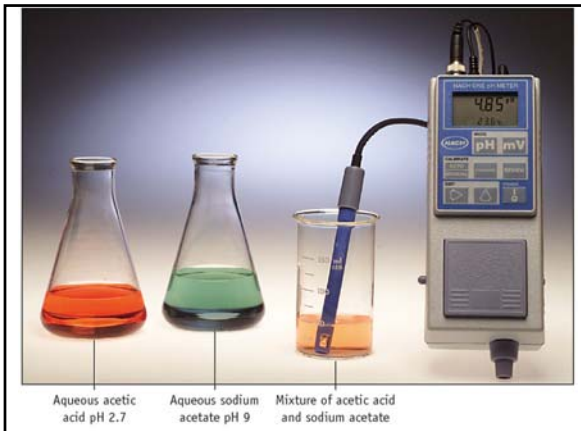


## Question:

- What happens when we add NaAcO to a solution of HAcO 0.25 M?

$$HAcO + H_2O \leftrightarrows AcO^- + H_3O^+$$

pH > 2.7

The common ion effect

18.1

## Buffer Solutions

**Problem:** What is the pH of a buffer that has [HAcO] = 0.700 M and [$AcO^-$] = 0.600 M?

$$HAcO + H_2O \leftrightarrows AcO^- + H_3O^+$$

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

| | [HAcO] | [$AcO^-$] | [$H_3O^+$] |
|---|---|---|---|
| initial | 0.700 | 0.600 | 0 |
| change | -x | +x | +x |
| equilib | 0.700 - x | 0.600 + x | x |

## Buffer Solutions

$$HAcO + H_2O \leftrightarrows AcO^- + H_3O^+$$

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

| | [HAcO] | [$AcO^-$] | [$H_3O^+$] |
|---|---|---|---|
| equilib | 0.700 - x | 0.600 + x | x |

Assuming that x << 0.700 and 0.600, we have

$$K_a = 1.8 \times 10^{-5} = \frac{[H_3O^+](0.600)}{0.700}$$

[$H_3O^+$] = $2.1 \times 10^{-5}$ and pH = 4.68

## Henderson-Hasselbalch Equation

$$[H_3O^+] = \frac{[Acid]}{[Conj.\ base]} \cdot K_a$$

Take the negative log of both sides of this equation

$$pH = pK_a - \log\frac{[Acid]}{[Conj.\ base]}$$

$$pH = pK_a + \log\frac{[Conj.\ base]}{[Acid]}$$

pH = 4.74 + log (0.600/0.700) = 4.68

## Adding an Acid to a Buffer

**Problem:** What is the pH when 1 mL of 1 M HCl is added to

a) 1 L of pure water (before HCl, pH = 7)

b) 1 L of buffer that has [HAcO] = 0.7 M and [$AcO^-$] = 0.6 M (pH = 4.68)

Solution to Part (a)

Calc. [HCl] after adding 1 mL of HCl to 1 L of water

$C_1 \cdot V_1 = C_2 \cdot V_2$

$1\ M \cdot 10^{-3}\ L = C_2 \cdot 1.001\ L$

$C_2 = 1 \times 10^{-3}\ M = [H_3O^+]$

pH = 3

7

3

b) 1 L of buffer that has [HAcO] = 0.7 M and [AcO$^-$] = 0.6 M (pH before = 4.7)

Solution to Part (b)

Step 1 — do the stoichiometry

$H_3O^+$ (from HCl) + $AcO^-$ → HAcO + $H_2O$ (l)

The reaction occurs completely because K is very large.

$K = 1/K_a = 1/1.8\ 10^{-5}$

$= 5.6\ 10^4$ >> 1 ⇨ product favored

| | | | |
|---|---|---|---|
| I | 0.001 | 0.600 | 0.700 |
| E | 0 | 0.599 | 0.701 |

Solution to Part (b): Step 2 –

Now we solve the exercise as a new problem

$HAcO + H_2O \leftrightharpoons H_3O^+ + AcO^-$

| | [HAcO] | [$H_3O^+$] | [$AcO^-$] |
|---|---|---|---|
| I (M) | 0.701 M | 0 | 0.599 M |
| C (M) | -x | +x | +x |
| E (M) | 0.701-x | x | 0.599 + x |

| | [HAcO] | [$AcO^-$] | [$H_3O^+$] |
|---|---|---|---|
| E | 0.701-x | 0.599+x | x |

Because $0.6 \geq 1.8\times10^{-5} \cdot 100$

$0.701-x \approx 0.701$ and $0.599-x \approx 0.599$

$$[H_3O^+] = \frac{[HOAc]}{[OAc^-]} \cdot K_a = \frac{0.701}{0.599} \cdot (1.8 \times 10^{-5})$$

$[H_3O^+] = 2.1 \times 10^{-5}$ M ------> pH = 4.7

The pH has not changed on adding HCl to the buffer!

4.7 ⇩ + HCl 4.7

## Controlling pH: Buffer Solutions

| Pure water | | Buffer |
|---|---|---|
| 7 | | 4.7 |
| ⇩ | + HCl | ⇩ |
| 3 | | 4.7 |

18.2

## Preparing a Buffer

You want to buffer a solution at pH = 4.30

This means $[H_3O^+] = 10^{-pH} = 5.0 \times 10^{-5}$ M

It is best to choose an acid such that $[H_3O^+]$ is about equal to $K_a$ (or pH ≈ $pK_a$).

—then you get the exact $[H_3O^+]$ by adjusting the ratio of acid to conjugate base.

$$[H_3O^+] = \frac{[Acid]}{[Conj.\ base]} \cdot K_a$$

## Preparing a Buffer

You want to buffer a solution at pH = 4.30 or $[H_3O^+] = 5.0 \times 10^{-5}$ M

| POSSIBLE ACIDS | $K_a$ |
|---|---|
| $HSO_4^-$ / $SO_4^{2-}$ | $1.2 \times 10^{-2}$ |
| HOAc / $OAc^-$ | $1.8 \times 10^{-5}$ |
| HCN / $CN^-$ | $4.0 \times 10^{-10}$ |

Best choice is acetic acid / acetate.

## Preparing a Buffer

You want to buffer a solution at pH = 4.30 or $[H_3O^+] = 5.0 \times 10^{-5}$ M

$$[H_3O^+] = 5.0 \times 10^{-5} = \frac{[HOAc]}{[OAc^-]}(1.8 \times 10^{-5})$$

Solve for $[HAcO]/[AcO^-]$ ratio = 2.78

Therefore, if you use 0.100 mol of NaAcO and 0.278 mol of HAcO, you will have pH = 4.30.

## Preparing a Buffer

A final point —

CONCENTRATION of the acid and conjugate base are not important.

It is the RATIO OF THE NUMBER OF MOLES of each.

Result: diluting a buffer solution does not change its pH

## Preparing a Buffer

Buffer prepared from

8.4 g $NaHCO_3$

weak acid

16.0 g $Na_2CO_3$

conjugate base

$HCO_3^- + H_2O \leftrightarrows H_3O^+ + CO_3^{2-}$

What is the pH?

$K_a = 4.8\ 10^{-11}$