



# ACIDS & BASES

BUFFERS & THE COMMON ION EFFECT

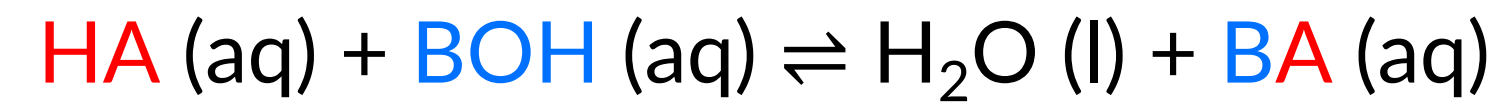
CHEMISTRY 165 // SPRING 2020

# Inventory of what we've covered so far

We have considered acids and bases separately:



We have considered mixing acids and bases together:



acid

base

water

salt

We have considered how aqueous salts (BA) can be acidic, basic, or neutral in water.

Now we will consider the mixture of weak acids/bases with salts to form buffers.

# What is a buffer?

**Buffers:** A solution that resists changes in pH when small amounts of acids or bases are added.

Buffers are typically made from solutions of a weak acid (HA) and its conjugate-base ( $A^-$ ),  
or from solutions of a weak base and its conjugate-acid.

We will also learn how to make buffers through titrations, but not now.

# Let's run through how to make buffers

**Buffers:** A solution that resists changes in pH when small amounts of acids or bases are added.

Buffers are typically made from solutions of a weak acid (HA) and its conjugate-base (A<sup>-</sup>).

Previously, we looked at the equilibrium for weak-acid dissociation.

Consider a solution of 0.40 M acetic acid (CH<sub>3</sub>COOH,  $K_a = 1.76 \times 10^{-5}$ ). We could calculate the pH using an ICE such as the one below.

	acid			conjugate-base
	CH <sub>3</sub> COOH	⇌	H <sup>+</sup>	+ CH <sub>3</sub> COO <sup>-</sup>
→ I	0.40 M		0	0
C	- x		+ x	+ x
E	0.40 - x		x	x

Notice that initially we only have **acid** in solution.

What if we add 0.20 M of Na(CH<sub>3</sub>COO) to the 0.40 M CH<sub>3</sub>COOH solution? We know the salt will dissociate:



Pay attention to how this affects the ICE chart now:

	acid			conjugate-base
	CH <sub>3</sub> COOH	⇌	H <sup>+</sup>	+ CH <sub>3</sub> COO <sup>-</sup>
→ I	0.40 M		0	0.20 ←
C	- x		+ x	+ x
E	0.40 - x		x	0.20 + x

Notice we now have **acid** and the **conjugate-base** in solution.

# Calculations of pH for buffers

Consider a solution of 0.40 M acetic acid ( $\text{CH}_3\text{COOH}$ ,  $K_a = 1.76 \times 10^{-5}$ ). We could calculate the pH using an ICE such as the one below.

	acid			conjugate-base
	$\text{CH}_3\text{COOH}$	$\rightleftharpoons$	$\text{H}^+$	+ $\text{CH}_3\text{COO}^-$
→	I		0	0
	0.40 M			
	C		+ x	+ x
	- x			
	E		x	x
	0.40 - x			

Notice that initially we only have **acid** in solution.

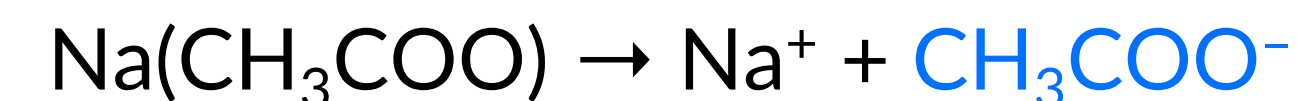
To find the pH of this weak acid solution, we can set up an equilibrium expression, approximate x to be negligibly small, solve for  $x = [\text{H}^+]$ , and then pH:

$$K_a = \frac{x^2}{0.40 - x} \approx \frac{x^2}{0.40} = 1.76 \times 10^{-5}$$

$$x = [\text{H}^+]$$

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

What if we add 0.20 M of  $\text{Na}(\text{CH}_3\text{COO})$  to the 0.40 M  $\text{CH}_3\text{COOH}$  solution? We know the salt will dissociate:



	acid			conjugate-base
	$\text{CH}_3\text{COOH}$	$\rightleftharpoons$	$\text{H}^+$	+ $\text{CH}_3\text{COO}^-$
→	I		0	0.20 ←
	0.40 M			
	C		+ x	+ x
	- x			
	E		x	0.20 + x
	0.40 - x			

Notice we now have **acid** and the **conjugate-base** in solution.

To find the pH of this weak acid buffer, we can set up an equilibrium expression, approximate x to be negligibly smaller, solve for  $x = [\text{H}^+]$ , and then pH:

$$K_a = \frac{(x)(0.20 + x)}{0.40 - x} \approx \frac{0.20x}{0.40} = 1.76 \times 10^{-5}$$

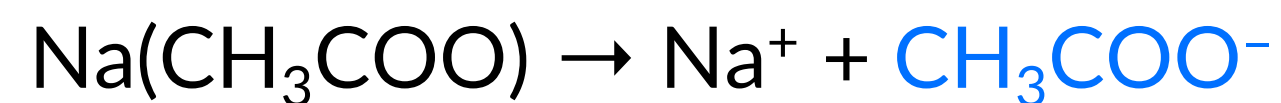
$$x = [\text{H}^+]$$

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

*Let's work this out more explicitly!*

# Henderson-Hasselbalch and pH of buffers

What if we add 0.20 M of  $\text{Na}(\text{CH}_3\text{COO})$  to the 0.40 M  $\text{CH}_3\text{COOH}$  solution? We know the salt will dissociate:



	acid		conjugate-base
	$\text{CH}_3\text{COOH}$	$\rightleftharpoons$	$\text{H}^+ + \text{CH}_3\text{COO}^-$
I	0.40 M		0
C	-x		+x
E	0.40 - x		x

Notice we now have *acid* and the *conjugate-base* in solution.

To find the pH of this weak acid buffer, we can set up an equilibrium expression, approximate x to be negligibly smaller, solve for  $x = [\text{H}^+]$ , and then pH:

$$K_a = \frac{(x)(0.20 + x)}{0.40 - x} \approx \frac{0.20x}{0.40} = 1.76 \times 10^{-5}$$

$$x = [\text{H}^+]$$

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

Let's pick apart this equation:

$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = 1.76 \times 10^{-5} \leftarrow K_a$$

↙  $[\text{A}^-]$  (0.20)  
↘  $[\text{H}^+]$  (x)  
→  $[\text{HA}]$  (0.40)

Now, take the log of both sides and rearrange a bit:

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

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

↑ pH

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

This is the Henderson-Hasselbalch equation and it allows you to *estimate* (or calculate) the pH of a buffer if you know the  $K_a$  of the acid and the concentrations of the weak acid and its conjugate-base in solution.

# What is a (good) buffer?

**Buffers:** A solution that resists changes in pH when small amounts of acids or bases are added.

Buffers are typically made from solutions of a weak acid (HA) and its conjugate-base ( $A^-$ ),  
or from solutions of a weak base and its conjugate-acid.

The buffer shown below is a very good buffer. But why? Think about how buffers work.

	acid			conjugate-base
	$CH_3COOH$	$\rightleftharpoons$	$H^+$	$+ CH_3COO^-$
I	0.40 M		0	0.40
C	- x		+ x	+ x
E	0.40 - x		x	0.40 + x

Good buffers have  $[HA] = [A^-]$ . What about their pH's?

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

$$pH = pK_a$$

Notice that we have equal amounts of **acid** and the **conjugate-base** in solution,  $[HA] = [A^-]$ .

Why is this good? Well, it means we have a system that can act as both an acid or base depending on what we throw into the solution.

- If we add acid, the acid will react with the conjugate-base side.
- If we add base, the base will react with the acid side.

Regardless of what we add, our buffer will have enough acid or conjugate-base to resist drastic changes in pH.

## PRACTICE PROBLEM 1

You have a 1.0 L solution containing 0.40 M  $\text{CH}_3\text{COOH}$  ( $K_a = 1.76 \times 10^{-5}$ ) and 0.20 M  $\text{Na}(\text{CH}_3\text{COO})$ .

Calculate the pH of this buffer solution if 0.10 mol HCl is added. Assume no volume change.

— *answer* —



# PRACTICE PROBLEM 1

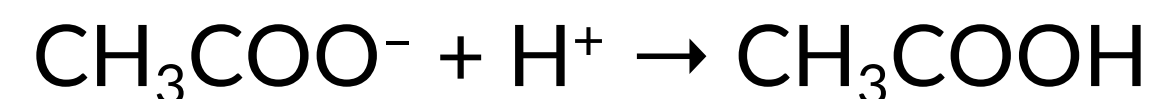
You have a 1.0 L solution containing 0.40 M  $\text{CH}_3\text{COOH}$  ( $K_a = 1.76 \times 10^{-5}$ ) and 0.20 M  $\text{Na}(\text{CH}_3\text{COO})$ .

Calculate the pH of this buffer solution if 0.10 mol HCl is added. Assume no volume change.

— answer —

First, ask yourself what HCl will react with in the weak-acid dissociation equilibrium: the acid or its conjugate-base?

Since HCl is an acid, it should react with the conjugate-base via:



We can construct an ICF chart in moles to help us out here.

	$\text{CH}_3\text{COO}^-$	+	$\text{H}^+$	$\rightarrow$	$\text{CH}_3\text{COOH}$
I	0.20 mol		0.10 mol		0.40 mol
C	- 0.10		- 0.10		+ 0.10
F	0.10		0		0.50

## Why ICF and not ICE?

Remember that ICE charts are for equilibrium processes. At the instant of mixing HCl into the buffer, we get a non-equilibrium and unidirectional reaction between the conjugate-base and  $\text{H}^+$  to form acid. The ICF chart is still *useful* because it simplifies the stoichiometry calculations we would normally have to do for non-equilibrium chemical reactions: (1) find the limiting reactant, (2) determine how much excess reactant is left, and (3) determine how much product is formed.

## How did I know what goes in the “C” (change) row?

Since this is a non-equilibrium reaction, we have a limiting reactant. You could figure out the limiting reactant through a number of ways. The easiest way is to notice that the reaction is 1:1 for  $\text{CH}_3\text{COO}^-:\text{H}^+$  but we have a ratio of 0.40:0.10, so  $\text{H}^+$  is limiting.

Now, just apply the Henderson-Hasselbalch equation to estimate the pH:

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log\left(\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}\right) \\ &= -\log(1.76 \times 10^{-5}) + \log\left(\frac{\frac{0.10 \text{ mol}}{1.0 \text{ L}}}{\frac{0.50 \text{ mol}}{1.0 \text{ L}}}\right) \\ &= 4.754_5 - 0.69_9 \\ \text{pH} &= 4.06\end{aligned}$$

## PRACTICE PROBLEM 2

You have a 1.0 L solution containing 0.40 M  $\text{CH}_3\text{COOH}$  ( $K_a = 1.76 \times 10^{-5}$ ) and 0.20 M  $\text{Na}(\text{CH}_3\text{COO})$ .

Calculate the pH of this buffer solution if 0.20 mol  $\text{NaOH}$  is added. Assume no volume change.

— *answer* —

## PRACTICE PROBLEM 2

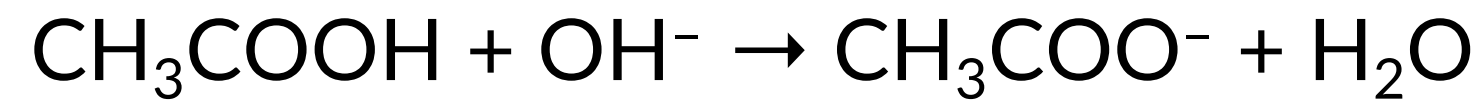
You have a 1.0 L solution containing 0.40 M  $\text{CH}_3\text{COOH}$  ( $K_a = 1.76 \times 10^{-5}$ ) and 0.20 M  $\text{Na}(\text{CH}_3\text{COO})$ .

Calculate the pH of this buffer solution if 0.20 mol  $\text{NaOH}$  is added. Assume no volume change.

— answer —

First, ask yourself what  $\text{NaOH}$  will react with in the weak-acid dissociation equilibrium: the acid or its conjugate-base?

Since  $\text{NaOH}$  is a base, it should react with the acid via:



We can construct an ICF chart in moles to help us out here.

	$\text{CH}_3\text{COOH}$	+	$\text{OH}^-$	→	$\text{CH}_3\text{COO}^-$
I	0.40 mol		0.20 mol		0.20 mol
C	- 0.20		- 0.20		+ 0.20
F	0.20		0		0.40

Now, just apply the Henderson-Hasselbach equation to estimate the pH:

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log\left(\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}\right) \\ &= -\log(1.76 \times 10^{-5}) + \log\left(\frac{\frac{0.40 \text{ mol}}{1.0 \text{ L}}}{\frac{0.20 \text{ mol}}{1.0 \text{ L}}}\right) \\ &= 4.754_5 - 0.30_1 \\ \text{pH} &= 5.06\end{aligned}$$