugars avoids an enormous increase in osmotic pressure in the storage cell.

Ionization of water

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

- Free H+ ions do not exist in solution; H+ ions formed in water are immediately hydrated to form hydronium ions (H3O+).

$$H-O\;|||\;H-O \rightleftharpoons H-\overset{+}{O}-H + OH^-$$
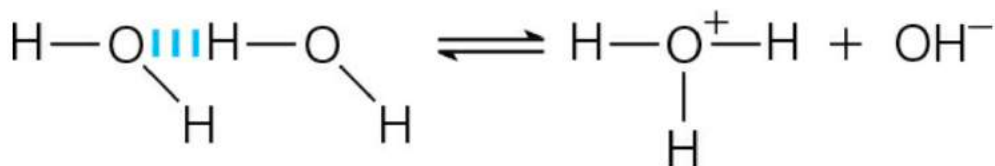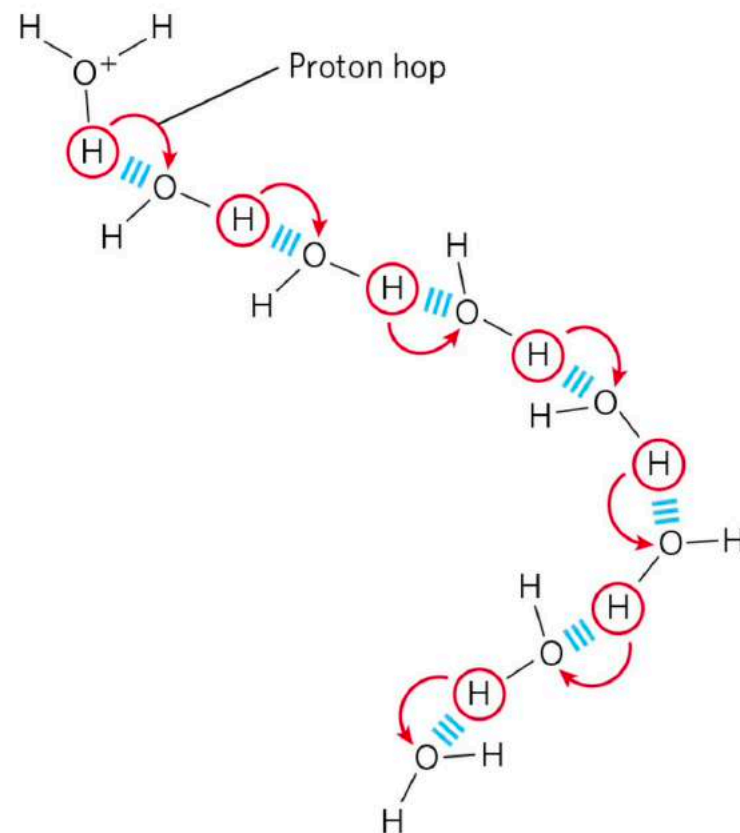
- Pure water ionizes slightly, forming equal numbers of hydrogen ions (hydronium ions, H_3O^+) and hydroxide ions

Hydronium ion gives up a proton.

Proton hop

Water accepts proton and becomes a hydronium ion.
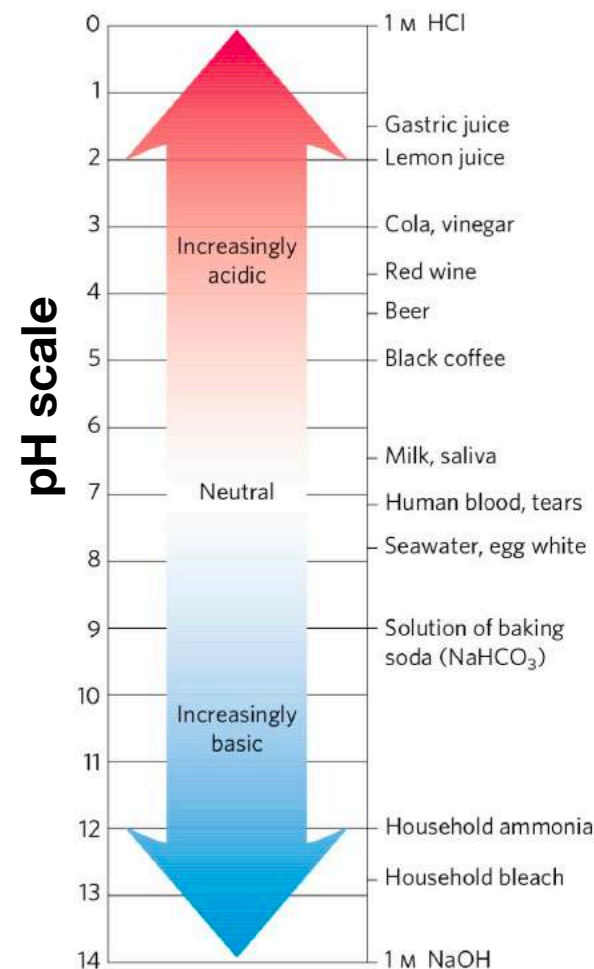
pH scale designates the [H+] and [OH−]

- The extent of ionization is described by an equilibrium constant

$$K_{eq} = \frac{[H^+] \, [OH^-]}{[H_2O]}$$

  - From K_{eq}, the ion product of water, K_w, is derived
  - At 25 °C, $K_w = 10^{-14}$ M^2
  - So, $[H+] = \sqrt{K_w} = 10^{-7}$ M

- **The pH of an aqueous solution reflects the conc. of H^+ (on a logarithmic scale)**

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

- The greater the acidity of a solution, the lower its pH.

pH scale

pH		
0		1 M HCl
1		
2	Increasingly acidic	Gastric juice / Lemon juice
3		Cola, vinegar
4		Red wine / Beer
5		Black coffee
6		Milk, saliva
7	Neutral	Human blood, tears
8		Seawater, egg white
9		Solution of baking soda (NaHCO$_3$)
10	Increasingly basic	
11		
12		Household ammonia
13		Household bleach
14		1 M NaOH

pKa

- Weak acids partially ionize to release a hydrogen ion, thus lowering the pH of the aqueous solution. Weak bases accept a H+, increasing the pH. The extent of these processes is characteristic of each particular weak acid or base and is expressed as an **acid dissociation constant(K_a)**:

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

- pKa expresses the relative strength of a weak acid or base, on a logarithmic scale:

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

- When pH = pKa the concentration of the weak acid and the conjugate base are equal.

Monoprotic acids
Acetic acid
($K_a = 1.74 \times 10^{-5}$ M)

Ammonium ion
($K_a = 5.62 \times 10^{-10}$ M)

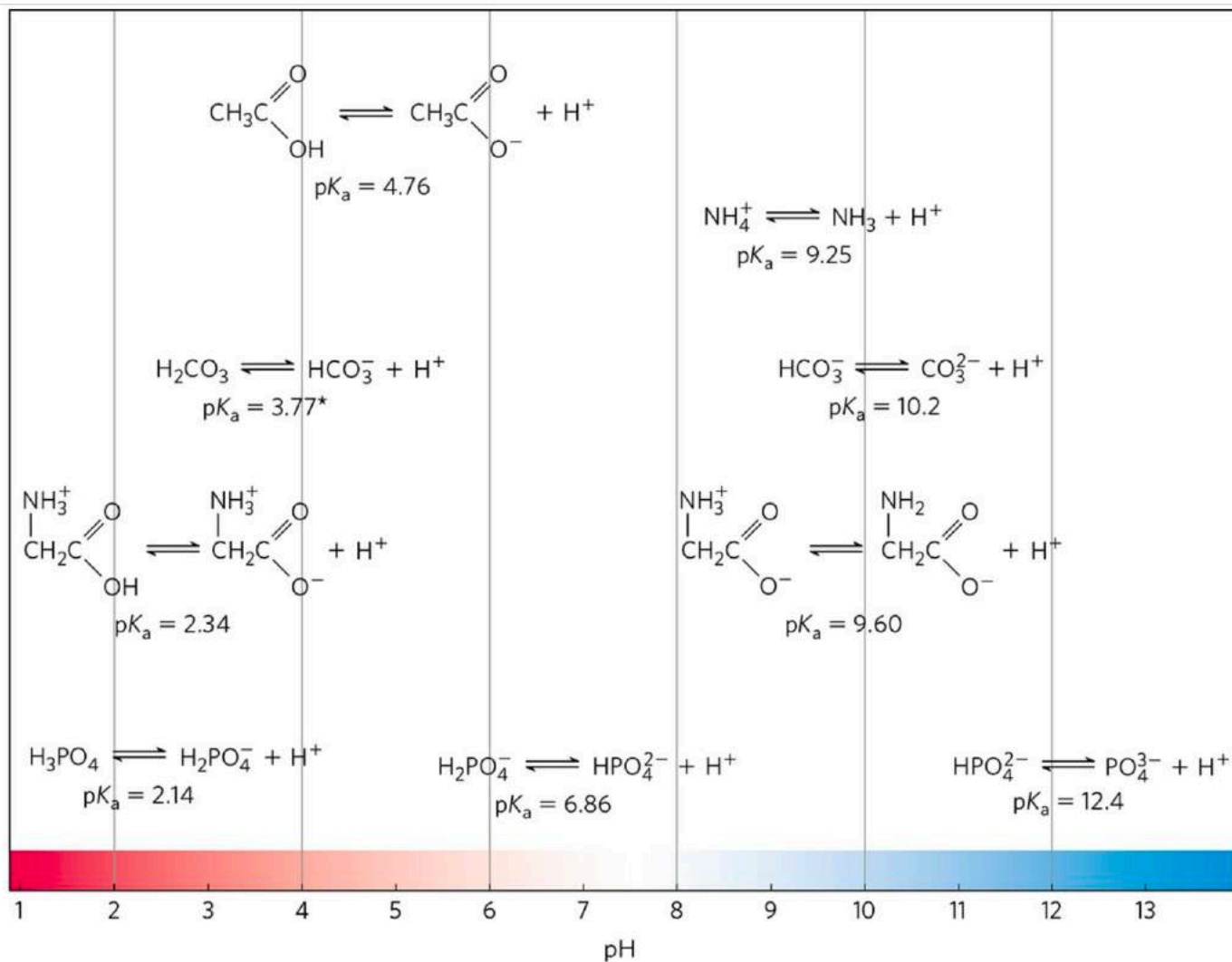**Diprotic acids**
Carbonic acid
($K_a = 1.70 \times 10^{-4}$ M);
Bicarbonate
($K_a = 6.31 \times 10^{-11}$ M)

Glycine, carboxyl
($K_a = 4.57 \times 10^{-3}$ M);
Glycine, amino
($K_a = 2.51 \times 10^{-10}$ M)

Triprotic acids
Phosphoric acid
($K_a = 7.25 \times 10^{-3}$ M);
Dihydrogen phosphate
($K_a = 1.38 \times 10^{-7}$ M);
Monohydrogen phosphate
($K_a = 3.98 \times 10^{-13}$ M)

$CH_3C(=O)OH \rightleftharpoons CH_3C(=O)O^- + H^+$
$pK_a = 4.76$

$NH_4^+ \rightleftharpoons NH_3 + H^+$
$pK_a = 9.25$

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$
$pK_a = 3.77^*$

$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$
$pK_a = 10.2$

$NH_3^+\text{-}CH_2C(=O)OH \rightleftharpoons NH_3^+\text{-}CH_2C(=O)O^- + H^+$
$pK_a = 2.34$

$NH_3^+\text{-}CH_2C(=O)O^- \rightleftharpoons NH_2\text{-}CH_2C(=O)O^- + H^+$
$pK_a = 9.60$

$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$
$pK_a = 2.14$

$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$
$pK_a = 6.86$

$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$
$pK_a = 12.4$

pH
1 2 3 4 5 6 7 8 9 10 11 12 13
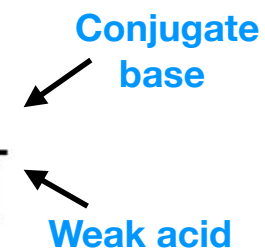
Henderson-Hasselbach equation
Buffering a system

- **Buffers are mixtures of weak acids (the proton donor) and their conjugate bases (the proton acceptor) in water**

- Such aqueous systems tend to resist changes in pH when small amounts of acid (H+) or base (OH–) are added.

- This equation fits the titration curve of all weak acids and enables us to deduce some important quantitative relationships.

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[A^-]}{[HA]}$$

Conjugate base (→ $[A^-]$)

Weak acid (→ $[HA]$)

Buffering range

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

Conjugate base

Weak acid