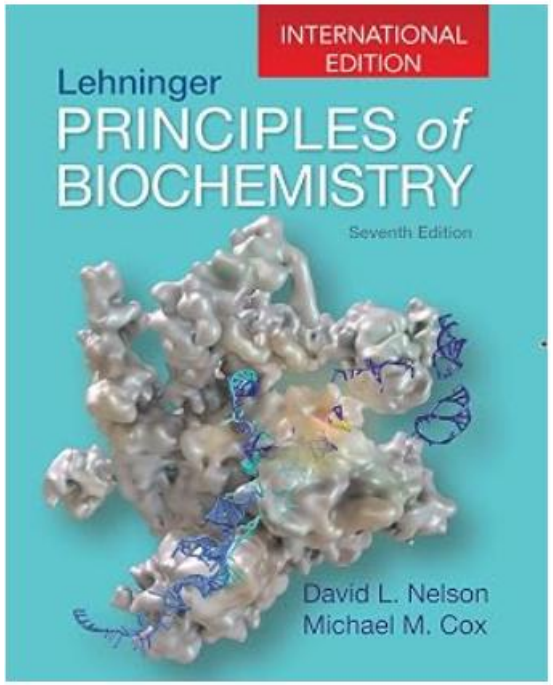
pH, Buffer, Handerson-Hasselbalch equation



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Ionization Product of H_2O

- Like all reversible reactions, the ionization of water can be described by an equilibrium constant.
- When weak acids are dissolved in water, they contribute H^+ by ionizing; weak bases consume H^+ by becoming protonated.
- The total hydrogen ion concentration from all sources is experimentally measurable and is expressed as the pH of the solution.
- Water molecules have a slight tendency to undergo reversible ionization to yield a hydrogen ion (a proton) and a hydroxide ion, giving the equilibrium:

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

- Although we commonly show the dissociation product of water as H^+, free protons do not exist in solution; hydrogen ions formed in water are immediately hydrated to **hydronium ions** (H_3O^+).
- 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.
- The movement of hydronium and hydroxide ions in the electric field is anomalously fast compared with that of other ions such as Na^+, K^+, and Cl^-.
- This high ionic mobility results from the kind of "proton hopping".

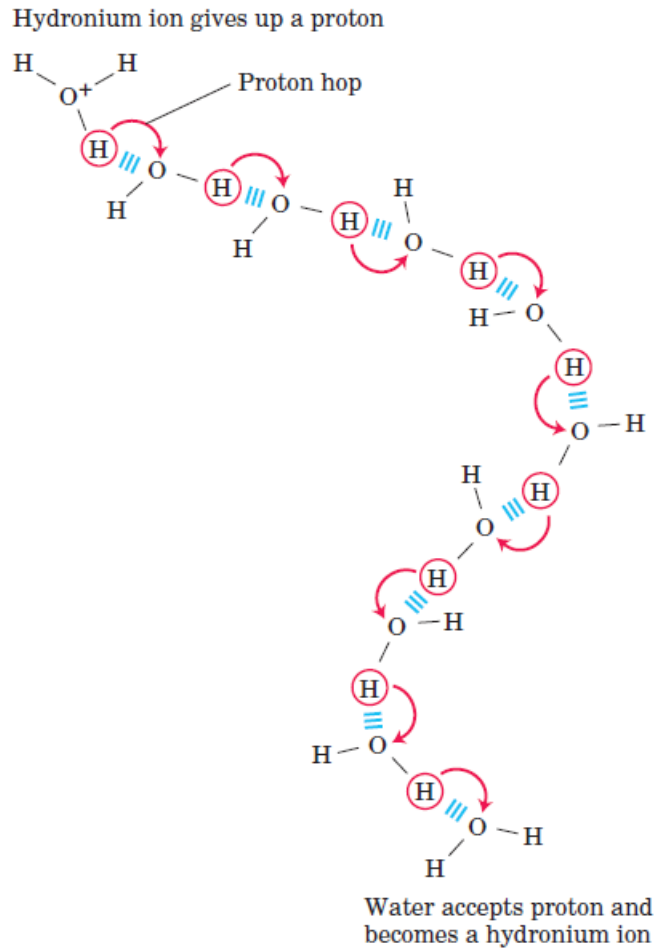

FIGURE 2–14 **Proton hopping.** Short "hops" of protons between a series of hydrogen-bonded water molecules effect an extremely rapid net movement of a proton over a long distance. As a hydronium ion (upper left) gives up a proton, a water molecule some distance away (lower right) acquires one, becoming a hydronium ion. Proton hopping is much faster than true diffusion and explains the remarkably high ionic mobility of H^+ ions compared with other monovalent cations such as Na^+ or K^+.

Ion Product

- The position of equilibrium of any chemical reaction is given by its **equilibrium constant, *K*eq** (sometimes expressed simply as *K*). For the generalized reaction an equilibrium constant can be defined in terms of the concentrations of reactants (A and B) and products (C and D) at equilibrium:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} + \mathrm{D}$$

$$K_{\mathrm{eq}} = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}$$

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-}$$

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

- In pure water at 25 C, the concentration of water is 55.5 M (grams of H2O in 1 L divided by its gram molecular weight: (1,000 g/L)/(18.015 g/mol)).

$$K_{\mathrm{eq}} = \frac{[\mathrm{H^+}][\mathrm{OH^-}]}{55.5\ \mathrm{M}},$$

$$(55.5\ \mathrm{M})(K_{\mathrm{eq}}) = [\mathrm{H^+}][\mathrm{OH^-}] = K_{\mathrm{w}}$$

- Where *K*w designates the product (55.5 M)(*K*eq), the **ion product of water** at 25 °C.

...Ion Product

- The value for *K*eq, determined by electrical-conductivity measurements of pure water, is 1.8 x10^{-16} M at 25° C.
- Substituting this value for *K*eq in Equation gives the value of the ion product of water:

$$K_w = [H^+][OH^-] = (55.5\ M)(1.8 \times 10^{-16}\ M)$$
$$= 1.0 \times 10^{-14}\ M^2$$

- Thus the product $[H^+][OH^-]$ in aqueous solutions at 25 C always equals 1 x 10^{-14} M^2.
- When there are exactly equal concentrations of H and OH, as in pure water, the solution is said to be at **neutral pH.**
- At this pH, the concentration of H^+ and OH^- can be calculated from the ion product of water as follows:

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

Solving for $[H^+]$ gives

$$[H^+] = \sqrt{K_w} = \sqrt{1 \times 10^{-14}\ M^2}$$

$$[H^+] = [OH^-] = 10^{-7}\ M$$

- As the ion product of water is constant, whenever $[H^+]$ is greater than 1 x 10^{-7} M, $[OH^-]$ must become less than 1 x 10^{-7} M, and vice versa.

pH

- The term **pH** is defined by the expression:

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

- The symbol p denotes “negative logarithm of.”
- For a precisely neutral solution at 25° C, in which the concentration of hydrogen ions is 1.0×10^{-7} M, the pH can be calculated as follows:

$$\text{pH} = \log \frac{1}{1.0 \times 10^{-7}} = \log (1.0 \times 10^{7})$$

$$= \log 1.0 + \log 10^{7} = 0 + 7 = 7$$

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 $\text{pOH} = -\log [OH^-]$, which is analogous to the expression for pH. Note that in all cases, pH + pOH = 14.

...pH

- Solutions having a pH greater than 7 are alkaline or basic; the concentration of OH^- is greater than that of H^+.
- Conversely, solutions having a pH less than 7 are acidic.
- Note that the pH scale is logarithmic, not arithmetic.
- To say that two solutions differ in pH by 1 pH unit means that one solution has ten times the H^+ concentration of the other, but it does not tell us the absolute magnitude of the difference.
- The pH of an aqueous solution can be approximately measured using various indicator dyes, including litmus, phenolphthalein, and phenol red, which undergo color changes as a proton dissociates from the dye molecule.
- Accurate determinations of pH in the chemical or clinical laboratory are made with a glass electrode that is selectively sensitive to H^+ concentration but insensitive to Na^+, K^+, and other cations.
- In a pH meter the signal from such an electrode is amplified and compared with the signal generated by a solution of accurately known pH.
- Measurement of pH is one of the most important and frequently used procedures in biochemistry.
- The pH affects the structure and activity of biological macromolecules; for example, the catalytic activity of enzymes is
- strongly dependent on pH.

Weak Acid/ Base

- Acids may be defined as proton donors and bases as proton acceptors.
- A proton donor and its corresponding proton acceptor make up a **conjugate acid-base pair**.
- Acetic acid (CH3COOH), a proton donor, and the acetate anion ($CH3COO^-$), the corresponding proton acceptor, constitute a conjugate acid base pair, related by the reversible reaction:

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

- Each acid has a characteristic tendency to lose its proton in an aqueous solution.
- The stronger the acid, the greater its tendency to lose its proton.
- The tendency of any acid (HA) to lose a proton and form its conjugate base (A^-) is defined by the equilibrium constant (*K*eq) for the reversible reaction:

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

which is

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

- Equilibrium constants for ionization reactions are usually called ionization or **dissociation constants,** often designated *K*a.

pK_a

- The p*K*a expresses, on a logarithmic scale, the relative strength of a weak acid or base:

$$\mathrm{p}K_\mathrm{a} = \log \frac{1}{K_\mathrm{a}} = -\log K_\mathrm{a}.$$

- The stronger the acid, the lower its p*K*a; the stronger the base, the higher its p*K*a.
- The p*K*a can be determined experimentally; it is the pH at the midpoint of the titration curve for the acid or base.

Buffering against pH Changes in Biological Systems

- Cells and organisms maintain a specific and constant cytosolic pH, keeping biomolecules in their optimal ionic state, usually near pH 7.
- In multicellular organisms, the pH of extracellular fluids is also tightly regulated.
- Constancy of pH is achieved primarily by biological buffers: mixtures of weak acids and their conjugate bases.
- In cells and tissues, phosphate and bicarbonate buffer systems maintain intracellular and extracellular fluids at their optimum (physiological) pH, which is usually close to pH 7.
- Enzymes generally work optimally at this pH.
- **Buffers** are aqueous systems that tend to resist changes in pH when small amounts of acid (H^+) or base (OH^-) are added.
- A buffer system consists of a weak acid (the proton donor) and its conjugate base (the proton acceptor).
- Each conjugate acid-base pair has a characteristic pH zone in which it is an effective buffer.
- The H_2PO_4 /HPO_4^{-2} pair has a p*K*a of 6.86 and thus can serve as an effective buffer system between approximatelypH 5.9 and pH 7.9; the NH_4^+ /NH_3 pair, with a p*K*a of 9.25, can act as a buffer between approximately pH 8.3 and pH 10.3.

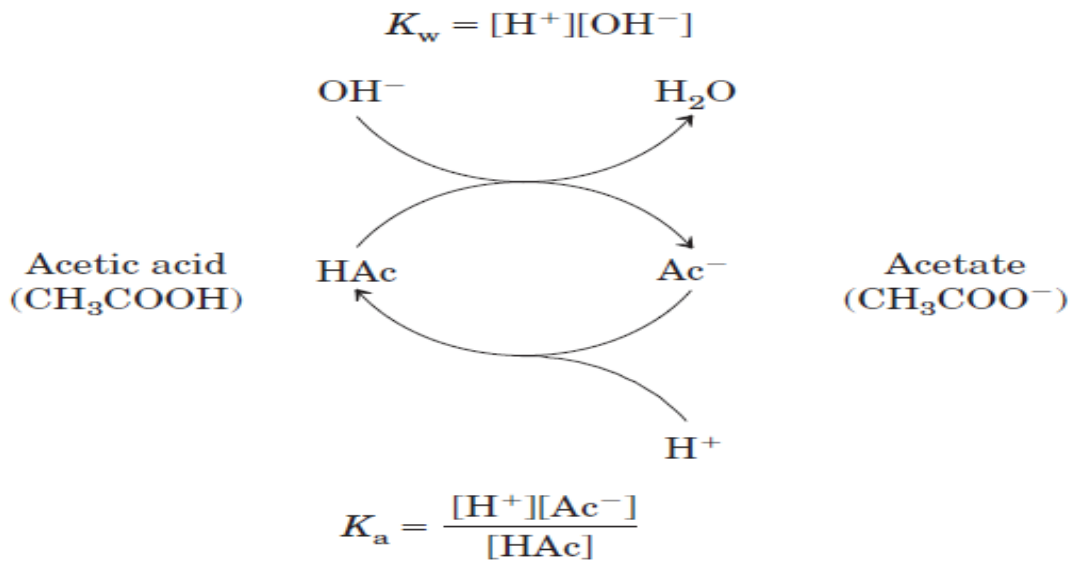

FIGURE 2–19 The acetic acid–acetate pair as a buffer system. The system is capable of absorbing either H^+ or OH^- through the reversibility of the dissociation of acetic acid. The proton donor, acetic acid (HAc), contains a reserve of bound H^+, which can be released to neutralize an addition of OH^- to the system, forming H_2O. This happens because the product $[H^+][OH^-]$ transiently exceeds K_w (1×10^{-14} M^2). The equilibrium quickly adjusts so that this product equals 1×10^{-14} M^2 (at 25 °C), thus transiently reducing the concentration of H^+. But now the quotient $[H^+][Ac^-] / [HAc]$ is less than K_a, so HAc dissociates further to restore equilibrium. Similarly, the conjugate base, Ac^-, can react with H^+ ions added to the system; again, the two ionization reactions simultaneously come to equilibrium. Thus a conjugate acid-base pair, such as acetic acid and acetate ion, tends to resist a change in pH when small amounts of acid or base are added. Buffering action is simply the consequence of two reversible reactions taking place simultaneously and reaching their points of equilibrium as governed by their equilibrium constants, K_W and K_a.

Henderson-Hasselbalch equation

- **Henderson-Hasselbalch equation,** which is important for understanding buffer action and acid-base balance in the blood and tissues of vertebrates.
- This equation is simply a useful way of restating the expression for thedissociation constant of an acid.
- For the dissociation of a weak acid HA into H^+ and A^-, the Henderson-Hasselbalch equation can be derived as follows:

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

First solve for $[H^+]$:

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

Then take the negative logarithm of both sides:

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

Substitute pH for $-\log [H^+]$ and pK_a for $-\log K_a$:

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

- Now invert -log [HA]/[A^-], which involves changing its sign, to obtain the Henderson-Hasselbalch equation:

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

Stated more generally,

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

- For week acid,

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log 1 = \mathrm{p}K_\mathrm{a} + 0 = \mathrm{p}K_\mathrm{a}$$