فصل 19 (کتاب سیلبربرگ)

تعادل های یونی در سیستم های آبی

Ionic Equilibria in Aqueous Systems

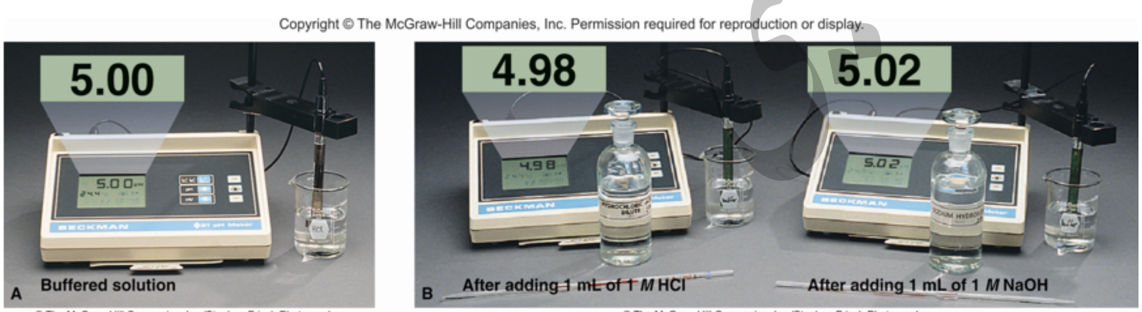
تعریف بافر اسید-باز

An acid-base buffer usually consists of a ***conjugate acid-base pair*** where both species are present in appreciable quantities in solution.

اجزای بافر با غلظت زیاد در محلول وجود دارند.

An acid-base buffer is therefore a ***solution of a weak acid and its conjugate base,*** or a ***weak base*** and its ***conjugate acid***.

Figure 19.2 **The effect of adding acid or base to a buffered solution.**



A 100-mL sample of an acetate buffer is adjusted to pH 5.00.

The addition of 1 mL of strong acid (*left*) or strong base (*right*) changes the pH very little.

The acetate buffer is made by mixing 1 *M* CH_3COOH (a weak acid) with 1 *M* CH_3COONa (which provides the conjugate base, CH_3COO^-).

بافر چگونه عمل می کند: اثر یون مشترک

A buffer works through the ***common-ion effect***.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

acetic acid — acetate ion

If $NaCH_3COO$ is added, it provides a source of CH_3COO^- ion, and the equilibrium shifts to the left. CH_3COO^- is ***common*** to both solutions.

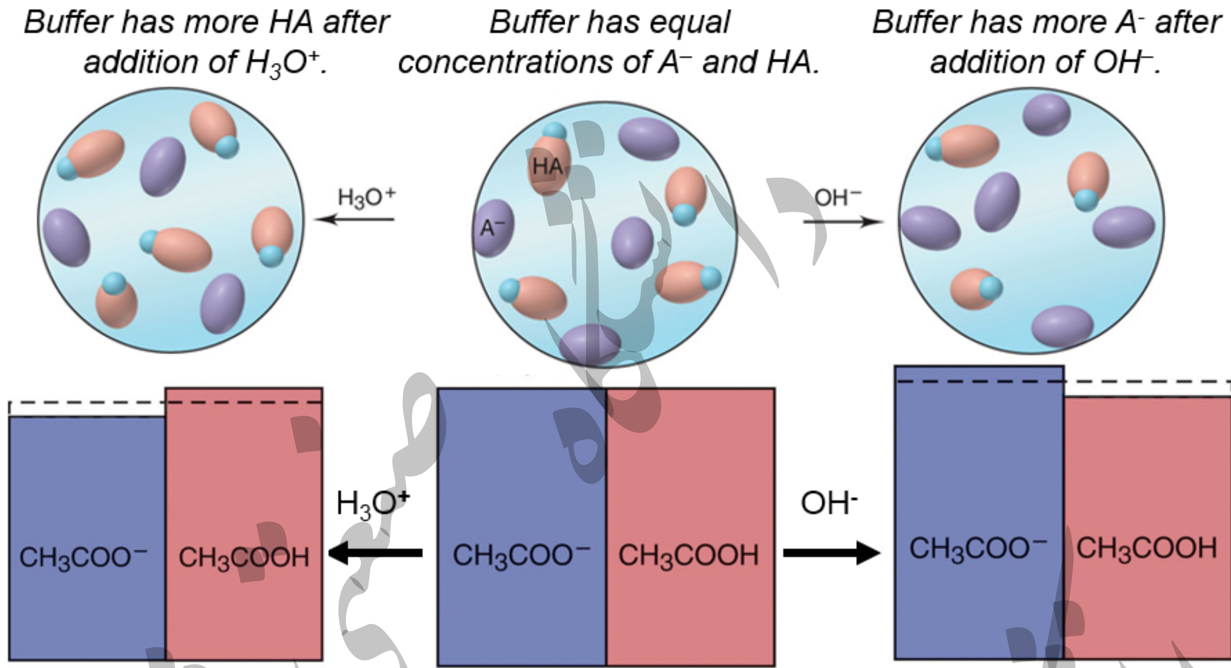
افزایش استات درصد تفکیک اسید را کاهش می دهد. جدول 19 – 1 را ببینید.

Table 19.1 The Effect of Added Acetate Ion on the Dissociation of Acetic Acid

$[CH_3COOH]_{init}$	$[CH_3COO^-]_{added}$	% Dissociation*	$[H_3O^+]$	pH
0.10	0.00	1.3	$1.3x10^{-3}$	2.89
0.10	0.050	0.036	$3.6x10^{-5}$	4.44
0.10	0.10	0.018	$1.8x10^{-5}$	4.74
0.10	0.15	0.012	$1.2x10^{-5}$	4.92

* $\% \text{ Dissociation} = \frac{[CH_3COOH]_{dissoc}}{[CH_3COOH]_{init}} \times 100$

Figure 19.3 **How a buffer works.**



$H_2O + CH_3COOH \leftarrow H_3O^+ + CH_3COO^-$ $\quad$ $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

بنابراین اجزای بافر درنهایت یون هیدرونیوم یا یون هیدروکسید اضافه شده را مصرف می کنند.

سوال: آیا با اضافه کردن اسید قوی یا باز قوی می توان pH بافر را تغییر داد؟

pH و نسبت غلظتی اجزای بافر

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \qquad [H_3O^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]}$$

Since K_a is constant, the $[H_3O^+]$ of the solution depends on the ***ratio of buffer component concentrations***.

If the ratio $\frac{[HA]}{[A^-]}$ increases, $[H_3O^+]$ increases.

If the ratio $\frac{[HA]}{[A^-]}$ decreases, $[H_3O^+]$ decreases.

معادله هندرسون هسل- باخ

The Henderson-Hasselbalch Equation

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

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

$$-\log[H_3O^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right)$$

$$\boxed{pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)}$$

تمرین: از مسائل آخر فصل 19 سیلبربرگ، دو مسئله 19-15 و 19-16 را در این زمینه حل کنید.

سوال: گستره pH بافر را به دست آورید.

Buffer Range

The ***buffer range*** is the pH range over which the buffer is effective.

Buffer range is related to the ratio of buffer component concentrations.

The closer $\frac{[HA]}{[A^-]}$ is to 1, the more effective the buffer.

If the concentration of one component is more than 10 times the concentration of the other, buffering action is poor. Since log10 = 1, ***buffers have a usable range within ± 1 pH unit of the*** pK_a ***of the acid component.***

تمرین: از مسائل آخر فصل 19 سیلبربرگ، مسئله 19-9 را در این زمینه حل کنید.

نمونه مسئله 19-1: محاسبه اثر افزایش اسید یا باز بر pH بافر

Sample Problem 19.1 **Calculating the Effect of Added H_3O^+ or OH^- on Buffer pH**

PROBLEM: Calculate the pH:

(a) Of a buffer solution consisting of 0.50 *M* CH_3COOH and 0.50 *M* CH_3COONa

(b) After adding 0.020 mol of solid NaOH to 1.0 L of the buffer solution in (a).

(c) After adding 0.020 mol of HCl to 1.0 L of the buffer solution in (a).

K_a of $CH_3COOH = 1.8 \times 10^{-5}$. (Assume the additions cause a negligible change in volume.)

PLAN: We can calculate $[CH_3COOH]_{init}$ and $[CH_3COO^-]_{init}$ from the given information. From this we can find the starting pH. For **(b)** and **(c)** we assume that the added OH^- or H_3O^+ reacts completely with the buffer components. We write a balanced equation in each case, set up a reaction table, and calculate the new $[H_3O^+]$.

با افزایش اسید یا باز قوی به بافر، فرض می کنیم که اسید یا باز اضافه شده کاملا با اجزاء بافر واکنش می دهد.

SOLUTION: (a)

Concentration (*M*)	$CH_3COOH(aq)$	$+ H_2O(l) \rightleftharpoons$	$CH_3COO^-(aq)$	$+ H_3O^+(aq)$
Initial	0.50	-	0.50	0
Change	$-x$	-	$+x$	$+x$
Equilibrium	$0.50 - x$	-	$0.50 + x$	x

Since K_a is small, x is small, so we assume

$[CH_3COOH] = 0.50 - x \approx 0.50$ *M* and $[CH_3COO^-] = 0.50 + x \approx 0.50$ *M*

$$x = [H_3O^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]} \approx 1.8\times10^{-5} \times \frac{0.50}{0.50} = 1.8\times10^{-5}\ M$$

pH = -log(1.8x10⁻⁵) = 4.74

Checking the assumption:

$$\frac{1.8\times10^{-5}\ M}{0.50\ M} \times 100 = 3.6\times10^{-3}\%$$ (< 5%; assumption is justified.)

(b) $[OH^-]_{added} = \dfrac{0.020 \text{ mol}}{1.0 \text{ L soln}} = 0.020\ M\ OH^-$

Setting up a reaction table for the ***stoichiometry***:

Concentration (*M*)	**$CH_3COOH(aq)$**	**+ $OH^-(aq)$ →**	**$CH_3COO^-(aq)$**	**+ $H_2O(l)$**
Initial	0.50	0.020	0.50	-
Change	−0.020	−0.020	+0.020	-
Equilibrium	0.48	0	0.52	-

Setting up a reaction table for the ***acid dissociation***, using new initial [ ]:

Concentration (*M*)	**$CH_3COOH(aq)$**	**+ $H_2O(l)$ ⇌**	**$CH_3COO^-(aq)$**	**+ $H_3O^+(aq)$**
Initial	0.48	-	0.52	0
Change	$-x$	-	$+x$	$+x$
Equilibrium	$0.48 - x$	-	$0.52 + x$	x

Since K_a is small, x is small, so we assume

$[CH_3COOH] = 0.48 - x \approx 0.48\ M$ and $[CH_3COO^-] = 0.52 + x \approx 0.52\ M$

$$x = [H_3O^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]} \approx 1.8\text{x}10^{-5} \times \frac{0.48}{0.52} = 1.7\text{x}10^{-5}\ M$$

pH = $-\log(1.7\text{x}10^{-5})$ = 4.77

Addition of a small amount of base caused the pH to rise only slightly, from 4.74 to 4.77.

(c) $[H_3O^+]_{added} = \dfrac{0.020 \text{ mol}}{1.0 \text{ L soln}} = 0.020\ M\ H_3O^+$

Setting up a reaction table for the ***stoichiometry***:

Concentration (*M*)	$CH_3COO^-(aq)$	$+\ H_3O^+(aq)$	$\rightarrow CH_3COOH(aq)$	$+\ H_2O(l)$
Initial	0.50	0.020	0.50	-
Change	−0.020	−0.020	+0.020	-
Equilibrium	0.48	0	0.52	-

Setting up a reaction table for the ***acid dissociation***, using new initial [ ]:

Concentration (*M*)	$CH_3COOH(aq)$	$+\ H_2O(l)$	$\rightleftharpoons CH_3COO^-(aq)$	$+\ H_3O^+(aq)$
Initial	0.52	-	0.48	0
Change	$-x$	-	$+x$	$+x$
Equilibrium	$0.52 - x$	-	$0.48 + x$	x

Since K_a is small, x is small, so we assume

$[CH_3COOH] = 0.52 - x \approx 0.52\ M$ and $[CH_3COO^-] = 0.48 + x \approx 0.48\ M$

$$x = [H_3O^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]} \approx 1.8\times10^{-5} \times \frac{0.52}{0.48} = 2.0\times10^{-5}\ M$$

pH = $-\log(2.0\times10^{-5})$ = 4.70

Addition of a small amount of acid caused the pH to drop only slightly, from 4.74 to 4.70.

تمرین:

از مسائل آخر فصل 19 سیلبربرگ، دو مسئله 19-18 و 19-19 را در این زمینه حل کنید.

منبع:

فصل 19 کتاب شیمی عمومی تالیف سیلبربرگ