Acid-Base Equilibria

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- A weak acid solution HF + Salt of conjugate base NaF

$$\mathrm{NaF}\,(s) \longrightarrow \mathrm{Na^+}\,(aq) + \boxed{\mathrm{F^-}\,(aq)}$$

$$\mathrm{HF}(aq) \rightleftharpoons \mathrm{H^+}\,(aq) + \boxed{\mathrm{F^-}\,(aq)}$$

common ion

- Major species HF, Na^+, F^- and H_2O

$$\mathrm{HF}(aq) \longrightarrow \mathrm{H^+}\,(aq) + \mathrm{F^-}\,(aq)$$

Equilibrium shifts away from added component. Less H^+ ion present

Added F- ion from NaF

The ***common ion effect*** is the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance.

The presence of a common ion **suppresses** the ionization of a weak acid or a weak base.

Consider mixture of CH_3COONa (strong electrolyte) and CH_3COOH (weak acid).

$$CH_3COONa\ (s) \longrightarrow Na^+\ (aq) + \boxed{CH_3COO^-\ (aq)}$$

$$CH_3COOH\ (aq) \rightleftharpoons H^+\ (aq) + \boxed{CH_3COO^-\ (aq)}$$

common ion

Example

15.1.a. The equilibrium concentration of H^+ in a solution containing only 1.0 M HF is 2.7×10^{-2} M and the percent dissociation is 2.7%.

b. Calculate $[H^+]$ and the percent dissociation in a solution containing 1.0 M HF ($K_a = 7.2 \times 10^{-4}$) and the 1.0 M NaF.

15.1.a. The equilibrium concentration of H^+ in a solution containing only 1.0 M HF is 2.7x 10^{-2} M and the percent dissociation is 2.7%.

Solution part- a

Calculate the pH of a 1.0 *M* HF solution

$$HF\ (aq) \rightleftharpoons H^+\ (aq) + F^-\ (aq)$$

$$K_a = \frac{[H^+][F^-]}{[HF]} = 7.2 \times 10^{-4}$$

	HF (*aq*) ⇌	**H^+ (*aq*) +**	**F^- (*aq*)**
Initial (*M*)	1.0	0.00	0.00
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$1.0 - x$	x	x

$$K_a = \frac{x^2}{1.0 - x} = 7.2 \times 10^{-4}$$

if $K_a << 1$ then $1.0 - x \approx 1.0$

$$K_a \approx \frac{x^2}{1.0} = 7.2 \times 10^{-4}$$

or $x^2 = 7.2 \times 10^{-4}$

$x = 2.7 \times 10^{-2} = 0.027\ M$

$X = [H^+] = [F^-] = 0.027\ M$

$pH = -\log [H^+] = 1.57$

$$\text{\% dissociation} = \frac{0.027\ M}{1.0\ M} \times 100\% = \boxed{2.7\%}$$

b. Calculate [H^+] and the percent dissociation in a solution containing 1.0 M HF(Ka = 7.2×10^{-4}) and the 1.0 M NaF.

Solution part- b

the pH of a 1.0 *M* HFand the 1.0 M NaF. Solution.

$$HF\ (aq) \rightleftharpoons H^+\ (aq) + F^-\ (aq)$$

$$K_a = \frac{[H^+][F^-]}{[HF]} = 7.2 \times 10^{-4}$$

	$HF\ (aq)$ $\rightleftharpoons$	$H^+\ (aq)$ +	$F^-\ (aq)$
Initial (*M*)	**1.0**	0.00	**1.00** from HF
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	**1.0 - *x***	x	**1.0+x**

$$K_a = 7.2 \times 10^{-4} = \frac{x\ (1.0+x)}{1.0 - x}$$

$K_a << 1$

$1.0 - x \approx 1.0$

$$K_a \approx \frac{(x)\ 1.0}{1.0} = 7.2 \times 10^{-4}$$

***or* $x = 7.2 \times 10^{-4}$**

Compare previous **$x = 0.027\ M$**

b. Calculate $[H^+]$ and the percent dissociation in a solution containing 1.0 M HF($K_a = 7.2 \times 10^{-4}$) and the 1.0 M NaF.

Solution part- b…contd…..

$[H^+] = \boxed{x = 7.2 \times 10^{-4}}$

$[H^+]$ concentration decreases in buffer solutions

Compare previous ***x*** = 2.7×10^{-2} = 0.027 *M*

pH increases in buffer solutions

$\boxed{pH = -\log [H^+] = 3.14}$

Compare previous **pH = 1.57**

$$\% \text{ dissociation} = \frac{[H^+]}{[HF]} \times 100\% = \frac{7.2\times10^{-4}\ M}{1.0\ M} \times 100\% = \mathbf{.072\%}$$

Compare the previous per cent dissociation is **2.7%.**

per cent dissociation decreases in buffer solutions

A ***buffer solution*** is a solution of:

1. **A weak acid or a weak base and**
2. **The salt** of the weak acid or weak base

Both must be present!

A buffer solution has the **ability to resist changes** in pH upon the **addition of small amounts of either acid or base**.

Which of the following are buffer systems?

(a) KF/HF

(b) KBr/HBr,

(c) $Na_2CO_3/NaHCO_3$

Which of the following are buffer systems?
(a) KF/HF (b) KBr/HBr,
(c) $Na_2CO_3/NaHCO_3$

(a) KF is a weak acid and F^- is its conjugate base

buffer solution

(b) HBr is a strong acid

not a buffer solution

(c) CO_3^{2-} is a weak base and HCO_3^- is it conjugate acid

buffer solution

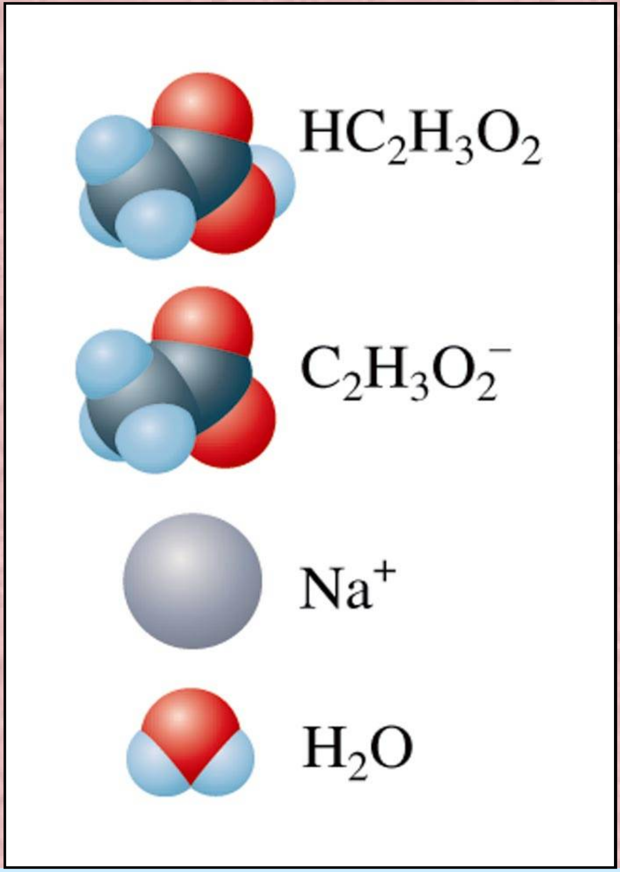
A ***buffer solution*** is a solution of:

1. **A weak acid or a weak base and**
2. **The salt** of the weak acid or weak base

Both must be present!

A buffer solution has the **ability to resist changes** in pH upon the **addition of small amounts of either acid or base.**

Consider an equal molar mixture of CH_3COOH and CH_3COONa



Sample Exercise 15.2

A buffered solution contains 0.50 M acetic acid $K_a = 1.8 \times 10^{-5}$ and 0.50 M sodium acetate $Na_2C_2H_3O_2$. Calculate the **pH** of this solution.

Ex. 15,2. A buffered solution contains 0.50 M acetic acid $K_a = 1.8 \times 10^{-5}$ and 0.50 M sodium acetate $Na_2C_2H_3O_2$. Calculate the pH of this solution.

mixture of salt CH_3COONa **[NaA]** and weak acid CH_3COOH **[HA]** .

$$CH_3COONa(s) \longrightarrow Na^+\ (aq) + CH_3COO^-\ (aq)$$

$$CH_3COOH\ (aq) \rightleftarrows H^+\ (aq) + CH_3COO^-\ (aq)$$

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

$$[H^+] = \frac{K_a\,[HA]}{[A^-]} = \frac{1.8\text{x } 10^{-5}\ [0.50]\ M}{[.50]} = 1.8 \text{ X } 10^{-5}$$

$[H^+] = 1.8 \text{ X } 10^{-5}$ and pH = 4.74

Now let us solve the same using

Henderson-Hasselbalch equation

$$pH = pK_a + \log\frac{[\text{conjugate base}]}{[\text{acid}]}$$

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

$pK_a = -\log K_a$

$$pH = 4.74 + \log\frac{[0.50]}{[0.50]} = 4.74$$

Consider mixture of salt NaA and weak acid HA.

$$\mathrm{NaA}\ (s) \longrightarrow \mathrm{Na^+}\ (aq) + \mathrm{A^-}\ (aq)$$

$$\mathrm{HA}\ (aq) \rightleftarrows \mathrm{H^+}\ (aq) + \mathrm{A^-}\ (aq)$$

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

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

Henderson-Hasselbalch equation

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

$$\mathbf{pH} = \mathrm{p}K_a + \log\frac{[\text{conjugate base}]}{[\text{acid}]}$$

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

or $\mathbf{pH} = \mathrm{p}K_a + \dfrac{[\mathrm{A^-}]}{[\mathrm{HA}]}$

$$\mathbf{p}\boldsymbol{K_a} \mathbf{= -log}\ \boldsymbol{K_a}$$

Experiment -2
Buffers

Objective : To learn how to prepare a buffer solution and to learn how buffers resist change in pH

Introduction : the pH of a buffer can be calculated using:

Henderson-Hasselbalch equation

$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} \quad \text{……………..eqn.1}$$

On the other hand, if the pH is known and the K_a value of the acid is given, the ratio of the [base]/[acid] can be calculating by rearranging the eqn.1

$$\log \frac{[\text{base}]}{[\text{acid}]} = (pH - pK_a) \quad \text{…………..eqn.2}$$

$$\frac{[\text{base}]}{[\text{acid}]} = \text{antilog } (pH - pK_a) \text{…………eqn.3}$$

P-6

Ex.2. A buffered solution contains 0.10 M acetic acid $K_a = 1.8 \times 10^{-5}$ and 0.10 M sodium acetate $Na_2C_2H_3O_2$. Calculate the pH of this solution.

mixture of salt CH_3COONa **[NaA]** and weak acid CH_3COOH **[HA]** .

$$CH_3COONa(s) \longrightarrow Na^+ (aq) + CH_3COO^- (aq)$$

$$CH_3COOH (aq) \rightleftharpoons H^+ (aq) + CH_3COO^- (aq)$$

$[H^+] = 1.8 \times 10^{-5}$ and pH = 4.74

Henderson-Hasselbalch equation

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

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

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

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

$pK_a = -\log K_a$

$$pH = 4.74 + \log \frac{[0.10]}{[0.10]} = \boxed{4.74}$$

Calc for pH = 5 ???

$pH = 4.74 + \mathbf{0.26}$

$\log [A^-]/[HA] = 0.26$

$[A^-]/[HA] = \text{antilog } 0.26$

$= \mathbf{1.82}$

See sample exercise 15.4 p-689 & exercise 15.37 ; 15.38

A ***buffer solution*** is a solution of:

1. **A weak acid or a weak base and**
2. **The salt** of the weak acid or weak base

Both must be present!

A buffer solution has the **ability to resist changes** in pH upon the addition of small amounts of either acid or base.

Consider an equal molar mixture of CH_3COOH and CH_3COONa

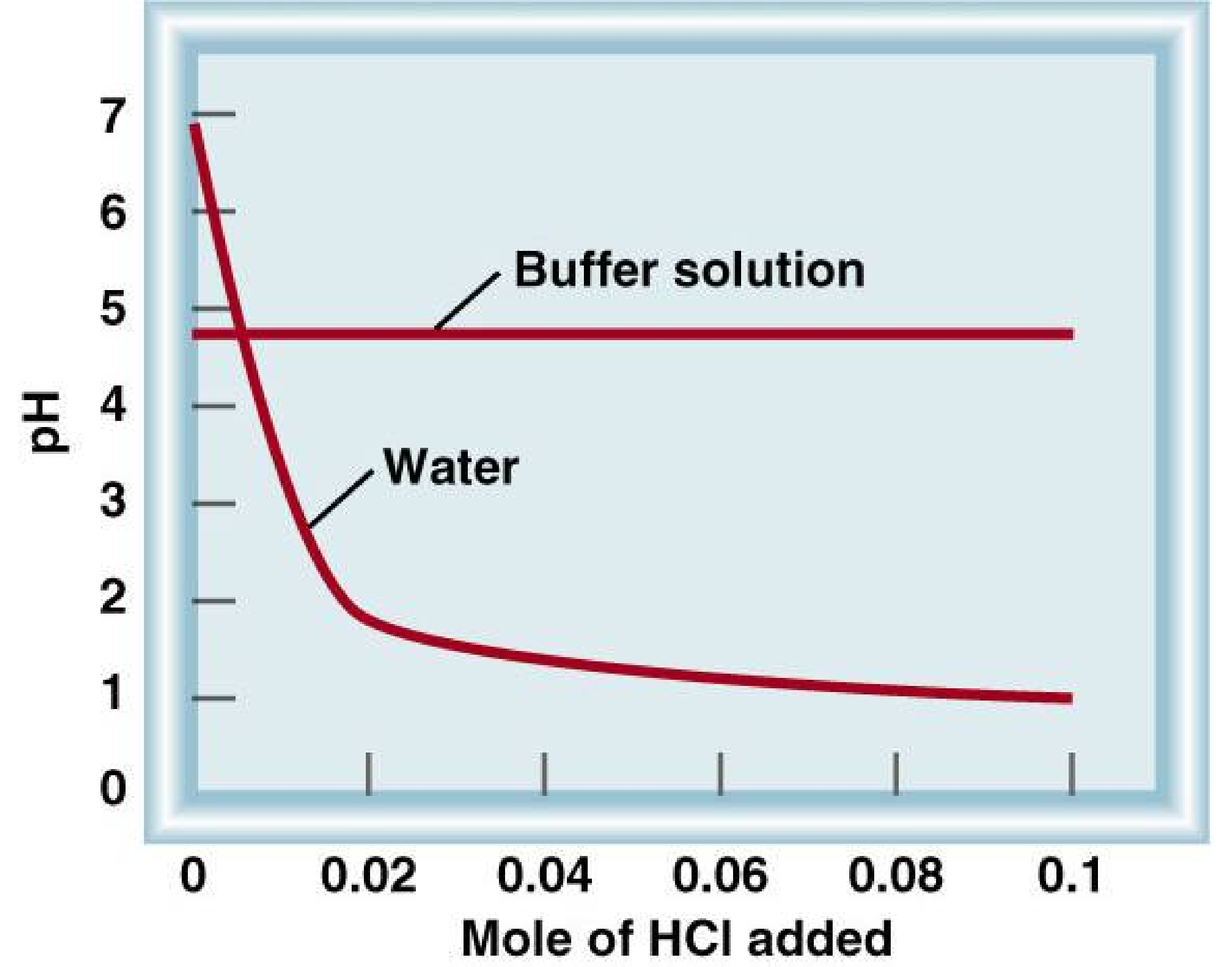
Add strong acid --- will **un-dissociate** some weak acid

$$H^+ (aq) + CH_3COO^- (aq) \longrightarrow CH_3COOH (aq)$$

Add strong base --- will **dissociate** some weak acid

$$OH^- (aq) + CH_3COOH (aq) \longrightarrow CH_3COO^- (aq) + H_2O (l)$$

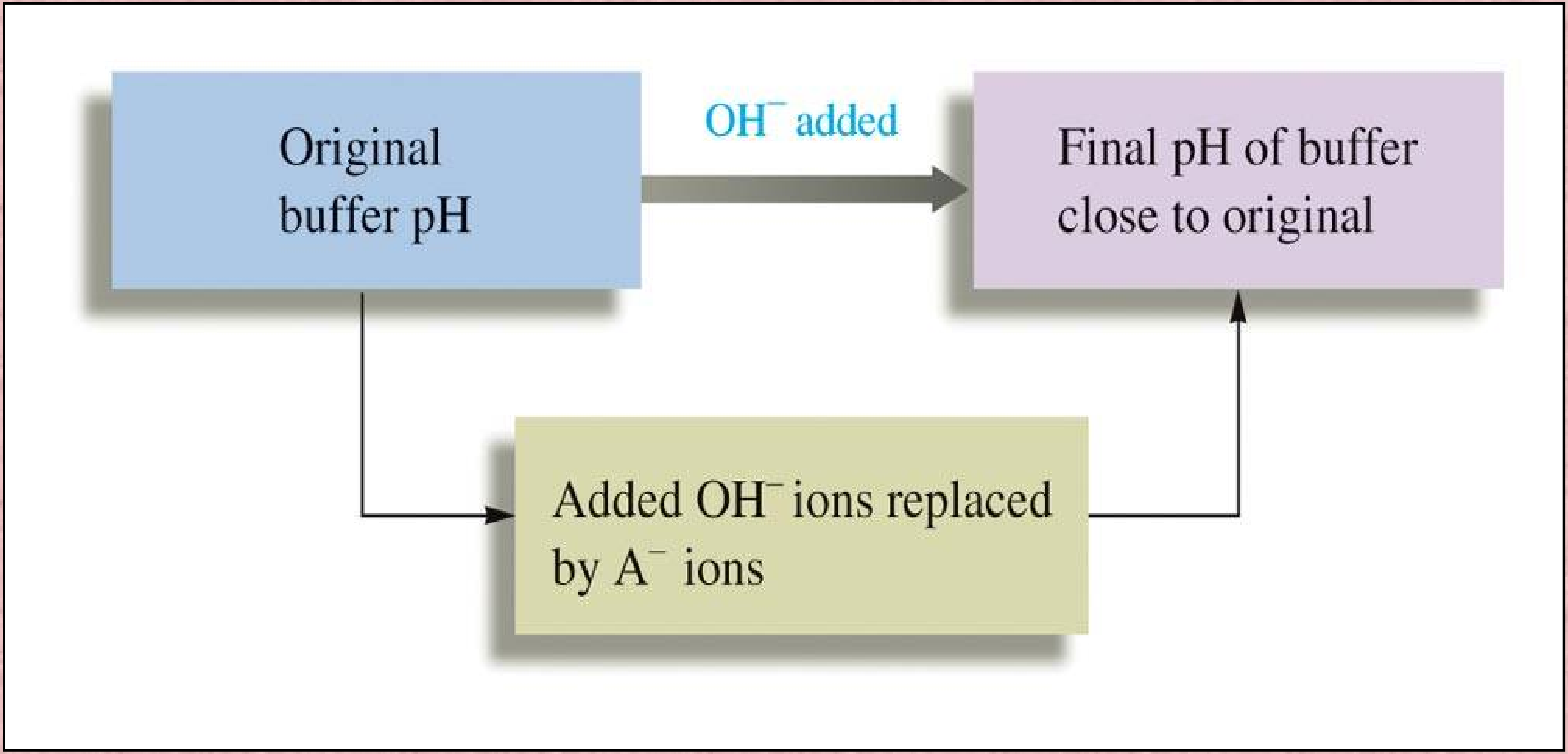
Add strong acid -- $HCl \longrightarrow H^+ + Cl^-$



Add strong acid -- will **un-dissociate** some weak acid

$HCl + CH_3COO^- \longrightarrow CH_3COOH + Cl^-$

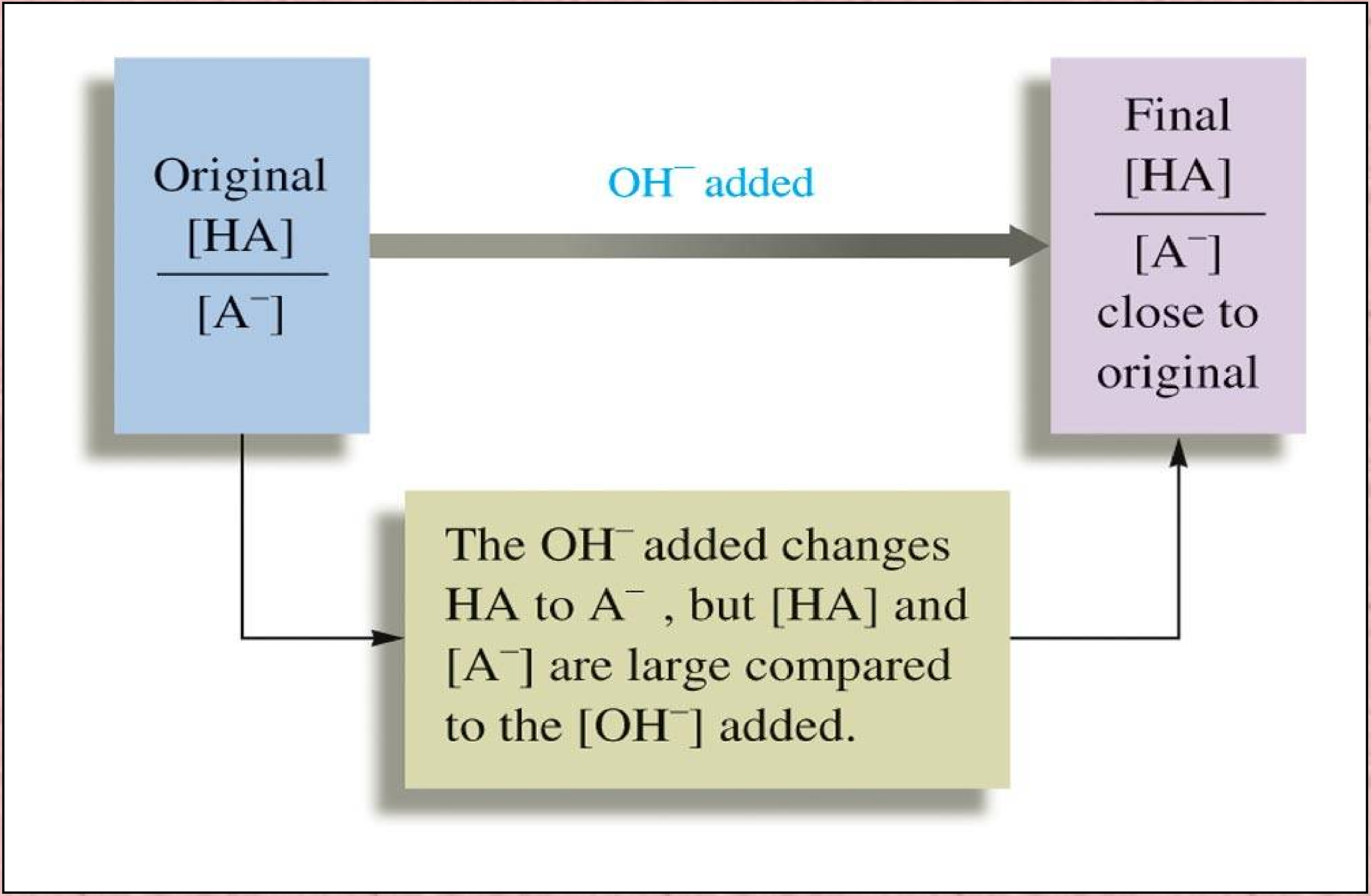
How Buffering Works



Add strong base --- will dissociate some weak acid

$OH^{-}\ (aq) + CH_3COOH\ (aq) \longrightarrow CH_3COO^{-}\ (aq) + H_2O\ (l)$

Buffering Schematic

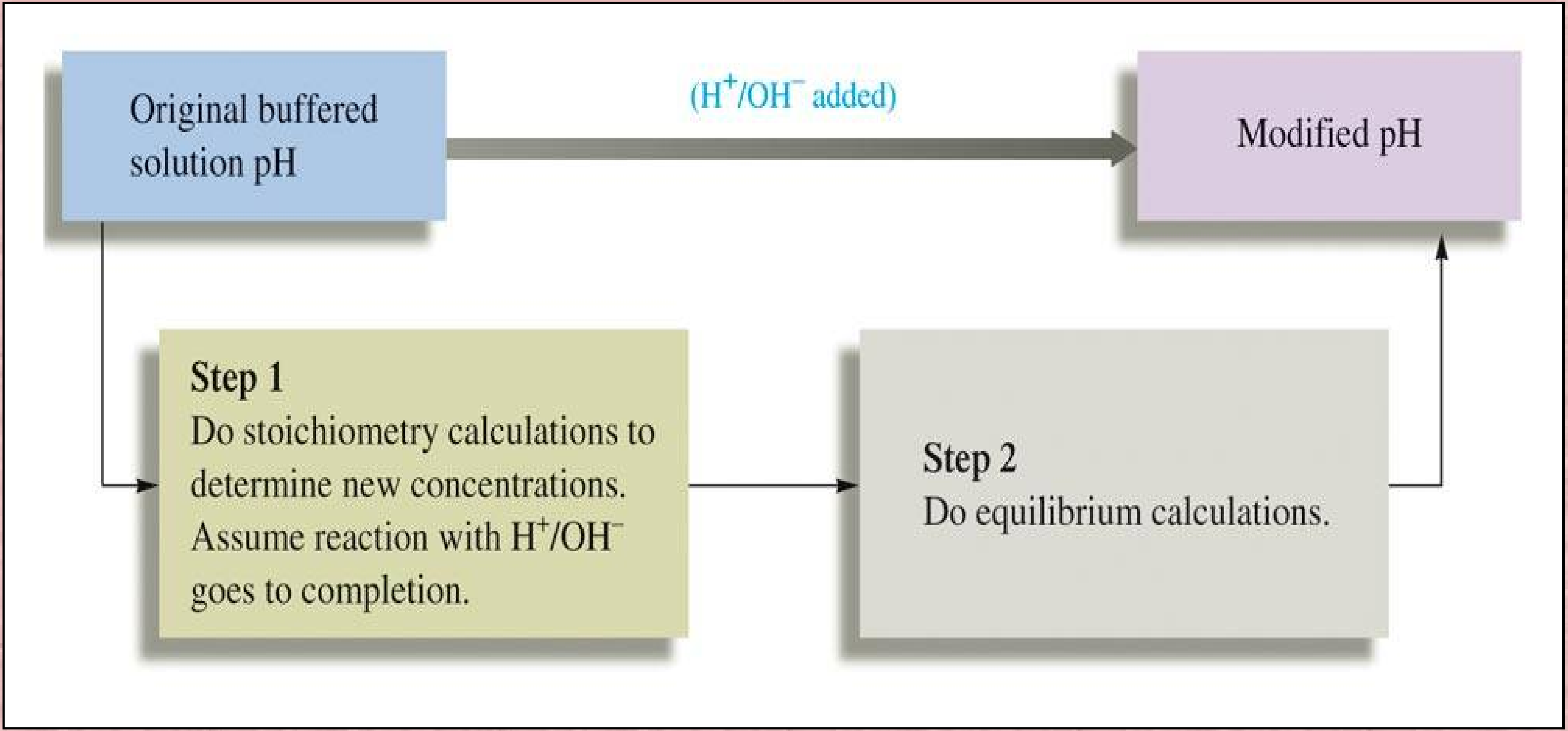


The OH^- added changes HA to A^-, but [HA] and $[A^-]$ are large compared to the $[OH^-]$ added.

Add strong base --- will **dissociate** some weak acid

$OH^- \ (aq) + CH_3COOH \ (aq) \longrightarrow CH_3COO^- \ (aq) + H_2O \ (l)$

Strong Acid or Base Being Added to a Buffered Solution



Original buffered solution pH

(H^+/OH^- added)

Modified pH

Step 1
Do stoichiometry calculations to determine new concentrations. Assume reaction with H^+/OH^- goes to completion.

Step 2
Do equilibrium calculations.

Add strong acid will **un-dissociate** some weak acid

$$\boxed{HCl + CH_3COO^- \longrightarrow CH_3COOH + Cl^-}$$

Ex.15.2. A buffered solution contains 0.50 M acetic acid $K_a = 1.8 \times 10^{-5}$ and 0.50 M sodium acetate $Na_2C_2H_3O_2$. Calculate the pH of this solution.

$$\mathbf{pH} = 4.74 + \log \frac{[0.50]}{[0.50]} = \mathbf{4.74}$$

Sample Exercise 15.3. Calculate the change in pH that occurs when 0.010 mol solid NaOH is added to 1.0 L of the buffered solution. Compare this pH with that which occur when 0.010 mol is added to 1.0 L of water.

solution: The strong base NaOH will completely dissociate. Although acetic acid is a weak acid but OH^- is a such a strong base **that the reaction will proceed to completion** until all OH^- ions are consumed.

$$\mathbf{OH^- (\mathit{aq}) + CH_3COOH (\mathit{aq}) \longrightarrow CH_3COO^- (\mathit{aq}) + H_2O (\mathit{l})}$$

Sample Exercise 15.3 Calculate the change in pH that occurs when 0.010 mol solid NaOH added to 1.0 L of the buffered solution. Compare this pH with that which occur when 0.010 mol is added to 1.0 L of water.

solution: ....that the reaction will proceed to completion until all OH^- ions are consumed.

1) Stoichiometry Problem

$$CH_3COOH\ (aq) + OH^-(aq) \longrightarrow CH_3COO^-\ (aq) + H_2O\ (l)$$

Before Reaction	0.50 mol	0.010 mol	0.50 mol
After reaction	0.50 - 0.010 **= 0.49 mol**	0.010 - 0.010 **= 0 mol**	0.50 + 0.010 **0.51 mol**

Note **that 0.010 mol acetic acid has been converted to**

CH_3COO^- by the added OH^- ions

Sample Exercise 15.3 Calculate the change in pH that occurs when 0.010 mol solid NaOH added to 1.0 L of the buffered solution. Compare this pH with that which occur when 0.010 mol is added to 1.0 L of water.

solution: ....that the reaction will proceed to completion until all OH^- ions are consumed.

2) Equilibrium Problem

The dominant equilibrium involves the dissociation of acetic acid

$$CH_3COOH\ (aq) \longrightarrow H^+(aq) + CH_3COO^-\ (aq)$$

Initial	**0.49 mol**	**0 mol**	**0.51 mol**
Change	-x	+ x	+x
Equilibrium	**0.49-x**	**x**	**0.51 + x**

Then $$K_a = 1.8 \times 10^{-5} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(0.51+x)}{(0.49-x)}$$

$$= \frac{(x)(0.51)}{(0.49)}$$ or

x= 1.73 x 10^{-5} and pH = 4.76

Sample Exercise 15.3 Calculate the change in pH that occurs when 0.010 mol solid NaOH added to 1.0 L of the buffered solution.Compare this pH with that which occur when 0.010 mol is added to 1.0 L of water.

solution: ....that the reaction will proceed to completion until all OH^- ions are consumed.

1) Stoichiometry Problem

$$CH_3COOH\ (aq) + OH^-(aq) \longrightarrow CH_3COO^-\ (aq) + H_2O\ (l)$$

2) Equilibrium Problem

$$\mathbf{CH_3COOH\ (aq) \longrightarrow H^+(aq) + CH_3COO^-\ (aq)}$$

Then

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][\,CH_3COO^-]}{[CH_3COOH]} = \frac{(x)\,(\,0.51+x)}{(0.49-x)}$$

$$= \frac{(x)\,(\,0.51)}{(0.49)}$$ or $x = 1.73 \times 10^{-5}$ and pH = 4.76

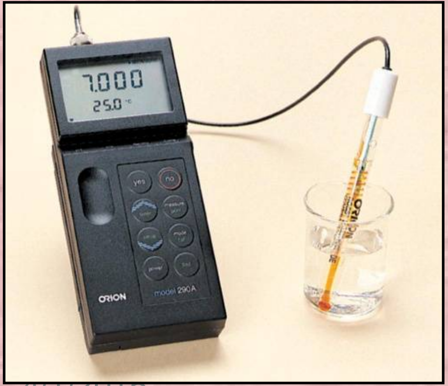
The change in pH by addition of 0.01 M NaOH in the buffered solution is then **4.76 – 4.74 = + 0.02**

Pure Water at pH 7.000. (bottom) When .01 mol NaOH is Added to 1.0L of Pure Water, the pH Jumps to 12.000

Sample Exercise 15.3 Calculate the change in pH that occurs when 0.010 mol solid NaOH added to 1.0 L of the buffered solution. Compare this pH with that which occur when 0.010 mol is added to 1.0 L of water.

……The change in pH by addition of 0.01 M NaOH in the buffered solution is then **4.76 – 4.74 = + 0.02**

Pure Water at pH 7.000. (bottom) When .01 mol NaOH is Added to 1.0L of Pure Water, the pH Jumps to 12.000



$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}}$$

$$= 1.0 \times 10^{-12}$$

pH = 12.00

Thus the change in pH is

12 - 7.00 = + 5.00

new solution **Pure water**

Consider mixture of salt NaA and weak acid HA.

$$\mathrm{NaA}\ (s) \longrightarrow \mathrm{Na}^{+}\ (aq) + \mathrm{A}^{-}\ (aq)$$

$$\mathrm{HA}\ (aq) \rightleftarrows \mathrm{H}^{+}\ (aq) + \mathrm{A}^{-}\ (aq)$$

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

$$[\mathrm{H}^{+}] = \mathrm{K}_{\mathrm{a}} \frac{[\mathrm{HA}]}{[\mathrm{A}^{-}]}$$

Henderson-Hasselbalch equation

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

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

$$\mathbf{pH} = \mathrm{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\text{or}\quad \mathbf{pH} = \mathrm{p}K_a + \frac{[\mathrm{A}^{-}]}{[\mathrm{HA}]}$$

$$\mathbf{p}K_a = -\log K_a$$

What is the pH of a solution containing 0.30 *M* HCOOH and 0.52 *M* HCOOK?

HCOOH $pK_a = 3.77$

Mixture of weak acid and conjugate base!

$$HCOOH\,(aq) \rightleftharpoons H^+\,(aq) + HCOO^-\,(aq)$$

	$HCOOH\,(aq)$	$H^+\,(aq)$	$HCOO^-\,(aq)$
Initial (*M*)	0.30	0.00	0.52
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.30 - x$	x	$0.52 + x$

Common ion effect

$$0.30 - x \approx 0.30$$

$$0.52 + x \approx 0.52$$

$$pH = pK_a + \log \frac{[HCOO^-]}{[HCOOH]}$$

HCOOH $pK_a = 3.77$

$$\mathbf{pH} = 3.77 + \log \frac{[0.52]}{[0.30]} \mathbf{= 4.01}$$

Calculate the pH of the 0.30 *M* NH_3/0.36 *M* NH_4Cl buffer system. What is the pH after the addition of 20.0 mL of 0.050 *M* NaOH to 80.0 mL of the buffer solution?

$$NH_4^+\ (aq) \rightleftharpoons H^+\ (aq) + NH_3\ (aq)$$

$$pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]} \qquad pK_a = 9.25 \qquad \textbf{pH} = 9.25 + \log \frac{[0.30]}{[0.36]} = 9.17$$

start (moles) 0.029 0.001 0.024

$$NH_4^+\ (aq) + OH^-\ (aq) \longrightarrow H_2O\ (l) + NH_3\ (aq)$$

end (moles) 0.028 0.0 0.025

final volume = 80.0 mL + 20.0 mL = 100 mL

$$[NH_4^+] = \frac{0.028}{0.10} \qquad [NH_3] = \frac{0.025}{0.10} \qquad \textbf{pH} = 9.25 + \log \frac{[0.25]}{[0.28]} = 9.20$$

Chemistry In Action: Maintaining the pH of Blood