

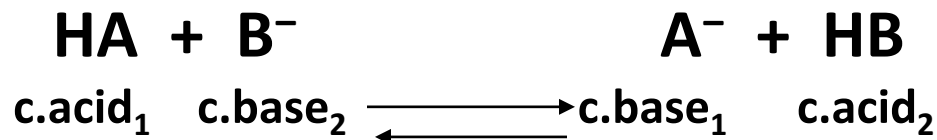
ACID-BASE AND BUFFER CONCEPTS

ACIDS AND BASES

- Many of the low-molecular weight metabolites and macromolecular components present in living cells are acids and bases.
- These molecules have the potential to ionize.
- The charges present on these molecules are important in the rate of enzyme-catalysed reactions, the stability of proteins and in the interactions with each other and with other small ions.

Bronsted concept of conjugate acid-conjugate base pairs:

- A substance that donates protons (hydrogen ions) is an “acid” and a substance that accepts protons is a “base”.
- When a Bronsted acid loses a proton, a Bronsted base is produced. The original acid and resulting base are named as a conjugate acid-conjugate base pair. The substance that accepts the proton is a different Bronsted base; by accepting the proton, another Bronsted acid is produced. So, in every ionization of an acid or base, two conjugate acid-conjugate base pairs are involved.



- **STRONG ACID – STRONG BASE:**

Strong acids and strong bases are substances that ionize almost 100% in aqueous solutions.

- **WEAK ACID – WEAK BASE :**

Weak acids and weak bases are substances that ionize partially in aqueous solutions.

- **pH:**

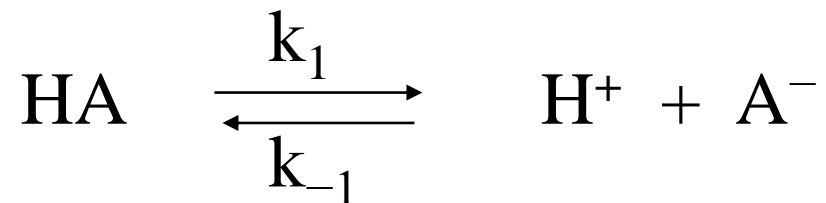
pH is a shorthand way of designating the hydrogen ion activity of a solution. By definition pH is the negative logarithm of the hydrogen ion concentration.

$$-\log [\text{H}^+] \quad \text{or} \quad \log 1 / [\text{H}^+]$$

EQUILIBRIUM CONSTANT

- A great many reactions that occur in nature are **reversible** and do not proceed to completion. Instead, they come to an apparent halt or **equilibrium** at some point between 0 and 100% completion. At equilibrium, the net velocity is zero because the absolute velocity in the forward direction exactly equals the absolute velocity in the reverse direction. The position of equilibrium is described by an **equilibrium constant, K_{eq}** .

- For example, if we consider the dissociation of a weak acid as in the reaction below, in which k_1 and k_{-1} are **rate constants**.



forward velocity: $v_f = k_1 [\text{HA}]$,

reverse velocity: $v_r = k_{-1} [\text{H}^+] [\text{A}^-]$

At equilibrium;

$$v_f = v_r$$



$$k_1 [\text{HA}] = k_{-1} [\text{H}^+] [\text{A}^-]$$



$$k_1 / k_{-1} = \frac{[\text{H}^+] [\text{A}^-]}{[\text{HA}]}$$

The ratio of the two constants (k_1 / k_{-1}) is itself a constant and is defined as K_{eq} . In this particular case, K_{eq} is an acid dissociation constant and would be indicated as K_{a} .

$$K_{\text{a}} = \frac{[\text{H}^+] [\text{A}^-]}{[\text{HA}]}$$

pH of Solutions of Weak Acids

- The dissociation of a weak acid, HA, yields H⁺ and A⁻ in equal concentrations. If K_a and the initial concentration of HA are known, H⁺ can be calculated easily:

$$K_a = \frac{[H^+][A^-]}{[HA]} \longrightarrow K_a = [H^+]^2 / [HA] \longrightarrow [H^+] = \sqrt{K_a [HA]}$$

- To obtain an expression giving pH, we put the above equation in the logarithmic form

$$-\log [H] = \frac{-\log K_a + -\log[HA]}{2} \longrightarrow \text{pH} = \frac{\text{p}K_a + \text{p}[HA]}{2}$$

Henderson-Hasselbalch Equation

- The Henderson – Hasselbalch equation was developed independently by the American biological chemist Henderson and the Swedish physiologist Hasselbalch, for relating the pH to the bicarbonate buffer system of the blood.
- In its general form, the Henderson–Hasselbalch equation is a useful expression for buffer calculations.

Henderson-Hasselbalch Equation

- An expression relating the K_a of a weak acid, HA, and the pH of a solution of the weak acid;

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

after rearranging terms;

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

- After taking logarithms of both sides and multiplying by -1;

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

$$\text{pH} = \text{pKa} + \log \frac{[\text{A}^-] \text{ (conjugated base)}}{[\text{HA}] \text{ (acid)}}$$

- When the concentrations of conjugate acid and conjugate base are equal;

$$\text{pH} = \text{pKa} \quad \text{or} \quad [\text{H}^+] = K_a$$

According to the above equations, the pH of a solution containing HA and A⁻ is independent of concentration; the pH established solely by the ratio of conjugate base to conjugate acid.

WHAT IS A BUFFER?

HOW DOES A BUFFER WORK?

- A 'buffer' is something that resists change.
- In common chemical usage, a pH buffer is a substance, or mixture of substances, that permits solutions to resist large changes in pH upon the addition of small amounts of H^+ or OH^- ions.
- If we describe it in another way, a buffer helps maintain a near constant pH upon the addition of small amounts of H^+ or OH^- ions to a solution.

- Common buffer mixtures contain two substances, a conjugate acid and a conjugate base.
- An 'acidic' buffer contains a weak acid and a salt of the weak acid (conjugate base).
- A 'basic' buffer contains a weak base and a salt of the weak base (conjugate acid).
- Together the two species (conjugate acid plus conjugate base) resist large changes in pH by partially absorbing additions of H^+ or OH^- ions to the system.

- If H^+ ions are added to the buffered solution, they react partially with the conjugate base present to form the conjugate acid. Thus, some H^+ ions are taken out of circulation.
- If OH^- ions are added to the buffered solution, they react partially with the conjugate acid present to form water and the conjugate base. Thus, some OH^- ions are taken out of circulation.

- Buffered solutions do change in pH upon the addition of H^+ or OH^- ions.
- However, the change is much less than that which would occur if no buffer were present.
- The amount of change depends on the strength of the buffer (buffer capacity) and the $[A^-] / [HA]$ ratio.
- **Buffer capacity** in the acid (or alkaline) direction: The number of moles of H^+ (or OH^-) that must be added to one liter of buffer in order to decrease (or increase) the pH by 1 unit.