Topic 6G - Buffers

Buffers

Solution containing a weak acid or base, plus the salt of its conjugate base or acid.

Acidic Buffer - weak acid + salt of conjugate base

$$CH_3COOH + Na^+CH_3COO^-$$

$$H_3PO_4 + K^+H_2PO_4^-$$

Maintains pH < 7

Basic Buffer - weak base + salt of conjugate acid

$$NH_3 + NH_4^+Cl^-$$

$$(Na^+)_3PO_4^{3-} + (Na^+)_2HPO_4^{2-}$$

Maintains pH > 7

Buffer Action

$$HA + H_2O \rightleftarrows A^- + H_3O^+$$

HA ↑ reacts with bases ("sink" for OH^-)

A^- ↑ reacts with acids ("sink" for H_3O^+)

Calculating pH of a Buffer

If [HA] = [A$^-$], then

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = [H_3O^+]$$

and pH = pK_a (maximum buffer capacity)

Since $$[H_3O^+] = K_a \frac{[HA]}{[A^-]}$$

then $$-\log[H_3O^+] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

Thus, $$pH = pK_a - \log\frac{[HA]}{[A^-]} = pK_a + \log\frac{[A^-]_{eq}}{[HA]_{eq}}$$

And since $[HA]_{eq} \approx [HA]_i$ and $[A^-]_{eq} \approx [A^-]_i$, then

$$pH \approx pK_a + \log\frac{[A^-]_i}{[HA]_i}$$

which is the so-called Henderson-Hasselbalch equation.

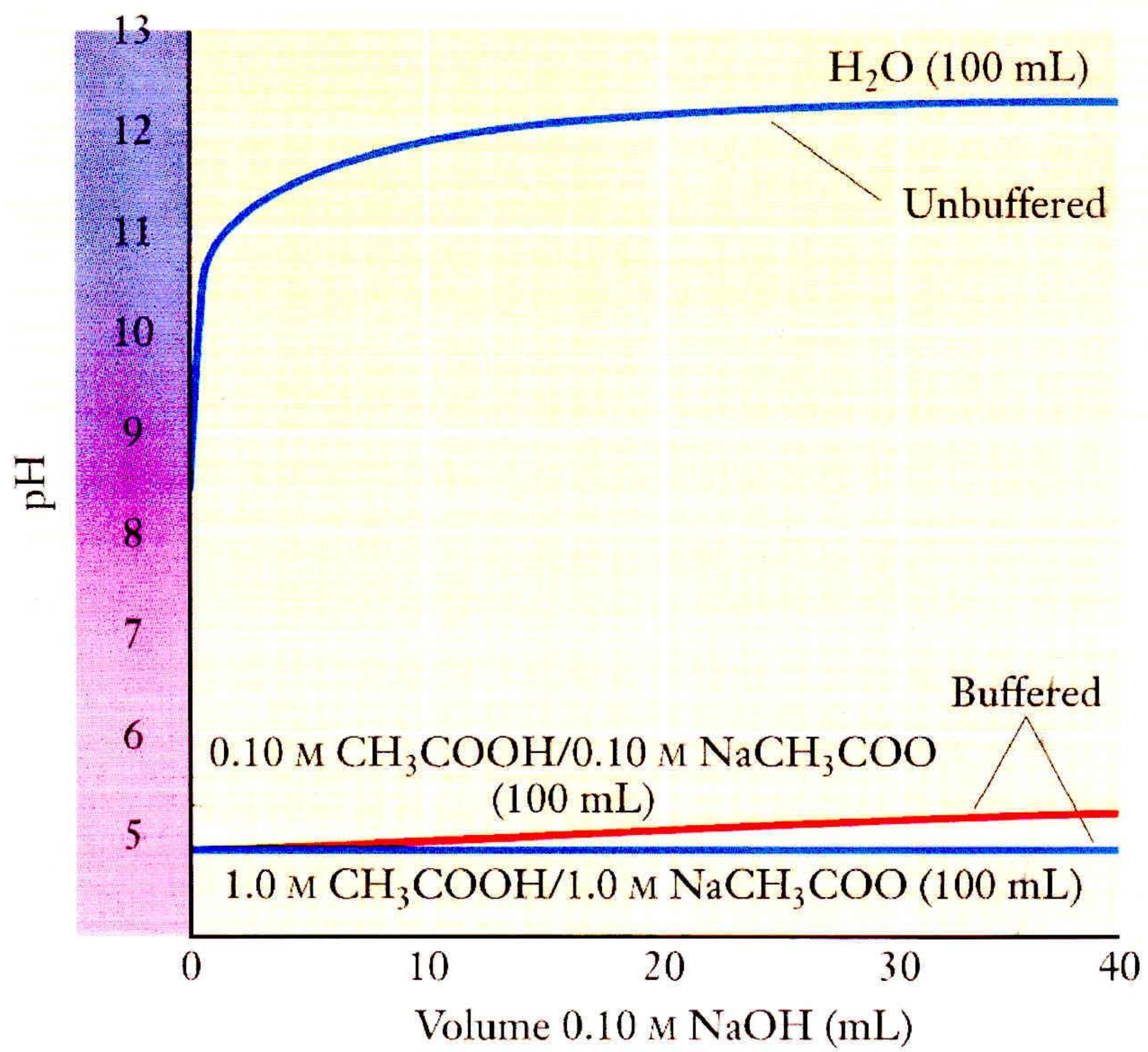


FIGURE 10.12 Addition of a given volume of base to buffered and unbuffered solutions causes a much greater change in the pH of the unbuffered solution. Of the two buffered solutions, the one with higher buffer concentration resists pH changes more effectively.

Buffer Capacity

The maximum amount of acid or base that can be added to a buffer before it loses its ability to resist pH changes.

If [HA] = 10 × [A⁻],

$$pH = pK_a + \log\frac{[A^-]}{10[A^-]} = pK_a + \log(0.1) = pK_a - 1$$

If [A⁻] = 10 × [HA],

$$pH = pK_a + \log\frac{10\,[HA]}{[HA]} = pK_a + \log(10) = pK_a + 1$$

Thus, buffers act effectively in the range ± 1 pK_a.

Buffering in Blood Plasma

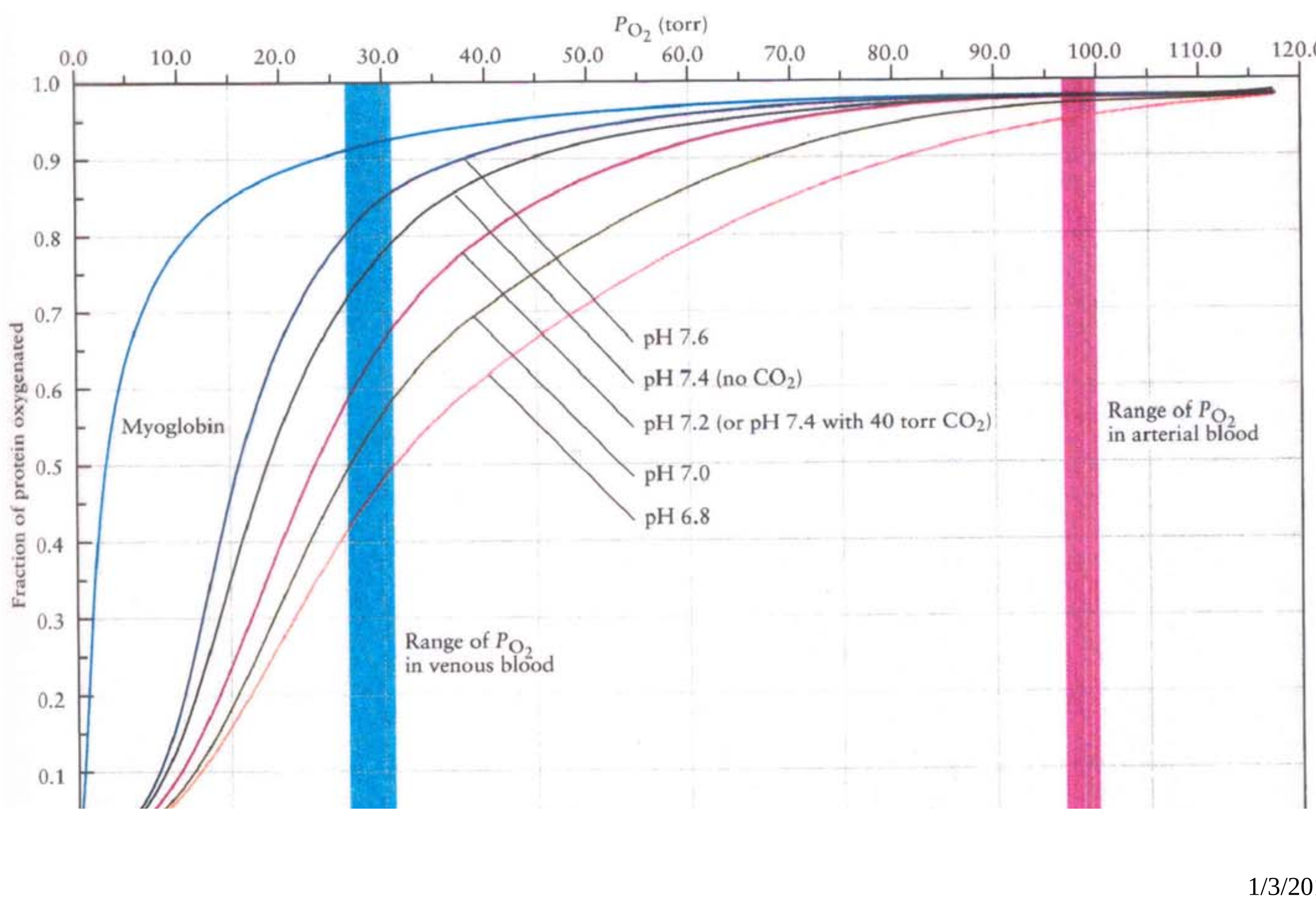
Behaviors of enzymes are markedly pH-dependent, and require the presence of buffers to optimize their effectiveness. The pH in cells is stabilized by a phosphate buffer system (HPO_4^{2-} / $H_2PO_4^-$), while that in fluids, such as blood plasma, is stabilized by a bicarbonate buffer system (HCO_3^- / H_2CO_3).

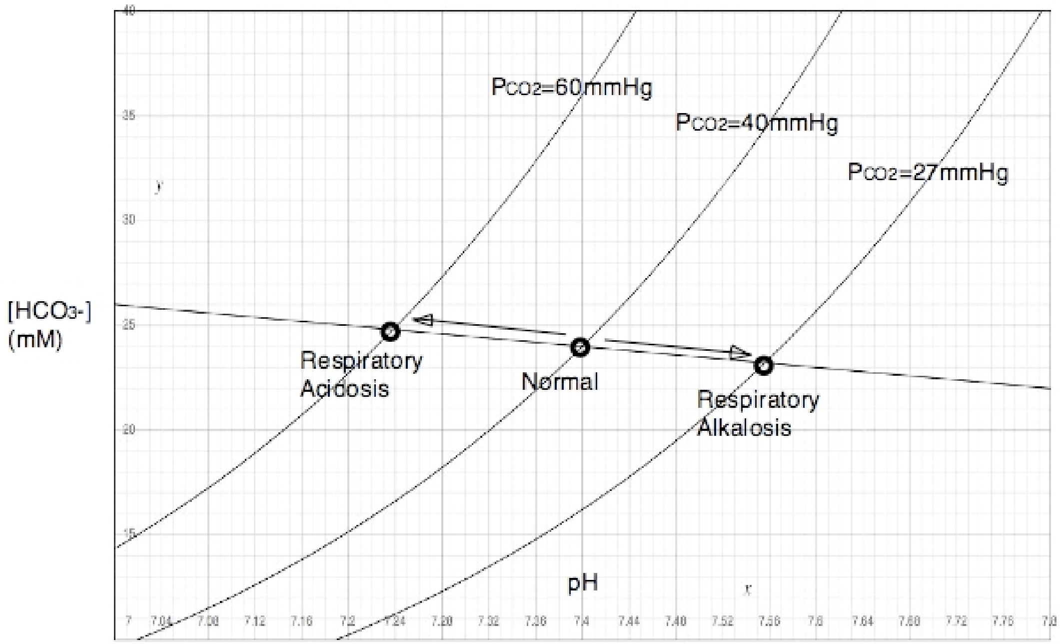
$$CO_2\,(g) \rightleftharpoons CO_2\,(aq)$$

$$CO_2\,(aq) + H_2O\,(\ell) \rightleftharpoons H_2CO_3\,(aq)$$

$$H_2CO_3\,(aq) + H_2O\,(\ell) \rightleftharpoons HCO_3^-\,(aq) + H_3O^+\,(aq)$$

Thus, blood pH is influenced by the amount of CO_2 that is present in the blood. As pH decreases, effectiveness of transferring O_2 from hemoglobin in blood to myoglobin in cells increases:




PCO2=60mmHg
PCO2=40mmHg
PCO2=27mmHg
[HCO3-]
(mM)
Respiratory
Acidosis
Normal
Respiratory
Alkalosis
pH