# M6 Part 1 - buffers

Chemistry - University Preparation (Castlebrooke SS Secondary School)

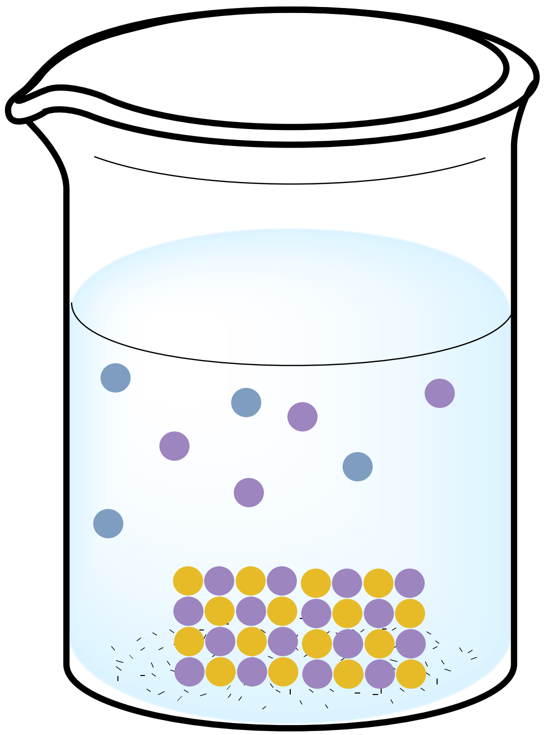
# MODULE 6

## Part 1: Buffer Solutions

# The Common-Ion Effect

Application of Le Chatelier's Principle:

- addition of a **common ion** to an equilibrium will cause it to shift in order to counter-act that addition



$$AgCl\,(s) \leftrightarrows Ag^{+}(aq) + Cl^{-}(aq)$$

**Add NaCl:** $NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$

# The Common-Ion Effect

Buffers are an example of the common ion effect:

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

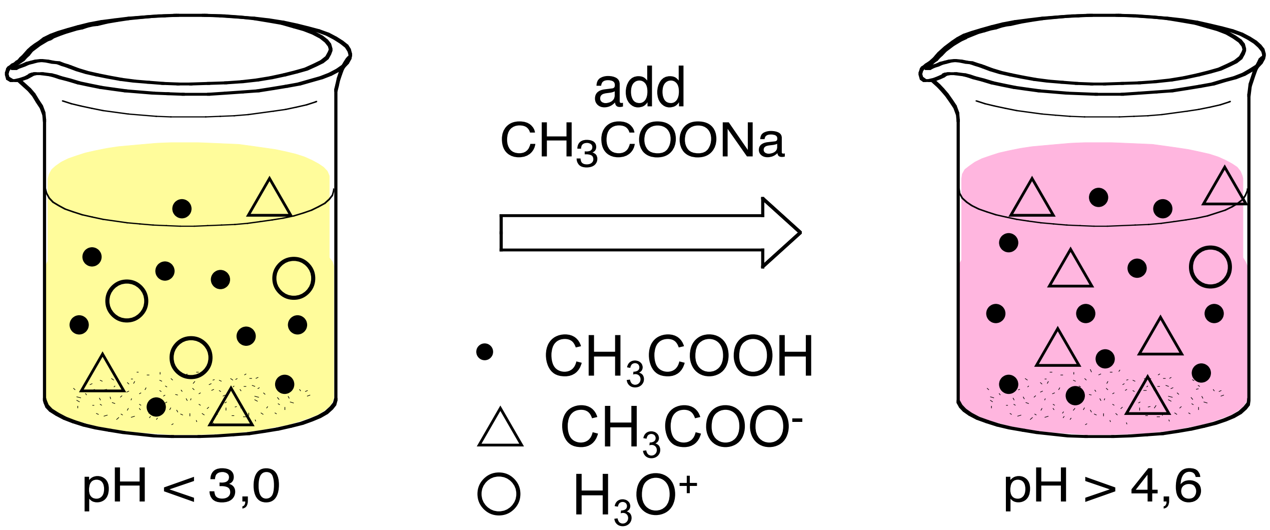
weak acid

conjugate base

If we add a salt of the conjugate base (example = **NaA**), according to Le Chatelier's Principle, the equilibrium will <u>move to the left</u>

- consequence: reduction of the ionization of the weak acid!

| | $CH_3COOH(aq)$ + | $H_2O(l)$ ⇆ | $H_3O^+(aq)$ + | $CH_3COO^-(aq)$ |
|---|---|---|---|---|
| Initial | 12 | – | 0 | 0 |
| Change | –3 | – | +3 | +3 |
| Equilibrium | 9 | – | 3 | 3 |
| Add | | – | | **+5** |
| Initial | 9 | – | 3 | 8 |
| Change | +2 | – | –2 | –2 |
| Equilibrium | 11 | – | 1 | 6 |



# Some real numbers...

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

**TABLE 17.1 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 | $1.3 \times 10^{-3}$ | 2.89 |
| 0.10 | 0.050 | 0.036 | $3.6 \times 10^{-5}$ | 4.44 |
| 0.10 | 0.10 | 0.018 | $1.8 \times 10^{-5}$ | 4.74 |
| 0.10 | 0.15 | 0.012 | $1.2 \times 10^{-5}$ | 4.92 |

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

# Your Turn...

What is the effect on the pH of adding $NH_4Cl$ to a solution of 0.25 M $NH_3(aq)$?

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

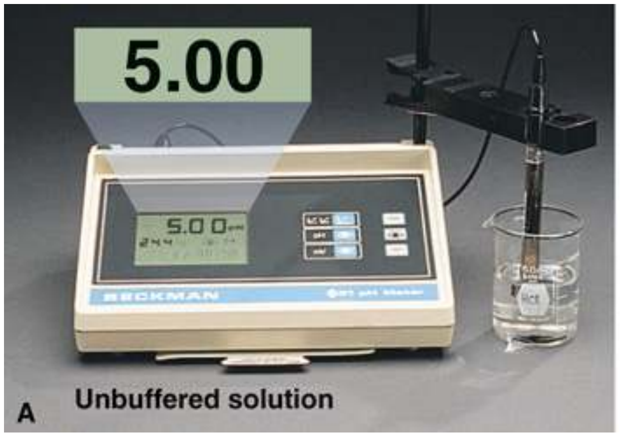
1. the pH will increase
2. the pH will decrease
3. the pH will not change
4. I'm not sure

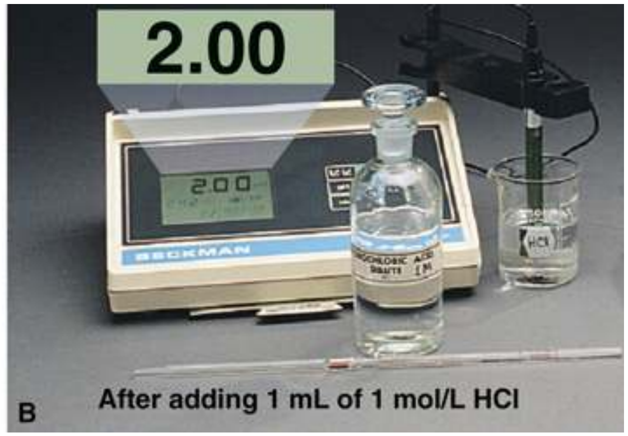
# Buffer Solutions

- The function of a buffer is to resist changes in the pH of a solution when either $H_3O^+$ or $OH^-$ are added
- Buffers are just a special case of the common ion effect

| a weak acid or base | + | the corresponding conjugate salt of that acid or base |
|---|---|---|
| HCN | + | NaCN |
| $NH_3$ | + | $NH_4Cl$ |

# Buffer Solutions







# Buffered Solution Characteristics

- in a buffer solution, the acid and base must not neutralize one another
  - we must therefore use **acid/base conjugate pairs**:

$$HA + A^- \leftrightharpoons A^- + HA \quad \textbf{Identity Reaction}$$

- a buffer contains relatively high amounts of a weak acid and its conjugate base (or vice-versa)
  - if $H_3O^+$ is added, it will react with the **base**
  - if $OH^-$ is added, it will react with the **acid**
- the pH is determined by the **ratio** of the concentrations of the acid and base

# Example: Preparing a buffer solution

What is the pH of a buffer that has [$CH_3COOH$] = 0.700 M and [$CH_3COO^-$] = 0.600 M?

$$CH_3COOH\,(aq) + H_2O \leftrightarrows H_3O^+(aq) + CH_3COO^-\,(aq) \quad K_a = 1.8 \times 10^{-5}$$

$$CH_3CO_2H + H_2O \leftrightarrows H_3O^+ + CH_3CO_2^-$$

| | | | | |
|---|---|---|---|---|
| I | 0.700 | - | 0 | 0.600 |
| C | $-x$ | - | $+x$ | $+x$ |
| E | $0.700 - x$ | - | $x$ | $0.600 + x$ |

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]}$$

# Example: Preparing a buffer solution

What is the pH of a buffer that has $[CH_3COOH] = 0.700$ M and $[CH_3COO^-] = 0.600$ M?

$$CH_3COOH\,(aq) + H_2O \leftrightharpoons H_3O^+(aq) + CH_3COO^-\,(aq) \quad K_a = 1.8 \times 10^{-5}$$

$$1.8 \times 10^{-5} = \frac{(0.600 + x)(x)}{0.700 - x}$$

**ASSUMPTION #2:**

Since $K_a \ll 1$, $x$ is small!

Therefore:

$0.600 + x \approx 0.600$

$0.700 - x \approx 0.700$

$$1.8 \times 10^{-5} = \frac{(0.600)(x)}{0.700}$$

$x = 2.1 \times 10^{-5}$ mol/L ✓

$x = [H_3O^+] = 2.1 \times 10^{-5}$ mol/L → **pH = –log(2.1x10$^{-5}$) = 4.68**

# pH of Buffer Solutions

- Note the key step in the previous calculation:

$$1.8 \times 10^{-5} = \frac{(0.600 + x)(x)}{0.700 - x}$$

$[A^-]_o$

$K_a$

$[HA]_o$

$$K_a = \frac{[H_3O^+]([A^-]_o + x)}{([HA]_o - x)}$$

$x$ is ALWAYS SMALL!

**(Common Ion Effect)**

For buffers, the equation simplifies to: $K_a = \dfrac{[H_3O^+][A^-]_o}{[HA]_o}$

# The Henderson-Hasselbalch Equation

Rearranging this equation for $[H_3O^+]$ gives:

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

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

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

pH

$pK_a$

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

Henderson-Hasselbalch Eqn

# Your Turn…

According to the H-H equation, when [HA] = [A-], the pH is equal to:

1. 1
2. 0
3. -pKa
4. pKa
5. I’m not sure

# The Henderson-Hasselbalch Equation

- buffer solutions are most effective when

**$[HA] \approx [A^-]$**

$$\log\frac{[A^-]}{[HA]} \approx \log(1.0) \approx 0.0$$

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

- therefore, a buffer solution is most effective when **$pH \approx pK_a$**

# The Two Criteria for the HH Equation

1

$$0.1 < \frac{[A^-]}{[HA]} < 10$$

Roughly equal amounts of acid and base

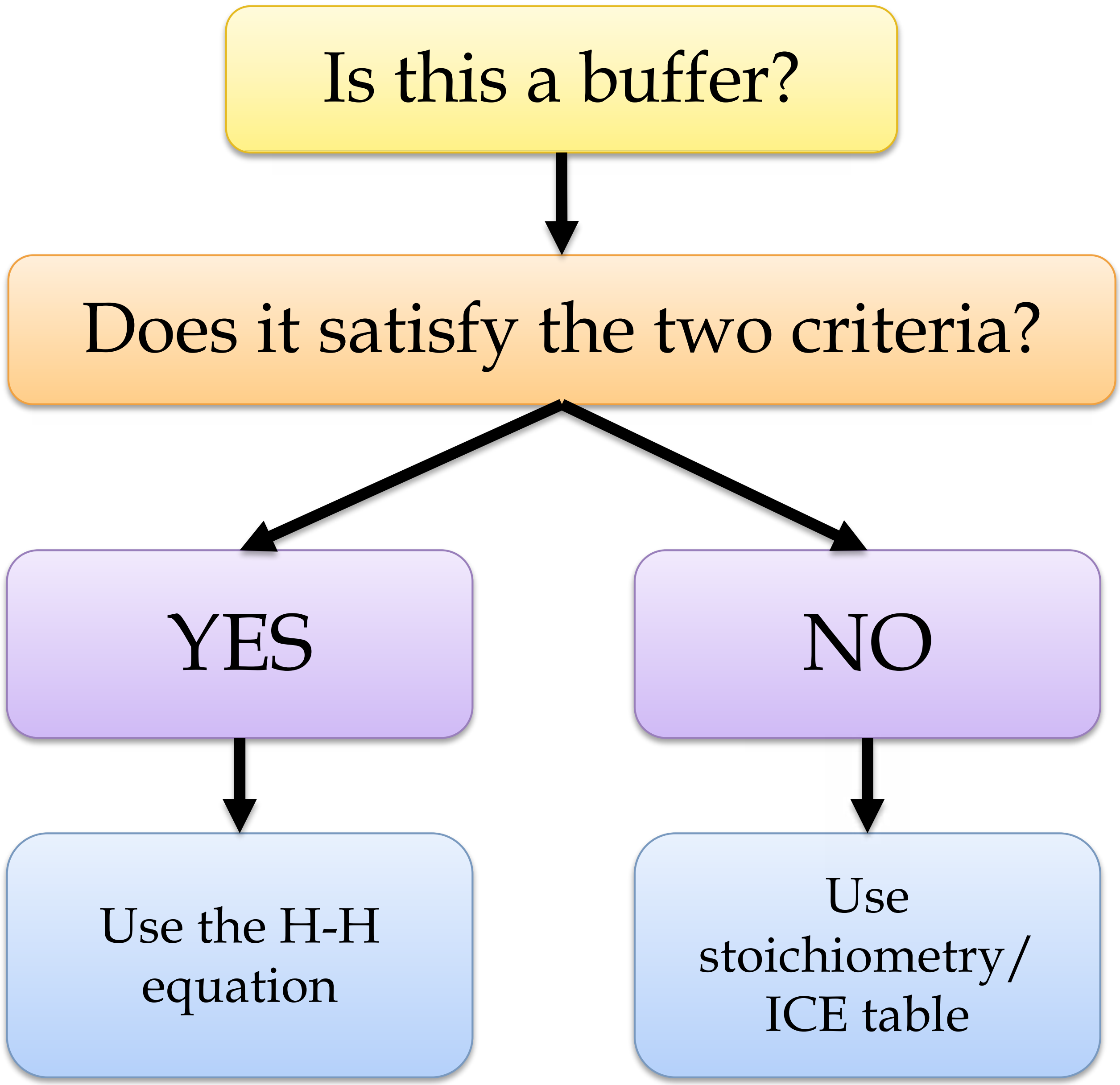
2

$$[A^-] > 100 \times K_a$$

and

$$[HA] > 100 \times K_a$$

Large amounts of acid and base


Is this a buffer?
Does it satisfy the two criteria?
YES
NO
Use the H-H equation
Use stoichiometry/ ICE table

# Example: Using the HH equation

25.0 g of propionic acid ($CH_3CH_2COOH$) and 36.2 g of sodium propionate ($CH_3CH_2COONa$) are mixed in a 1.00 L of solution. What is the pH?

**WANT:** pH = ?

**HAVE:** V = 1.00 L
m HA = 25.0 g    m NaA= 36.2 g

**NEED:** $K_a = 1.30 \times 10^{-5}$
MM of HA = 74.1 g/mol    MM of NaA = 96.1 g/mol

$$? \frac{\text{mol HA}}{\text{L}} = \frac{25.0\text{ g HA}}{1.00\text{ L}} \times \frac{\text{mol HA}}{74.1\text{ g HA}} = 0.337\text{ mol/L}$$

$$? \frac{\text{mol A}^-}{\text{L}} = \frac{36.2\text{ g NaA}}{1.00\text{ L}} \times \frac{\text{mol NaA}}{96.1\text{ g NaA}} \times \frac{1\text{ mol A}^-}{1\text{ mol NaA}} = 0.377\text{ mol/L}$$

# Example: Using the HH equation

25.0 g of propionic acid ($CH_3CH_2COOH$) and 36.2 g of sodium propionate ($CH_3CH_2COONa$) are mixed in a 1.00 L of solution. What is the pH?

<u>Is this a buffer?</u>

1 $$0.1 < \frac{[A^-]}{[HA]} < 10$$

2 $$[HA] \text{ and } [A^-] > 100 \times K_a$$

$$= 1.12$$

$$10^{-1}\text{ M} >> 10^{-5}$$

# Example: Using the HH equation

25.0 g of propionic acid ($CH_3CH_2COOH$) and 36.2 g of sodium propionate ($CH_3CH_2COONa$) are mixed in a 1.00 L of solution. What is the pH?

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

$$= -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.377}{0.337}\right)$$

$$= 4.89 + 0.0487$$

$$= 4.94$$

# Your Turn…

Without using a calculator, which of the following HA/$A^-$ buffers has the lowest pH?

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \qquad K_a = 4.8 \times 10^{-5}$$

1. 0.100 M HA / 0.200 M $A^-$
2. 0.200 M HA / 0.200 M $A^-$
3. 0.200 M HA / 0.100 M $A^-$
4. I'm not sure

# 6 ways to make a buffer…

**1** Weak acid (HA)

Titrate with NaOH
$HA + OH^- \longrightarrow A^- + H_2O$
to adjust
$\frac{[HA]}{[A^-]}$
to give

**2** Weak acid (HA) and salt (NaA)

Mix HA and $A^-$ to give

**3** Salt of weak acid (NaA)

Titrate with HCl
$A^- + H^+ \longrightarrow HA$
to adjust
$\frac{[HA]}{[A^-]}$
to give

**Desired pH**

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

$$[H_3O^+] = K_a\frac{[BH^+]}{[B]} = \frac{K_w}{K_b}\frac{[BH^+]}{[B]}$$

**4** Weak base (B)

Titrate with HCl
$B + H^+ \longrightarrow BH^+$
to adjust
$\frac{[BH^+]}{[B]}$
to give

**5** Weak base (B) and salt (BHCl)

Mix B and $BH^+$
to give

**6** Salt of weak base (BHCl)

Titrate with NaOH
$BH^+ + OH^- \longrightarrow B + H_2O$
to adjust
$\frac{[BH^+]}{[B]}$
to give

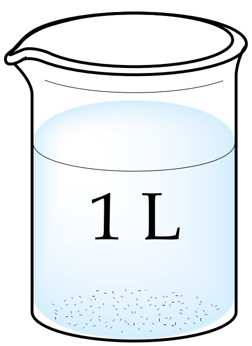
## ACIDIC = HA & $A^-$

- high [HA] and [$A^-$]
- [HA] ~ [$A^-$]

2

Weak acid (HA) and salt (NaA)

Mix HA and $A^-$ to give




0.1 mol HCN
0.1 mol NaCN

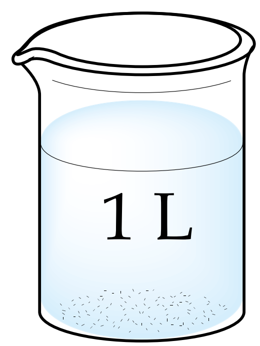
## BASIC = B & $HB^+$

- high [B] and [$HB^+$]
- [B] ~ [$HB^+$]

Weak base (B) and salt (BHCl)

Mix B and $BH^+$ to give

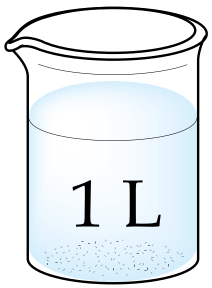
5




0.1 mol $NH_3$
0.1 mol $NH_4Cl$

# ACIDIC = HA & $A^-$

What if we have HA but no NaA?




0.2 mol HCN
0.1 mol NaOH

| | HCN | + $OH^-$ → | $CN^-$ + | $H_2O$ |
|---|---|---|---|---|
| BEFORE | 0.2 M | 0.1 M | 0 | – |
| AFTER | 0.1 M | 0 | 0.1 M | – |

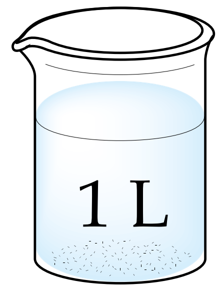
1

Weak acid (HA)

Titrate with NaOH
$HA + OH^- \longrightarrow A^- + H_2O$
to adjust
$$\frac{[HA]}{[A^-]}$$
to give

# BASIC = B & $HB^+$

What if we have B but no HBCl?




0.2 mol $NH_3$
0.1 mol HCl

| | $NH_3$ | + $H_3O^+$ → | $NH_4^+$ + | $H_2O$ |
|---|---|---|---|---|
| BEFORE | 0.2 M | 0.1 M | 0 | – |
| AFTER | 0.1 M | 0 | 0.1 M | – |

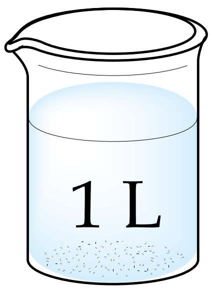
Weak base (B)

Titrate with HCl
$B + H^+ \longrightarrow BH^+$
to adjust
$$\frac{[BH^+]}{[B]}$$
to give

4

# ACIDIC = HA & $A^-$

What if we have NaA but no HA?




0.2 mol NaCN
0.1 mol HCl

| | $CN^-$ + | $H_3O^+$ → | HCN + | $H_2O$ |
|---|---|---|---|---|
| BEFORE | 0.2 M | 0.1 M | 0 | – |
| AFTER | 0.1 M | 0 | 0.1 M | – |

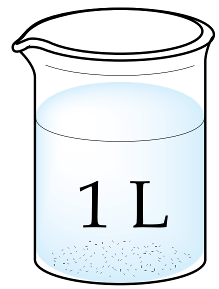
3

**Salt of weak acid (NaA)**

Titrate with HCl
$A^- + H^+ \longrightarrow HA$
to adjust
$\frac{[HA]}{[A^-]}$
to give

# BASIC = B & $HB^+$

What if we have HBCl but no B?




0.2 mol $NH_4Cl$
0.1 mol NaOH

| | $NH_4^+$ + | $OH^-$ → | $NH_3$ + | $H_2O$ |
|---|---|---|---|---|
| BEFORE | 0.2 M | 0.1 M | 0 | – |
| AFTER | 0.1 M | 0 | 0.1 M | – |

**Salt of weak base (BHCl)**

Titrate with NaOH
$BH^+ + OH^- \longrightarrow B + H_2O$
to adjust
$\frac{[BH^+]}{[B]}$
to give

6

# How do buffers work?

- now we know how to make a buffer, but how exactly do they maintain pH?

**1. neutralize external sources of acid or base**

**2. maintain a roughly constant ratio of [HA]/[A$^-$]**

# Module 5 Acid-Base Equilibria

- **IONIZATION:**

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

$$B\,(aq) + H_2O\,(l) \leftrightarrows HB^+\,(aq) + OH^-\,(aq)$$

- **HYDROLYSIS:**

$$A^-\,(aq) + H_2O\,(l) \leftrightarrows HA\,(aq) + OH^-\,(aq)$$

$$HB^+\,(aq) + H_2O\,(l) \leftrightarrows H_3O^+\,(aq) + B\,(aq)$$

**WATER IS ALWAYS A REACTANT → EQUILIBRIA!**

# Acid-Base Neutralization

Buffers protect against externally added $H_3O^+$ or $OH^-$ *via* **NEUTRALIZATION** reactions:

- **ACIDIC BUFFER:**

$$HA\ (aq) + OH^-\ (aq) \rightarrow A^-\ (aq) + H_2O\ (l)$$

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

- **BASIC BUFFER:**

$$HB^+\ (aq) + OH^-\ (aq) \rightarrow B\ (aq) + H_2O\ (l)$$

$$B\ (aq) + H_3O^+\ (aq) \rightarrow HB^+\ (aq) + H_2O\ (l)$$

**WATER IS A PRODUCT → NOT EQUILIBRIA!**

# Acid-Base Neutralizations

**Why is there a 'one-way' arrow?**

1 $HA\,(aq) + H_2O\,(l) \leftrightarrows H_3O^+\,(aq) + A^-\,(aq)$ $K_a = 1.0\text{x}10^{-5}$

2 $2\,H_2O\,(l) \leftrightarrows H_3O^+\,(aq) + OH^-\,(aq)$ $K_W = 1.0\text{x}10^{-14}$

3 = rev of 2

$H_3O^+\,(aq) + OH^-\,(aq) \leftrightarrows 2\,H_2O\,(l)$ $K' = 1/K_W = 1.0\text{x}10^{14}$

4 = 1 + 3

$HA\,(aq) + OH^-\,(aq) \leftrightarrows A^-\,(aq) + H_2O\,(l)$

$K_{overall} = K_a \times K' = 1.0\text{x}10^9$

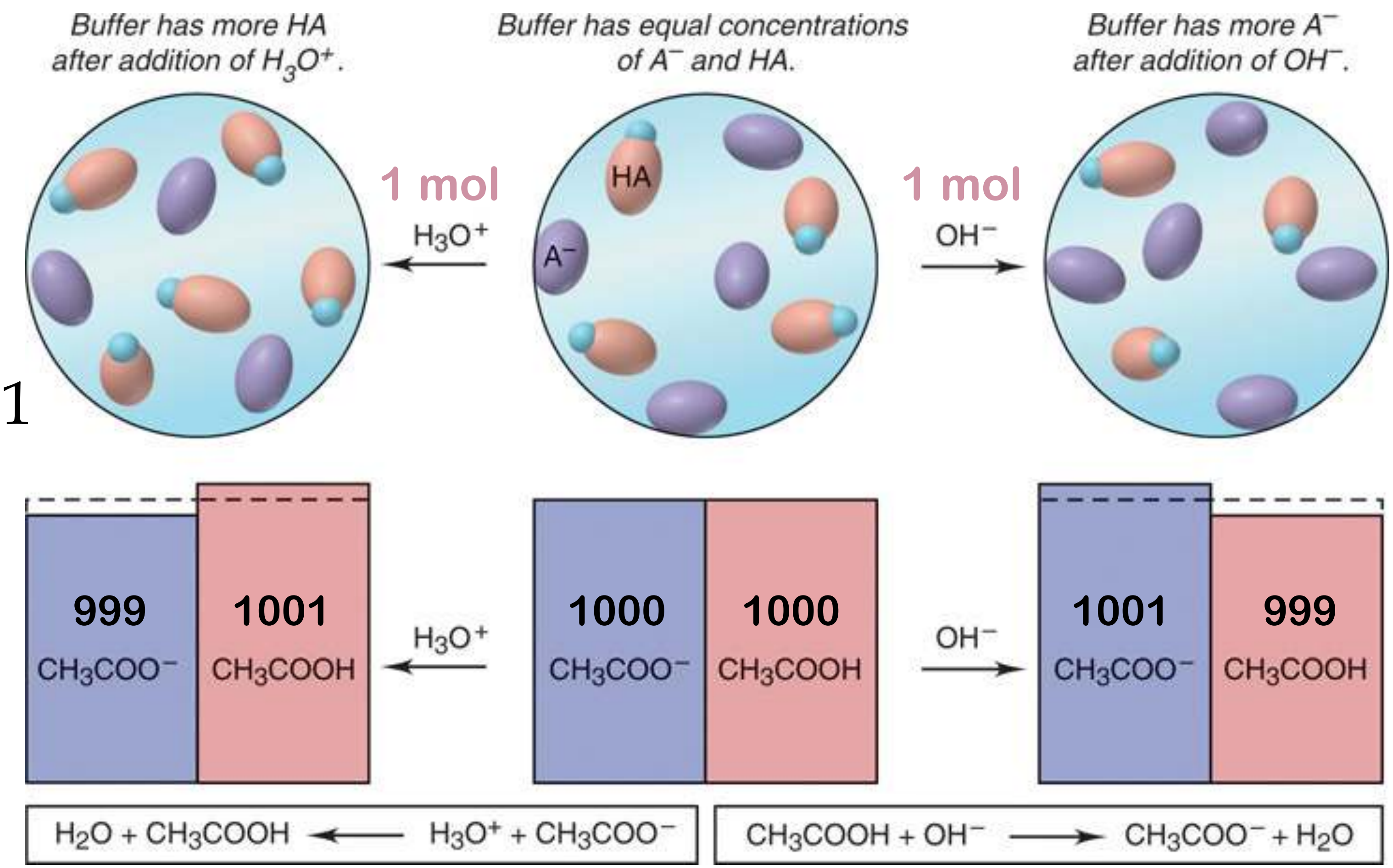
# Why Does Buffering Work?

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

$$\frac{[HA]_o}{[A^-]_o} = 1$$

$$[H_3O^+] \propto \frac{[HA]_o}{[A^-]_o}$$

$$\frac{[HA]_o}{[A^-]_o} \approx 1$$



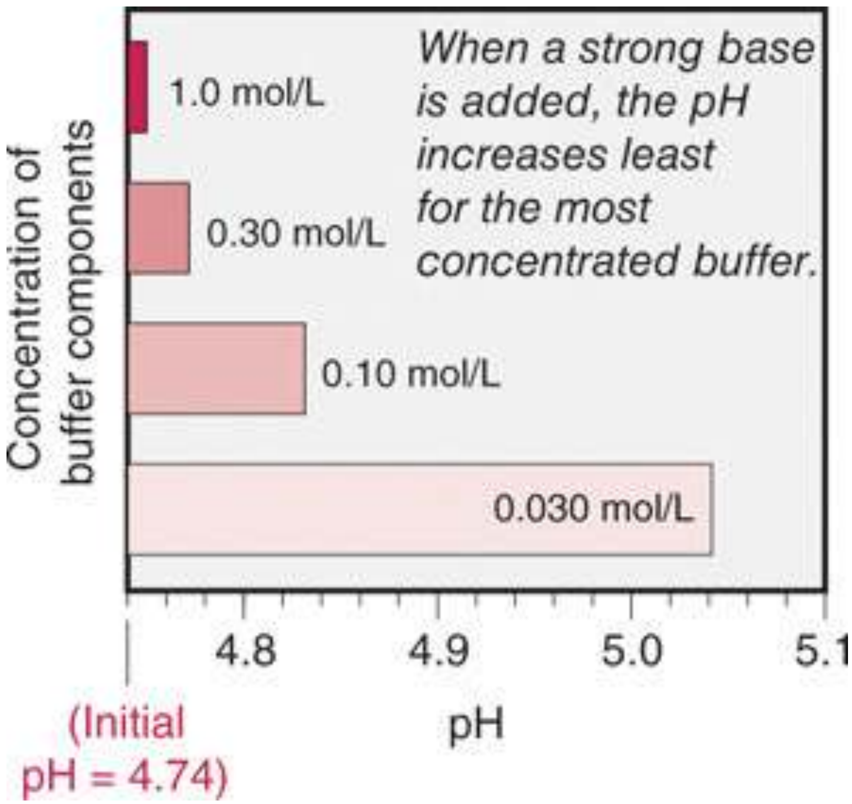

$$\frac{[HA]_o}{[A^-]_o} \approx 1$$

# Buffer Capacity

- **Buffer capacity** is the amount of acid or base that a buffer can neutralize before its pH changes appreciably.
  - Maximum buffer capacity exists when [HA] and [A-] are large and approximately equal to each other.

# Buffer Capacity Illustrated

## 4 different $CH_3COOH/CH_3COO^-$ buffers:




- All 4 have $[HA]_o = [A^-]_o$
- All 4 have the same initial pH = pKa

<u>Add 0.010 mol/L NaOH:</u>

- Top buffer changes by 1%
- Bottom buffer changes by 33%!

# Buffer Range

- **Buffer range** is the pH range over which a buffer effectively neutralizes added acids and bases.

$$0.1 < \frac{[A^-]}{[HA]} < 10$$

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

$$\frac{[A^-]}{[HA]} = 0.1 \qquad \frac{[A^-]}{[HA]} = 1 \qquad \frac{[A^-]}{[HA]} = 10$$

# Buffer Range

- **Buffer range** is the pH range over which a buffer effectively neutralizes added acids and bases.

$$0.1 < \frac{[A^-]}{[HA]} < 10$$

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

$$pH = pK_a - 1$$

$$pH = pK_a + 1$$

$$pH = pK_a \pm 1$$

# Example: Working with Buffers

A buffer contains 0.131 M acetic acid and 0.153 M acetate.

a) What is the pH of the buffer?

b) 10.0 mL of 1.00 M HBr is added to 500 mL of the buffer. What is the new pH?

c) 70.0 mL of 1.00 M NaOH is added to 500 mL of the buffer. What is the new pH?

a)

**WANT:** pH = ?

**HAVE:** [HA] = 0.131 M

$[A^-] = 0.153$ M

$K_a = 1.8 \times 10^{-5}$

1 $$0.1 < \frac{[A^-]}{[HA]} < 10$$

**= 1.17**

2 [HA] and $[A^-]$ $> 100 \times K_a$

**$10^{-1}$ M >> $10^{-5}$**

# Example: Working with Buffers

A buffer contains 0.131 M acetic acid and 0.153 M acetate.

a) What is the pH of the buffer?

b) 10.0 mL of 1.00 M HBr is added to 500 mL of the buffer. What is the new pH?

c) 70.0 mL of 1.00 M NaOH is added to 500 mL of the buffer. What is the new pH?

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

$$= -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.153}{0.131}\right)$$

$$= 4.74 + 0.067$$

$$= 4.81$$

# Example: Working with Buffers

A buffer contains 0.131 M acetic acid and 0.153 M acetate.

a) What is the pH of the buffer?

b) 10.0 mL of 1.00 M HBr is added to 500 mL of the buffer. What is the new pH?

c) 70.0 mL of 1.00 M NaOH is added to 500 mL of the buffer. What is the new pH?

b) We have a choice: **WORK IN MOLES** **WORK IN CONCENTRATIONS**

$$? \text{ mol HA} = 0.500 \text{ L} \times \frac{0.131 \text{ mol}}{\text{L}} = 0.0655 \text{ mol}$$

$$? \text{ mol A}^{-} = 0.500 \text{ L} \times \frac{0.153 \text{ mol}}{\text{L}} = 0.0765 \text{ mol}$$

$$? \text{ mol H}_3\text{O}^{+} \text{ added} = 0.0100 \text{ L} \times \frac{1.00 \text{ mol}}{\text{L}} = 0.0100 \text{ mol}$$

# Example: Working with Buffers

A buffer contains 0.131 M acetic acid and 0.153 M acetate.

a) What is the pH of the buffer?
b) 10.0 mL of 1.00 M HBr is added to 500 mL of the buffer. What is the new pH?
c) 70.0 mL of 1.00 M NaOH is added to 500 mL of the buffer. What is the new pH?

b) We use a 'BAMA' table to keep track of the neutralization:

| | $A^-$ + | $H_3O^+$ → | HA + | $H_2O$ |
|---|---|---|---|---|
| **BEFORE** | 0.0765 | | 0.0655 | – |
| **ADDITION** | | 0.0100 | | – |
| **MODIFICATION** | –0.0100 | –0.0100 | +0.0100 | – |
| **AFTER** | 0.0665 | 0 | 0.0755 | – |

# Example: Working with Buffers

A buffer contains 0.131 M acetic acid and 0.153 M acetate.

a) What is the pH of the buffer?
b) 10.0 mL of 1.00 M HBr is added to 500 mL of the buffer. What is the new pH?
c) 70.0 mL of 1.00 M NaOH is added to 500 mL of the buffer. What is the new pH?

b) $V_{total} = 0.500\text{ L} + 0.0100\text{ L} = 0.510\text{ L}$

mol HA = 0.0755 mol → $[HA] = 0.0755\text{ mol}/0.510\text{ L} = \mathbf{0.148\ M}$

mol $A^-$ = 0.0665 mol → $[A^-] = 0.0665\text{ mol}/0.510\text{ L} = \mathbf{0.130\ M}$

***IS THIS STILL A BUFFER?***

# Example: Working with Buffers

A buffer contains 0.131 M acetic acid and 0.153 M acetate.

a) What is the pH of the buffer?
b) 10.0 mL of 1.00 M HBr is added to 500 mL of the buffer. What is the new pH?
c) 70.0 mL of 1.00 M NaOH is added to 500 mL of the buffer. What is the new pH?

b)

1 $$0.1 < \frac{[A^-]}{[HA]} < 10$$

$= 0.878$

2 [HA] and [$A^-$] $> 100 \times K_a$

$10^{-1}$ M >> $10^{-5}$

# Example: Working with Buffers

A buffer contains 0.131 M acetic acid and 0.153 M acetate.

a) What is the pH of the buffer?

b) 10.0 mL of 1.00 M HBr is added to 500 mL of the buffer. What is the new pH?

c) 70.0 mL of 1.00 M NaOH is added to 500 mL of the buffer. What is the new pH?

b)

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

$$= -\log(1.8\times10^{-5}) + \log\left(\frac{0.130}{0.148}\right)$$

$$= 4.74 - 0.056$$

$$= 4.68$$

initial pH = 4.81 → added HBr → new pH = 4.68 → ΔpH = –0.13

# Example: Working with Buffers

A buffer contains 0.131 M acetic acid and 0.153 M acetate.

c) 70.0 mL of 1.00 M NaOH is added to 500 mL of the buffer. What is the new pH?

We have a choice: **WORK IN MOLES** **WORK IN CONCENTRATIONS**

$$V_{total} = 0.500\ \text{L} + 0.0700\ \text{L} = 0.570\ \text{L} \qquad C_2 = \frac{C_1V_1}{V_2}$$

$$?\ \frac{\text{mol HA}}{\text{L}} = \frac{(0.131\ \text{M})(0.500\ \text{L})}{(0.570\ \text{L})} = 0.115\ \text{M}$$

$$?\ \frac{\text{mol A}^-}{\text{L}} = \frac{(0.153\ \text{M})(0.500\ \text{L})}{(0.570\ \text{L})} = 0.134\ \text{M}$$

$$?\ \frac{\text{mol OH}^-\ \text{added}}{\text{L}} = \frac{(1.00\ \text{M})(0.0700\ \text{L})}{(0.570\ \text{L})} = 0.122\ \text{M}$$

# Example: Working with Buffers

A buffer contains 0.131 M acetic acid and 0.153 M acetate.

c) 70.0 mL of 1.00 M NaOH is added to 500 mL of the buffer. What is the new pH?

We use a 'BAMA' table to keep track of the neutralization:

| | HA | + $OH^-$ | → $A^-$ | + $H_2O$ |
|---|---|---|---|---|
| **BEFORE** | 0.115 | | 0.134 | – |
| **ADDITION** | | 0.122 | | – |
| **MODIFICATION** | –0.115 | –0.115 | +0.115 | – |
| **AFTER** | 0 | 0.007 | 0.249 | – |

# Example: Working with Buffers

A buffer contains 0.131 M acetic acid and 0.153 M acetate.

c) 70.0 mL of 1.00 M NaOH is added to 500 mL of the buffer. What is the new pH?

$[OH^-]$ leftover = **0.007 M** — ***STRONG BASE, BUT LOWER CONC'N***

$[A^-]$ = **0.249 M** — ***WEAK BASE, BUT HIGHER CONC'N***

What's more important?

**STRENGTH (QUALITY)**

**CONCENTRATION (QUANTITY)**

# Example: Working with Buffers

A buffer contains 0.131 M acetic acid and 0.153 M acetate.

c) 70.0 mL of 1.00 M NaOH is added to 500 mL of the buffer. What is the new pH?

How much of 0.249 M $A^-$ hydrolyzes in the presence of 0.007 M $OH^-$?

| | $A^-$ | + $H_2O$ | $\leftrightarrows$ HA | + $OH^-$ |
|---|---|---|---|---|
| I | 0.249 | - | 0 | 0.007 |
| C | $-x$ | - | $+x$ | $+x$ |
| E | $0.249 - x$ | - | $x$ | $0.007 + x$ |

$$K_b = \frac{K_W}{K_a} = \frac{1.0\text{x}10^{-14}}{1.8\text{x}10^{-5}} = 5.6 \times 10^{-10}$$

# Example: Working with Buffers

A buffer contains 0.131 M acetic acid and 0.153 M acetate.

c) 70.0 mL of 1.00 M NaOH is added to 500 mL of the buffer. What is the new pH?

How much of 0.249 M $A^-$ hydrolyzes in the presence of 0.007 M $OH^-$?

$$5.6 \times 10^{-10} = \frac{(x)(0.007 + x)}{0.249 - x}$$

**ASSUMPTION**

Since $K_b << 1$, $x$ is small!

$$5.6 \times 10^{-10} = \frac{(x)(0.007)}{0.249}$$

$$x = 2.0 \times 10^{-8} \text{ mol/L}$$

# Example: Working with Buffers

A buffer contains 0.131 M acetic acid and 0.153 M acetate.

c) 70.0 mL of 1.00 M NaOH is added to 500 mL of the buffer. What is the new pH?

How much of 0.249 M $A^-$ hydrolyzes in the presence of 0.007 M $OH^-$?

| | $A^-$ + | $H_2O$ ⇆ | HA + | $OH^-$ |
|---|---|---|---|---|
| I | 0.249 | - | 0 | 0.007 |
| C | $-x$ | - | $+x$ | $+x$ |
| E | $0.249 - x$ | - | $x$ | $0.007 + x$ |

# Example: Working with Buffers

A buffer contains 0.131 M acetic acid and 0.153 M acetate.

c) 70.0 mL of 1.00 M NaOH is added to 500 mL of the buffer. What is the new pH?

$$[OH^-]_{eq} = 0.0070 + x = 0.0070 + 2.0 \times 10^{-5}\ mol/L$$

$$= 0.0070\ M$$

What's more important?

**STRENGTH (QUALITY)**

**CONCENTRATION (QUANTITY)**

# Example: Working with Buffers

A buffer contains 0.131 M acetic acid and 0.153 M acetate.

c) 70.0 mL of 1.00 M NaOH is added to 500 mL of the buffer. What is the new pH?

We use a 'BAMA' table to keep track of the neutralization:

| | HA | + $OH^-$ | → $A^-$ | + $H_2O$ |
|---|---|---|---|---|
| BEFORE | 0.115 | | 0.134 | – |
| ADDITION | | 0.122 | | – |
| MODIFICATION | –0.115 | –0.115 | +0.115 | – |
| AFTER | 0 | 0.007 | 0.249 | – |

EXCEEDED THE BUFFER CAPACITY !

$$pOH = -\log(0.007) = 2.2$$

$$pH = 14 - 2.2 = 11.8$$

# Buffer Solutions

1. Common Ion Effect
2. Buffer solutions
3. The Henderson-Hasselbalch Equation

# Cumulative Problem: Preparing buffers

Your lab TA asks you to prepare a buffer solution with a pH of 7.40. The following reagents are all available to you:

- 550 mL of 0.200 M $HCOOH$
- 450 mL of 0.200 M $HOCl$
- solid $NaHCOO$
- solid $NaOCl$

a) Which 2 ingredients will you use to prepare the desired buffer?
b) What is the base/acid ratio in the desired buffer?
c) What mass (in g) of solid base must you dissolve in the corresponding acid solution to achieve the desired buffer pH?
d) If 1.00 mL of 1.00 M $NaOH$ is added to the buffer solution, what will be the new pH?