## N39 – Acid Base

## Henderson-Hasselbalch "He-Ha"

Link to YouTube Presentation: <a href="https://youtu.be/1c8eybhSmck">https://youtu.be/1c8eybhSmck</a>

## N39 – Acid Base

## Henderson-Hasselbalch "He-Ha"

**Target:** I can identify when a solution is a buffer and can perform calculations for buffered solutions. **Buffer** - A solution that resists a change in pH when either hydroxide ions <u>or</u> protons are added.

#### **Buffered solutions contain:**

- A weak acid and some extra conjugate A<sup>-</sup>
- A weak base and some extra conjugate BH<sup>+</sup>

### How do you make/form a buffer?

#### **Buffered solutions contain either:**

- A weak acid and its "matching" salt (A- in salt)
- A weak base and its "matching" salt (BH+ in salt)
- A weak acid and <u>smaller</u> amount of a strong base
- A weak base and <u>smaller</u> amount of strong acid

### How do you make/form a buffer?

#### **Buffered solutions contain either:**

- Because those end up with leftover weak A/B and forming some conjugate ions (so you don't need to add a salt)!
- A weak acid and its "matching" salt (A- in salt)
- A weak base and its "matching" salt (BH+ in salt)
- A weak acid and <u>smaller</u> amount of a strong base
- A weak base and <u>smaller</u> amount of strong acid

## **Acid/Salt Buffering Pairs**



The salt will contain the anion of the acid, A<sup>-</sup> and the cation of a strong base (NaOH, KOH)

Weak Acid	Formula of the acid	Example of a salt of the weak acid
Hydrofluoric	HF	KF – Potassium fluoride
Formic	НСООН	KHCOO – Potassium formate
Benzoic	C <sub>6</sub> H <sub>5</sub> COOH	NaC <sub>6</sub> H <sub>5</sub> COO – Sodium benzoate
Acetic	CH <sub>3</sub> COOH	NaH <sub>3</sub> COO – Sodium acetate
Carbonic	H <sub>2</sub> CO <sub>3</sub> (HHCO <sub>3</sub> )	NaHCO <sub>3</sub> - Sodium bicarbonate
Propanoic	HC <sub>3</sub> H <sub>5</sub> O <sub>2</sub>	NaC <sub>3</sub> H <sub>5</sub> O <sub>2</sub> - Sodium propanoate
Hydrocyanic	HCN	KCN - potassium cyanide

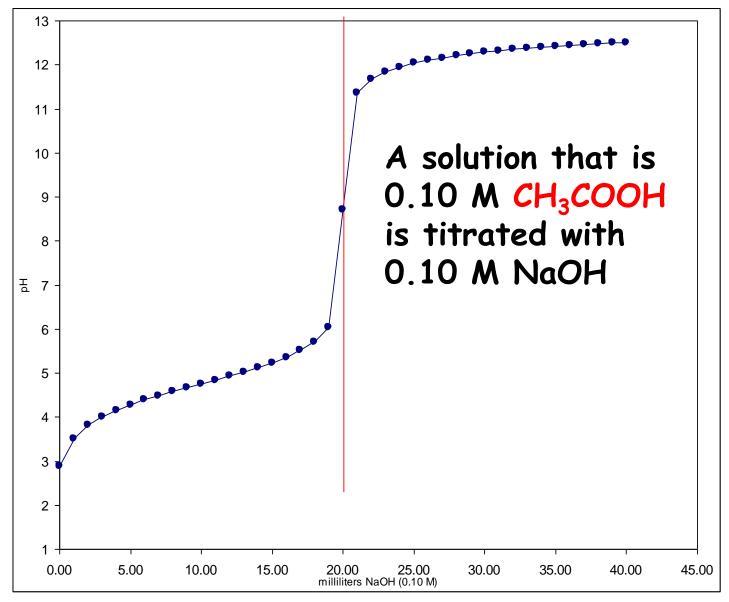
## **Base/Salt Buffering Pairs**



#### The salt will contain the cation of the base, BH<sup>+</sup> (base plus an extra hydrogen), and the anion of a strong acid (HCI, HNO<sub>3</sub>)

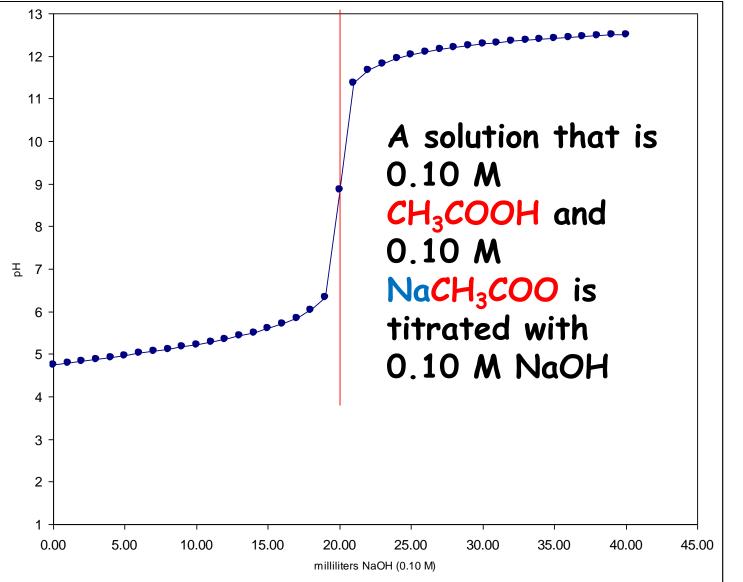
Weak Base	Formula of the base	Formula of the cation of the base	Example of a salt of the weak acid
Ammonia	NH <sub>3</sub>	NH <sub>4</sub> +	NH <sub>4</sub> CI - ammonium chloride
Methylamine	CH <sub>3</sub> NH <sub>2</sub>	CH <sub>3</sub> NH <sub>3</sub> +	CH <sub>3</sub> NH <sub>3</sub> CI – methylammonium chloride
Ethylamine	$C_2H_5NH_2$	C <sub>2</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup>	C <sub>2</sub> H <sub>5</sub> NH <sub>3</sub> NO <sub>3</sub> - ethylammonium nitrate
Aniline	$C_6H_5NH_2$	C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> +	C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> CI – aniline hydrochloride
Pyridine	C₅H₅N	C <sub>5</sub> H <sub>5</sub> NH +	C <sub>5</sub> H <sub>5</sub> NHCI – pyridine hydrochloride

## **Titration of an Unbuffered Solution**





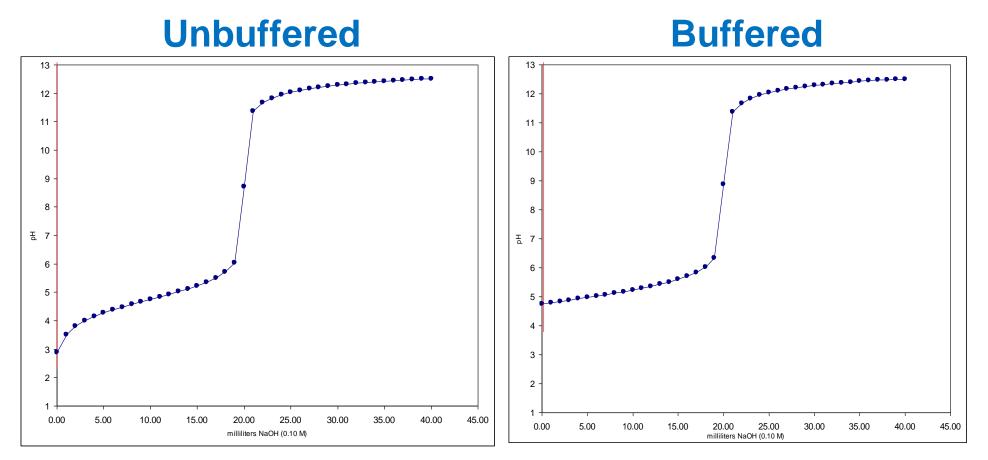
## **Titration of a Buffered Solution**





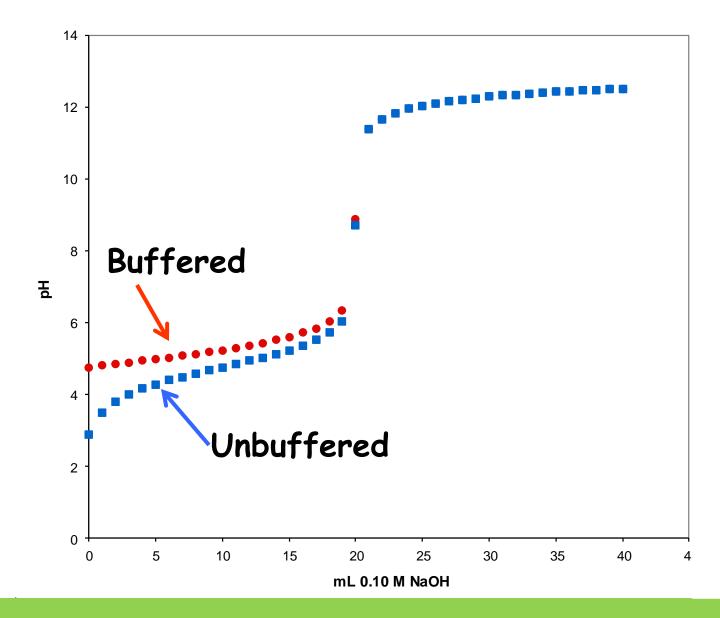
What do you notice about the shape of the curve?

## **Comparing Results**



- In what ways are the graphs different?
- In what ways are the graphs similar?

## **Comparing Results**



A buffered solution "resists changes in pH" as you add the acid or base! Slower pH change.

## **One way of doing these calculations**

**Rearrange your Law of Mass Action:** 

$$Ka = \frac{[H^+][A^-]}{[HA]} \rightarrow [H^+] = Ka \frac{[HA]}{[A^-]} \rightarrow = Ka \frac{[Acid]}{[conj.Base]}$$
salt

$$Kb = \frac{[BH^+][OH^-]}{[B]} \rightarrow [OH^-] = Kb \frac{[B]}{[BH^+]} \rightarrow = Kb \frac{[Base]}{[conj.Acid]}$$
salt

7.2 x 10<sup>-4</sup> M

2.0 M

 $HF \leftrightarrow H^+ + F^-$ 



B





### 0.20 M



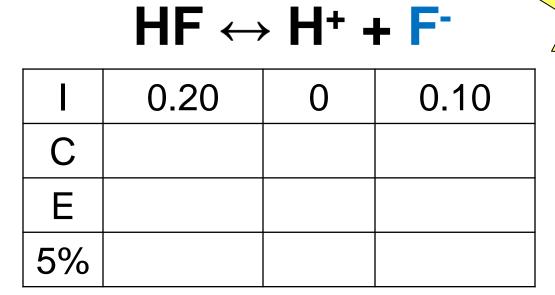
A	7.2	x 10 <sup>-4</sup> M
B	2.0	Μ

1.4 x 10<sup>-3</sup> M

none of these

) 0.20 M

C



Common

**Ion Effect!** 

5%

$\smile$			
B	2.0	Μ	



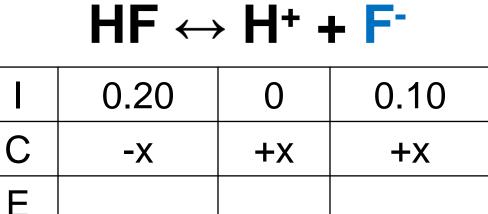


none of these

7.2 x 10<sup>-4</sup> M



### 0.20 M



Common **Ion Effect!** 

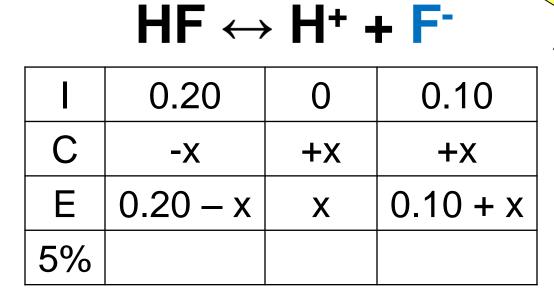
B	2.0	Μ	
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1.4 x 10<sup>-3</sup> M

none of these

7.2 x 10<sup>-4</sup> M

0.20 M



Common Ion Effect!

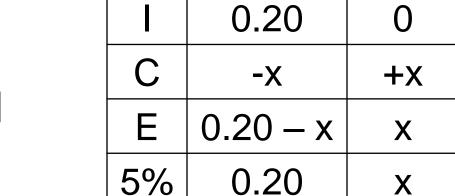
<b>B</b> 2.0 M
----------------

1.4 x 10<sup>-3</sup> M

none of these

7.2 x 10<sup>-4</sup> M

**)** 0.20 M



 $HF \leftrightarrow H^+ + F^-$ 

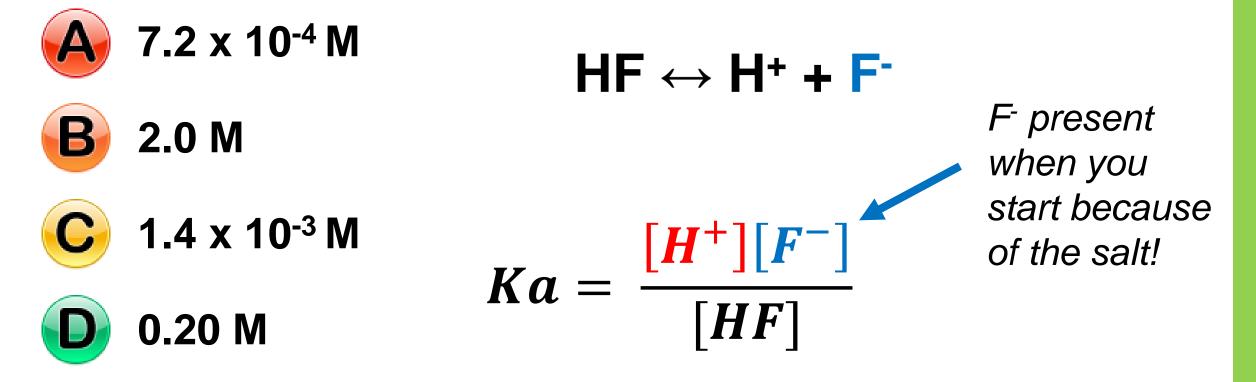
0.10

+X

0.10 + x

0.10

Common Ion Effect!





A 7.2 x 10<sup>-4</sup> M B 2.0 M C 1.4 x 10<sup>-3</sup> M D 0.20 M  $[H^+] = 1.44 x 10^{-3} M$  $[H^+] = 1.44 x 10^{-3} M$ 



A 7.2 x 10<sup>-4</sup> M 7.2 x 10<sup>-4</sup> =  $\frac{[H^+][0.10]}{[0.20]};$ **B** 2.0 M **C** 1.4 x 10<sup>-3</sup> M 0.20 M  $[H^+] = 1.44 \times 10^{-3} M$ none of these

Now...calculate the pH in a solution that is 0.10 M in NaF and 0.20 M in HF. ( $K_a = 7.2 \times 10^{-4}$ )

2.84  $[H^+] = 1.44 \times 10^{-3} M$ 0.70 B **C** 11.2  $pH = -log(1.44 \ x \ 10^{-3}M)$ 3.14 pH = 2.84none of these

Now...calculate the pH in a solution that is 0.10 M in NaF and 0.20 M in HF. ( $K_a = 7.2 \times 10^{-4}$ )

**A** 2.84  $[H^+] = 1.44 \times 10^{-3} M$ 0.70 B **C** 11.2  $pH = -log(1.44 \times 10^{-3}M)$ 3.14 pH = 2.84



### Another way to do these calculations!

#### **Henderson-Hasselbalch Equation**

#### A helpful shortcut equation to find the pH or pOH of a buffered solution.

You could also do ICE Tables but those can be really time consuming.



### **Henderson-Hasselbalch Equation**

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

$$pOH = pKb + log\left(\frac{[BH^+]}{[B]}\right) = pKb + log\left(\frac{[Acid]}{[Base]}\right)$$

pKa = -log(Ka) pKb = -log(Kb)

Just like 
$$pH = -log[H^+]$$

#### The acids or bases may be conjugates from the salt!

### **Henderson-Hasselbalch Equation**

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

$$pOH = pKb + log\left(\frac{[BH^+]}{[B]}\right) = pKb + log\left(\frac{[Acid]}{[Base]}\right)$$

pKa = -log(Ka) pKb = -log(Kb)

Just like 
$$pH = -log[H^+]$$

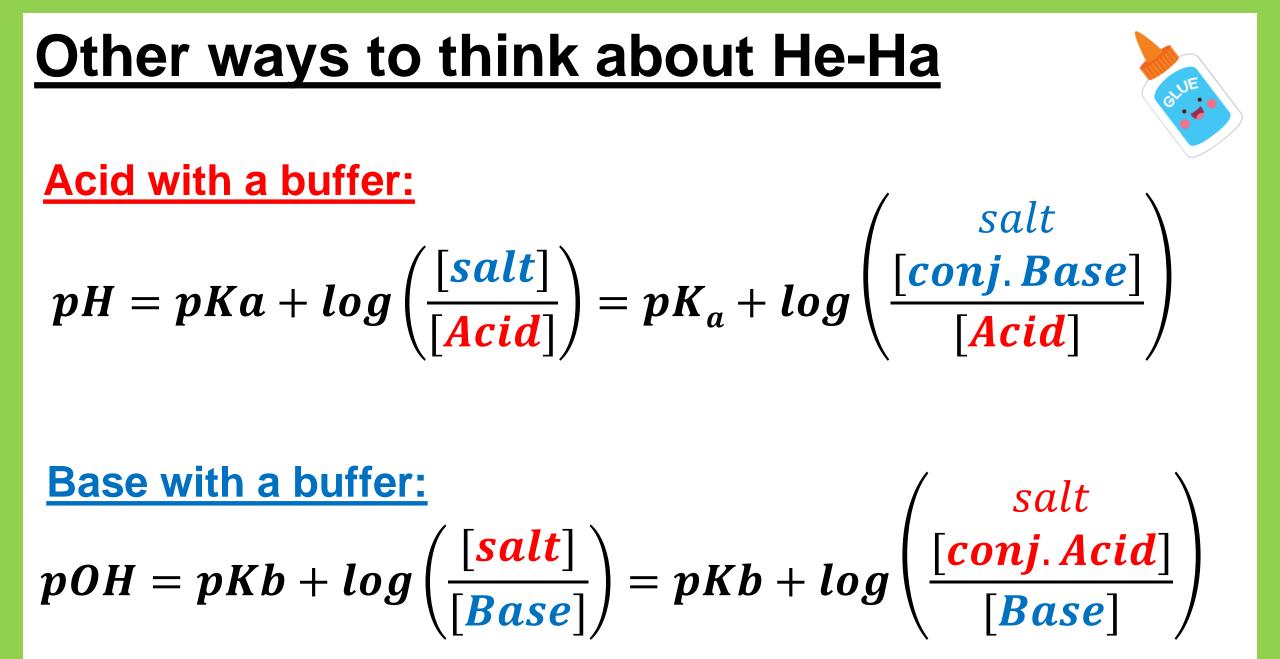
#### The acids or bases may be conjugates from the salt!

### **Careful!**

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

$$pOH = pKb + log\left(\frac{[BH^+]}{[B]}\right) = pKb + log\left(\frac{[Acid]}{[Base]}\right)$$

People get these backwards all the time! If you want pH then ACID goes on the BOTTOM. If you want pOH then BASE goes on the BOTTOM

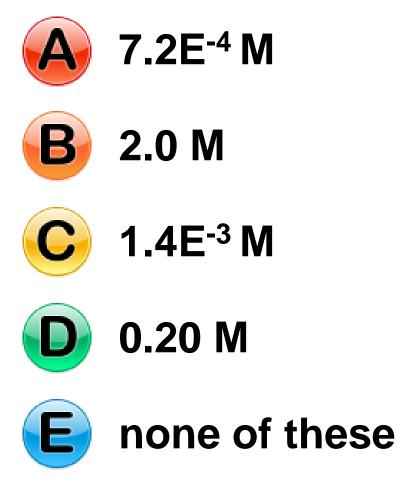




#### **Check your formulas!**

## 1.00 M MgCl<sub>2</sub> = 2.00 M Cl<sup>-</sup>

#### Be on the lookout for salts that have a van't Hoff factor of more than 2...is your [salt] the same as your [ion]



7.2E<sup>-4</sup> M Acid solution with a salt added. • HF = acid2.0 M B • NaF = salt1.4E<sup>-3</sup> M The salt has the conjugate base of the acid. • F<sup>-</sup> 0.20 M  $pH = pKa + Log \frac{[conj. Base Salt]}{[Acid]}$ none of these

<b>7.2E</b> <sup>-4</sup> M	pH = pKa + Log <mark>[conj. Base salt]</mark> [Acid]
<b>B</b> 2.0 M	
<b>C</b> 1.4E <sup>-3</sup> M	$pH = -log[7.2E^{-4}] + log\frac{[0.1M]}{[0.2M]}$
<b>D</b> 0.20 M	= 2.84
<b>E</b> none of these	[H <sup>+</sup> ] = 10 <sup>-pH</sup> = 10 <sup>-2.84</sup> = 0.00144 <i>M</i>

 $pH = pKa + Log \frac{[conj. Base salt]}{[Acid]}$ 7.2E<sup>-4</sup> M **B** 2.0 M  $pH = -log[7.2E^{-4}] + log\frac{[0.1M]}{[0.2M]}$ C 1.4E<sup>-3</sup> M 0.20 M = 2.84 $[H^+] = 10^{-pH} = 10^{-2.84} = 0.00144M$ none of these

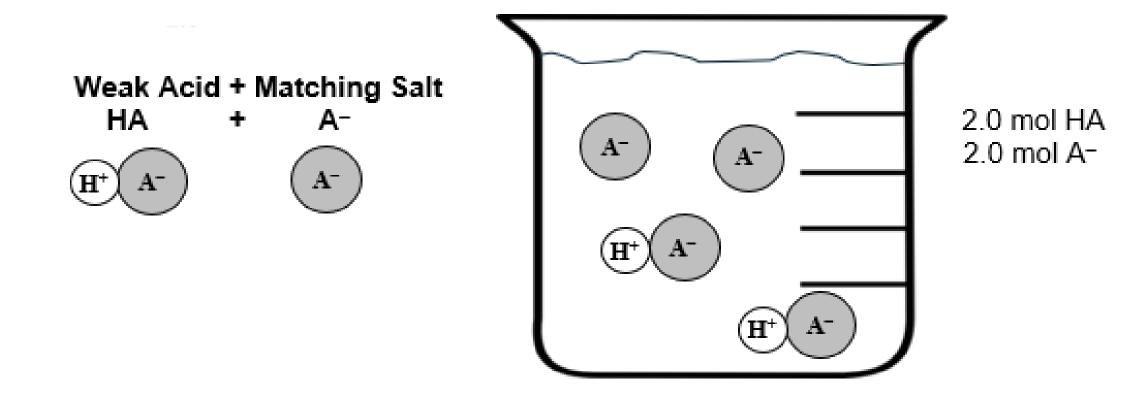
### Adding Acid or Base to a Buffer

**Buffer** - A solution that resists a change in pH when either hydroxide ions <u>or</u> protons are added.

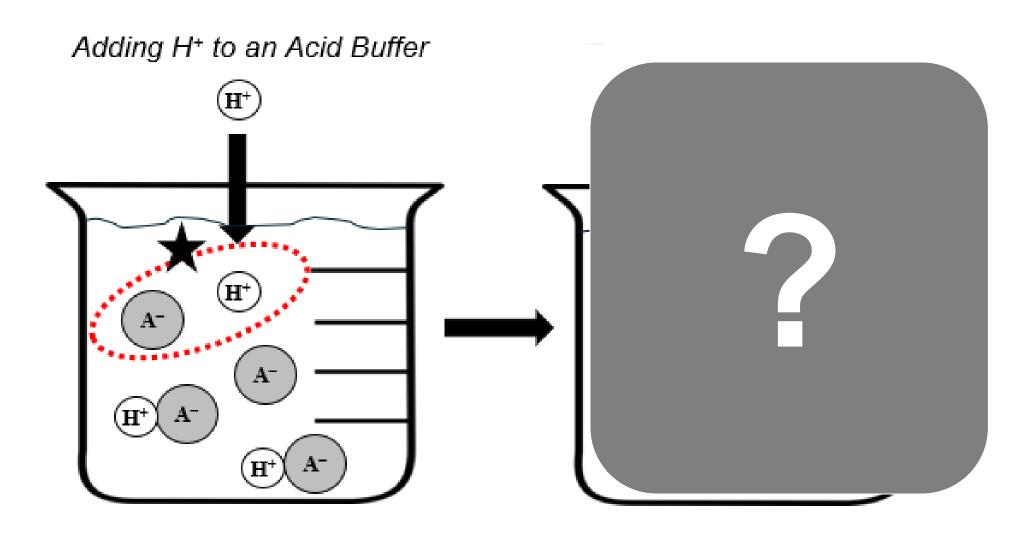
#### That means...

- If I add acid (H<sup>+</sup>) something in the buffer will react with the H<sup>+</sup> to use it up!
- If I add base (OH<sup>-</sup>) something in the buffer will react with the OH<sup>-</sup> to use it up!

## **ACID BUFFER**

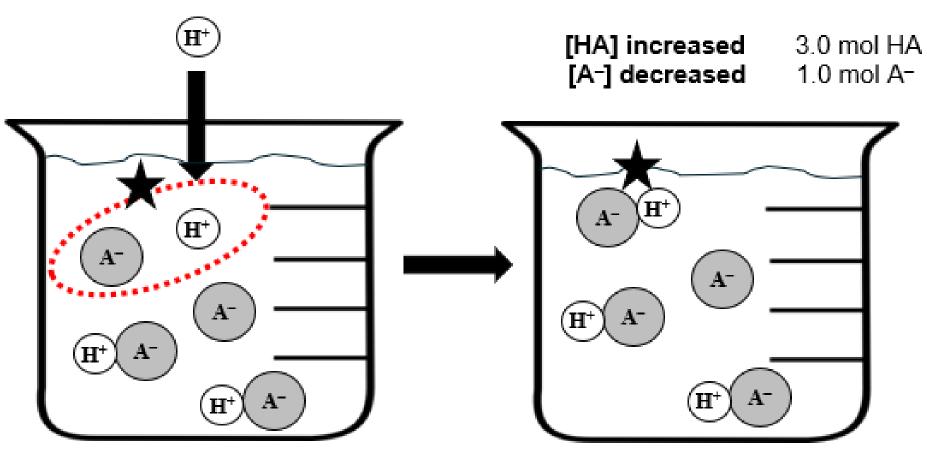


## <u>ACID BUFFER</u> – Add H<sup>+</sup>

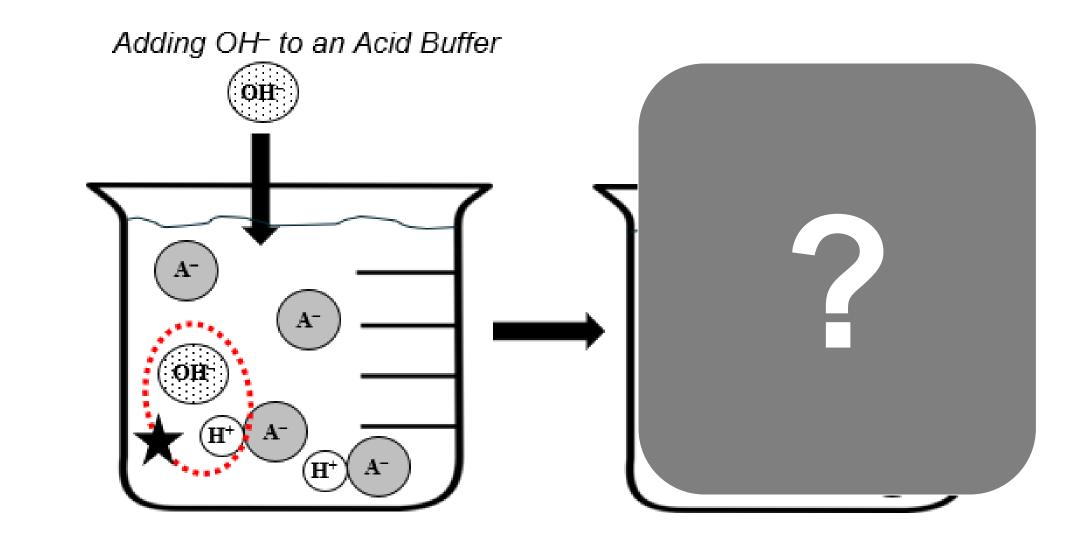


## ACID BUFFER – Add H<sup>+</sup>

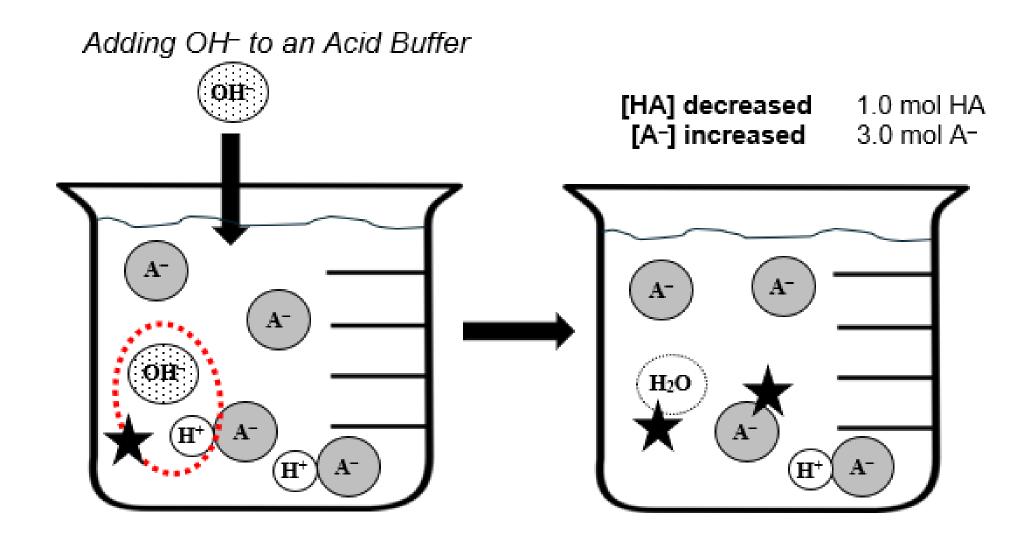
Adding H<sup>+</sup> to an Acid Buffer



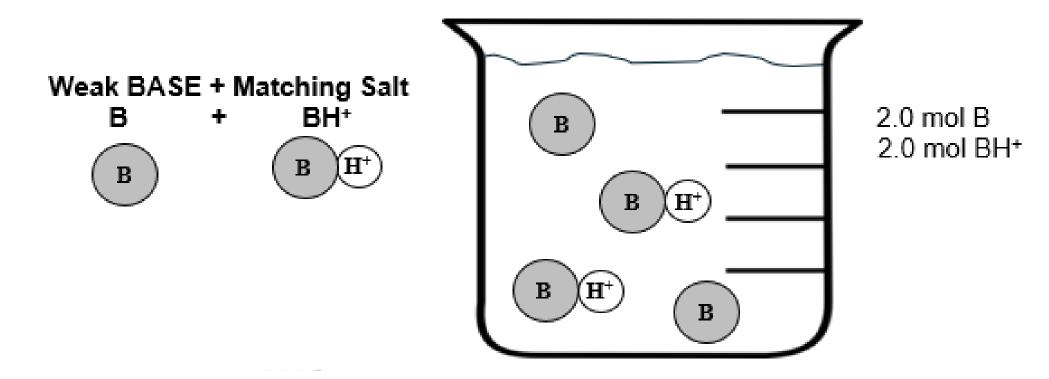
#### <u>ACID BUFFER</u> – Add OH<sup>-</sup>



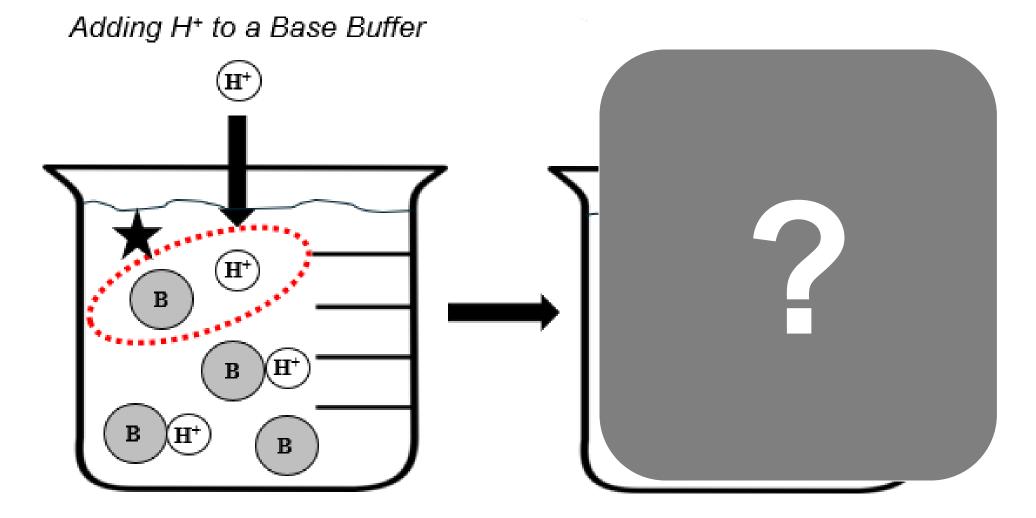
#### <u>ACID BUFFER</u> – Add OH<sup>-</sup>



#### **BASE BUFFER**

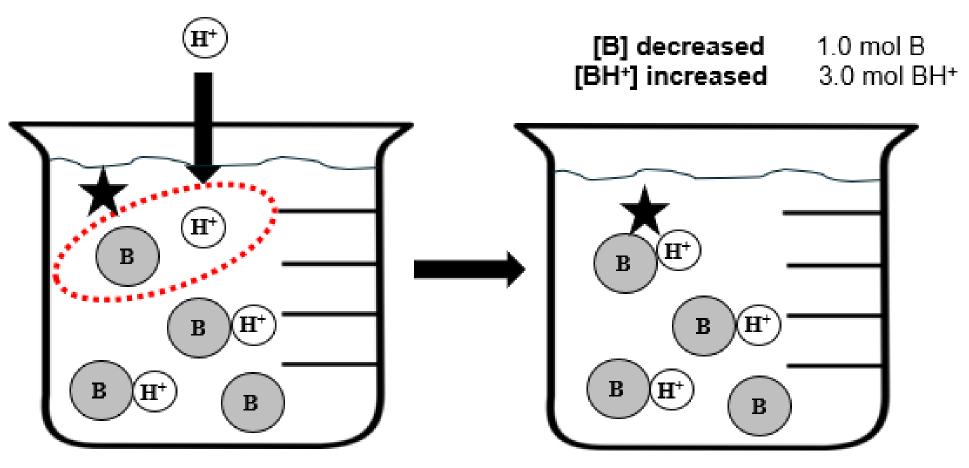


#### **BASE BUFFER** – Add H<sup>+</sup>

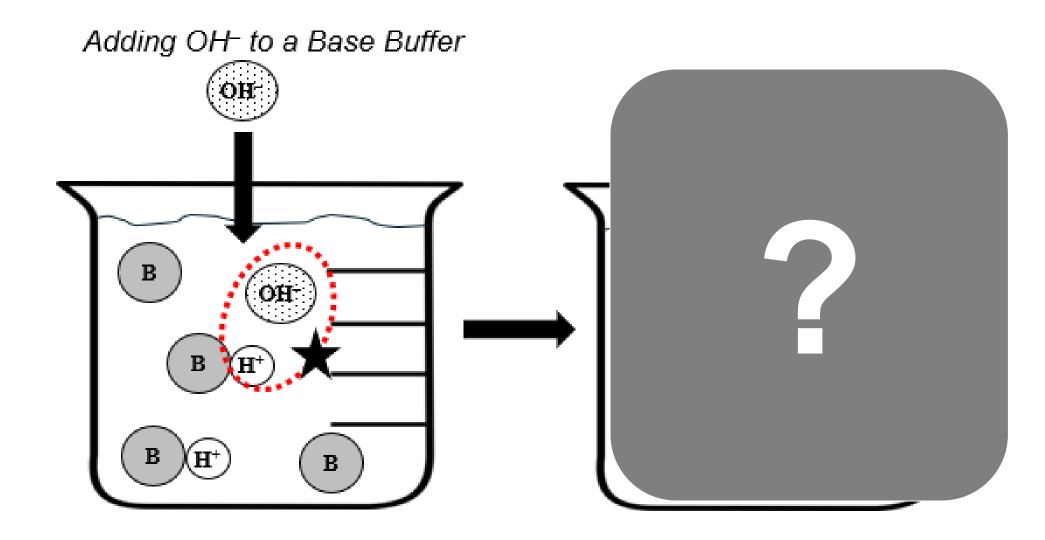


#### **BASE BUFFER – Add H**<sup>+</sup>

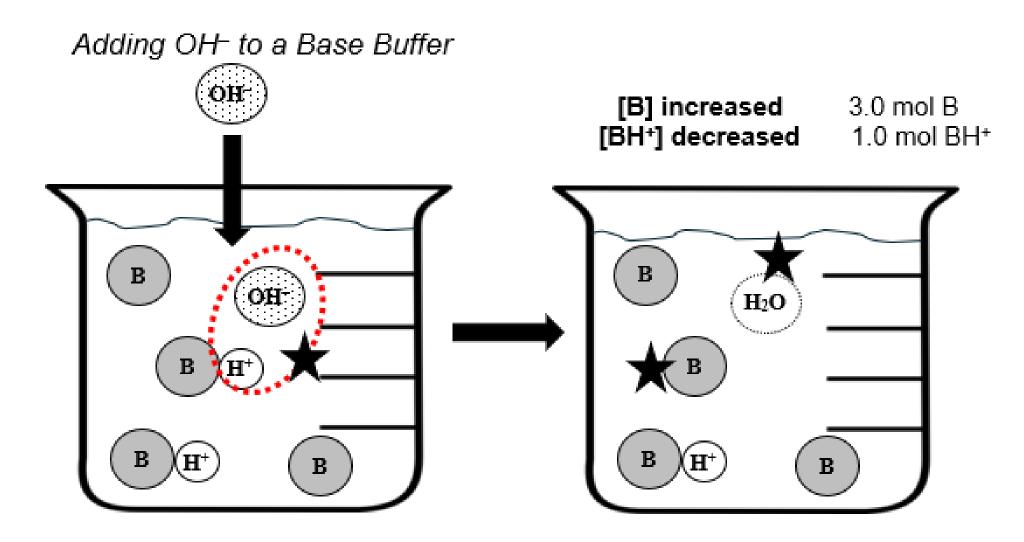
Adding H<sup>+</sup> to a Base Buffer



#### **BASE BUFFER** – Add OH<sup>-</sup>



#### BASE BUFFER – Add OH<sup>-</sup>



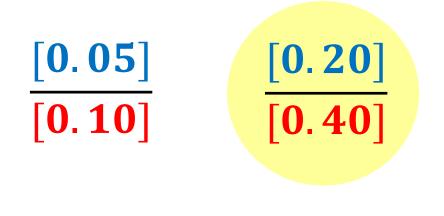
The degree to which a solution resists change in pH when adding acid/base is called the **buffer capacity**.

If you keep the <u>RATIO</u> of salt to acid the same but increase the <u>QUANTITIES</u> of each, the pH will stay the same but you have a greater buffer capacity – you can add more acid/base before the pH starts to change

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

#### **Buffer Capacity**

Two solutions are made with the same type of acid and same type of salt. Which has a higher buffer capacity?  $[A^-]$ 



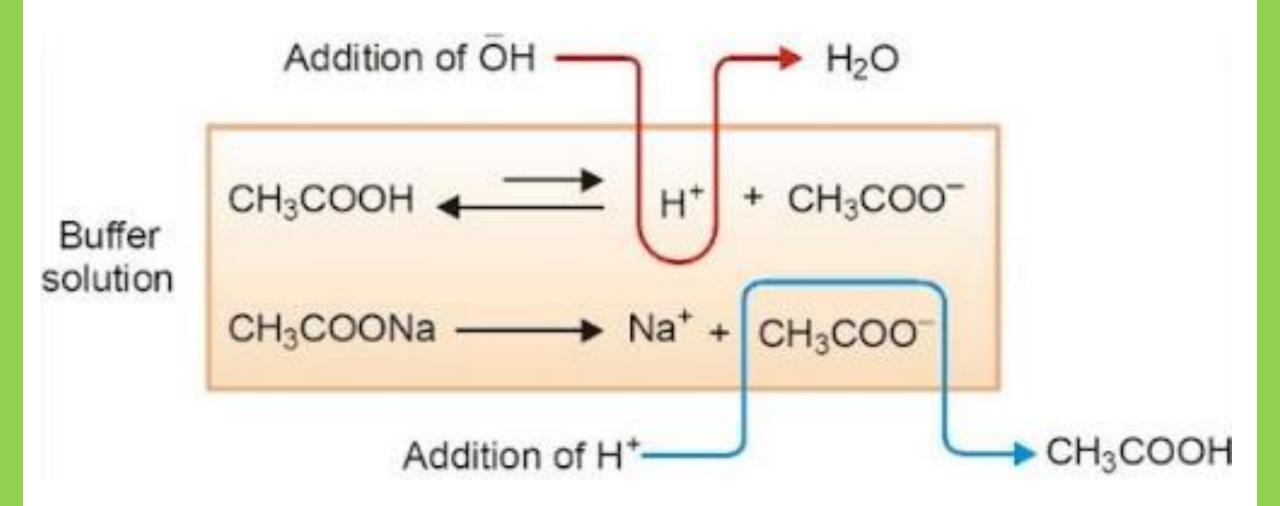
Max buffer capacity if you want it to work best for <u>BOTH</u> adding acid OR base, the "best" buffer would be a 1:1 ratio of salt to acid (or base)

[*HA*]

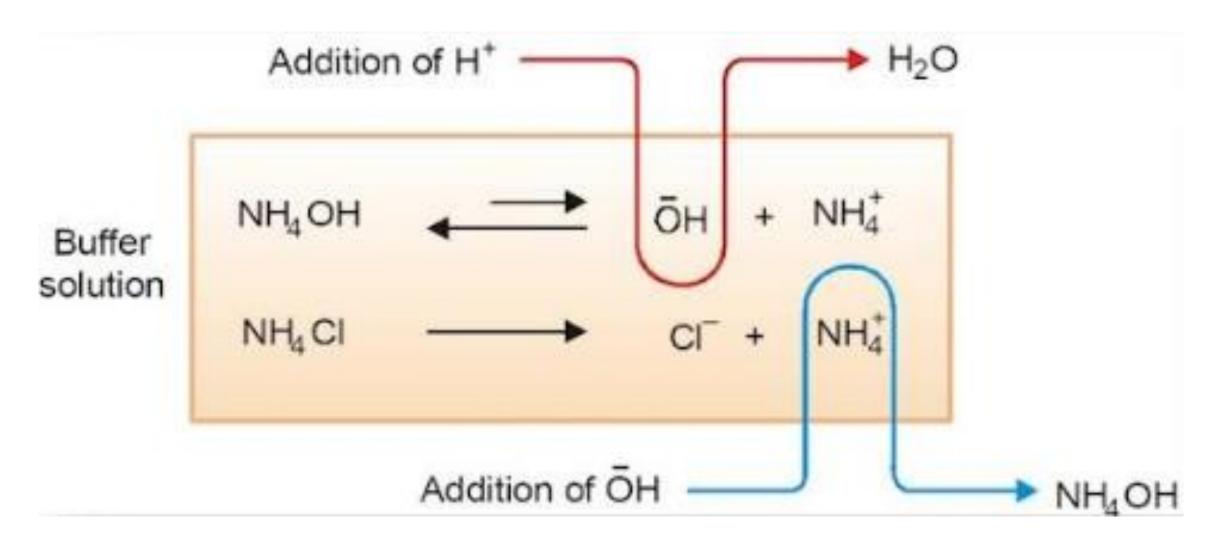
Will the pH of the buffered solution be the same or different if these were made with the same acid and the same salt? Why?

The same pH. The pKa will be the same and the ratio of the salt to acid is the same. So, no change in pH

#### **Buffer Capacity**



## **Buffer Capacity**



$$CH_{3}COOH(aq) + H_{2}O(l) \iff H_{3}O^{+}(aq) + CH_{3}COO^{-}(aq)$$

$$H_{3}O^{+} added, equilibrium position shifts to the left 
CH_{3}COOH(aq) \leftarrow CH_{3}COO^{-}(aq) + H_{3}O^{+}$$

$$OH^{-} added, equilibrium position shifts to the right 
OH^{-} + CH_{3}COOH(aq) \rightarrow H_{2}O(l) + CH_{3}COO^{-}(aq)$$
Buffer solution   
after addition   
of strong acid
$$Buffer solution 
acid and base$$

$$H_{3}O^{+} = Add H_{3}O^{+} = H$$

. .

- 10

> u ot a u ou ooo-( )

Figure 14.6.2: This diagram shows the buffer action of these reactions.

Repetition to build muscle memory is more important than ever with buffer problems.

Commit to eating, sleeping, and doing buffer problems for a few weeks. Your time/efforts will build muscle memory!

When you are in a play you have periods of higher time commitment as you get closer to the play. Must practice!

When you have a big game coming up you have periods of higher time commitment. Must practice!

Find your preferred method. They all have pros and cons. <u>Ice tables</u>

Pro = familiar Con = takes forever, lots of steps

#### <u>He-Ha</u>

Pro = fast, on theCon = Have to recognize to use it,AP eq. sheetnot always solving for pH

#### **Rearranging Law of Mass Action**

Pro = simpleCon = Have to recognize to use it,<br/>extra step to get to pH or pOH

Make sure to practice ALL methods once in a while. You never know which info they will give you... You want to be able to solve any variety of problems!

## <u>YES</u>, it is fine if I used one method on a key and you used another method. No big deal.

Just make sure you are careful about rounding issues.

#### Make sure to practice ALL methods once in a while.

You never know which info they will give you... You want to be able to solve any variety of problems!

# <u>YES</u>, it is fine if I used one method on a key and you used another method. No big deal.

Just make sure you are careful about rounding issues. <u>Example</u> - Some people like to always use the pH version of He-Ha instead of pOH version when dealing with a base, so they just need to convert  $K_b$  into  $K_a$  and be careful of where you put your base and conjugate acid.

These can get long, hard, and overwhelming Skip it and come back if you need to!

Sometimes you need to do stoichiometry first! Keep track of when you are using moles versus concentration!

- When things react use stoich to see what is made and what is left over. Write the chemical reaction out if you need to!
- "Mole tables" can be helpful. Sometimes called BCA tables or "Stoichiometry tables." Just a way of organizing your numbers. LABEL if a mole table, do NOT call it an ICE table!
- Make sure you go BACK to [ ] values for He-Ha or Law of Mass Action type calculations! BE CAREFUL!

(a) Calculate the pH of a 0.500 L buffer solution composed of 0.700 M formic acid (HCOOH , Ka =  $1.77 \times 10^{-4}$ ) and 0.500 M sodium formate (NaCOOH)

$$pH = pKa + Log \frac{[conj. Base salt]}{[Acid]}$$
$$pH = -log[1.77 x 10^{-4}] + log \frac{[0.500 M]}{[0.700 M]}$$
$$= 3.61$$

(a) Calculate the pH of a 0.500 L buffer solution composed of 0.700 M formic acid (HCOOH, Ka =  $1.77 \times 10^{-4}$ ) and 0.500 M sodium formate (NaCOOH) 3.61

(b) Calculate the pH after adding 60.0 mL of a 1.00 M NaOH solution

(a) Calculate the pH of a 0.500 L buffer solution composed of 0.700 M formic acid (HCOOH, Ka =  $1.77 \times 10^{-4}$ ) and 0.500 M sodium formate (NaCOOH) **3.61** (b) Calculate the pH after adding 60.0 mL of a 1.00 M NaOH solution HCOOH  $\stackrel{\bullet}{+}$  NaOH  $\rightarrow$  H<sub>2</sub>O + Na<sup>+</sup>  $\stackrel{\bullet}{+}$  COOH<sup>-</sup> Weak Conj. Weak Strong Conj. Sase Base Acid 🧳 Acid SAL

Weak Acid + corresponding Salt = BUFFER!

(a) Calculate the pH of a 0.500 L buffer solution composed of 0.700 M formic acid (HCOOH, Ka =  $1.77 \times 10^{-4}$ ) and 0.500 M sodium formate (NaCOOH) 3.61 (b) Calculate the pH after adding 60.0 mL of a 1.00 M NaOH solution

**HCOOH + NaOH**  $\rightarrow$  H<sub>2</sub>O + Na<sup>+</sup> + COOH<sup>-</sup>

Time for some stoichiometry to figure out how many moles of everything we have to start with

(a) Calculate the pH of a 0.500 L buffer solution composed of 0.700 M formic acid (HCOOH, Ka =  $1.77 \times 10^{-4}$ ) and 0.500 M sodium formate (NaCOOH) 3.61 (b) Calculate the pH after adding 60.0 mL of a 1.00 M NaOH solution

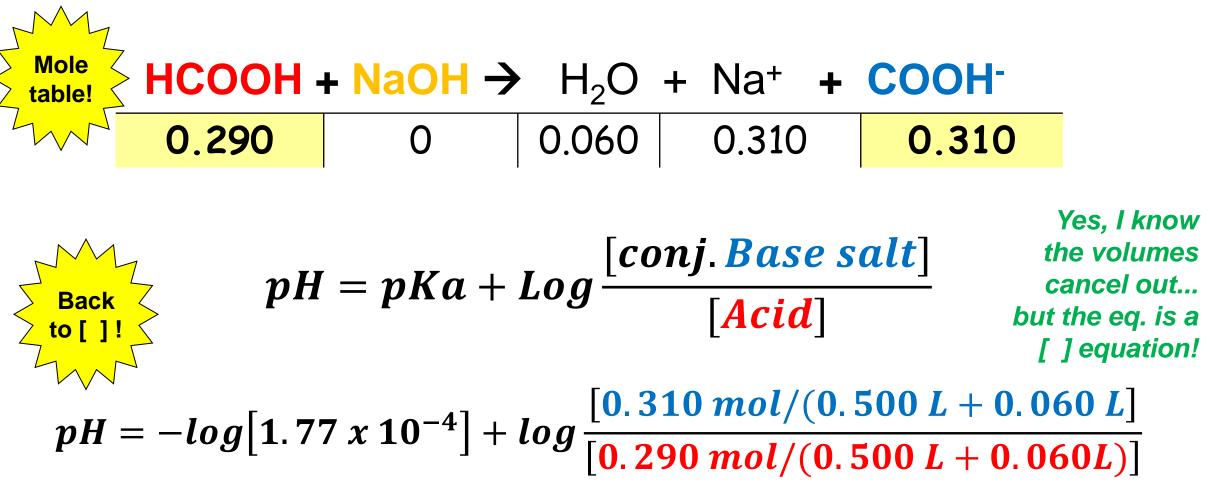
<b>HCOOH + NaOH</b> $\rightarrow$ H <sub>2</sub> O + Na <sup>+</sup> + COOH <sup>-</sup>					
0.500 L HCOOH	0.700 mol	= 0.350 mol HCOOH	0.060 L OH <sup>-</sup>	1 mol	
	1 L	to start with		1 mol	
	• <b>•</b>			1 L	
		= 0.250 mol COOH <sup>-</sup>	= 0.060 mol OH <sup>-</sup>		
0.500 L COOH <sup>-</sup>	0.500 mol	(and also mol Na+)		added	
	1 L	salt to start with			

```
(a) Calculate the pH of a 0.500 L buffer solution composed of 0.700 M formic acid (HCOOH , Ka = 1.77 \times 10^{-4}) and 0.500 M sodium formate (NaCOOH) 3.61
(b) Calculate the pH after adding 60.0 mL of a 1.00 M NaOH solution
HCOOH + NaOH → H<sub>2</sub>O + Na<sup>+</sup> + COOH<sup>-</sup>
0.350 mol | 0.060 mol | 0 | 0.250 mol | 0.250 mol
```

(a) Calculate the pH of a 0.500 L buffer solution composed of 0.700 M formic acid (HCOOH, Ka =  $1.77 \times 10^{-4}$ ) and 0.500 M sodium formate (NaCOOH) **3.61** (b) Calculate the pH after adding 60.0 mL of a 1.00 M NaOH solution Mole **HCOOH + NaOH**  $\rightarrow$  H<sub>2</sub>O + Na<sup>+</sup> + COOH<sup>-</sup> table! 0.350 mol 0.060 mol 0 0.250 mol 0.250 mol -0.060 -0.060 +0.060 +0.060 +0.060

(a) Calculate the pH of a 0.500 L buffer solution composed of 0.700 M formic acid (HCOOH, Ka =  $1.77 \times 10^{-4}$ ) and 0.500 M sodium formate (NaCOOH) **3.61** (b) Calculate the pH after adding 60.0 mL of a 1.00 M NaOH solution Mole **HCOOH + NaOH**  $\rightarrow$  H<sub>2</sub>O + Na<sup>+</sup> + COOH<sup>-</sup> table! 0 | 0.250 mol | 0.250 mol 0.350 mol 0.060 mol -0.060 -0.060 +0.060 +0.060 +0.0600.290 0.060 0.310 0.310 0

#### BACK TO [] FOR THE HE-HA CALCULATIONS!



TOTAL solution volume!!! Your volume changed as you added the NaOH!

= 3.78

Crash Course Video Buffers, the Acid Rain Slayer https://youtu.be/8Fdt5WnYn1k?si=gaA6JxbNHhhlN-Nt

#### **Bozeman Science Video** *pH and Buffers* <u>https://youtu.be/rlvEvwViJGk?si=CrPu5FtV0xLr8Amu</u>

#### **Professor Dave Video**

Acid-Base Equilibria and Buffer Solutions <a href="https://youtu.be/jdmHjFp\_35l?si=jncpa2ZlOWpPH72Z">https://youtu.be/jdmHjFp\_35l?si=jncpa2ZlOWpPH72Z</a>

#### Buffer capacity

#### 2017 3(d)

Nitrogen monoxide, NO(g), can undergo further reactions to produce acids, such as HNO<sub>2</sub>, a weak acid with a  $K_a$  of  $4.0 \times 10^{-4}$  and a p $K_a$  of 3.40.

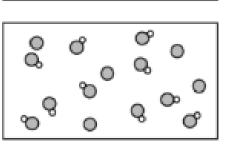
- (c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M HNO<sub>2</sub>(aq) and 0.100 M NaOH(aq).
- (d) A second student makes a buffer by dissolving 0.100 mol of NaNO<sub>2</sub>(s) in 100. mL of 1.00 M HNO<sub>2</sub>(aq). Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (c) ? Justify your answer.

The buffer made by the second student is more resistant to changes in pH because it contains a higher concentration of $HNO_2$ and $NO_2^-$ to react with added H <sup>+</sup> or OH <sup>-</sup> ions.	1 point is earned for the correct choice and a valid justification.

(e) A new buffer is made using HNO<sub>2</sub>(aq) as one of the ingredients. A particulate representation of a small representative portion of the buffer solution is shown below. (Cations and water molecules are not shown.) Is the pH of the buffer represented in the diagram greater than, less than, or equal to 3.40? Justify your answer.

D HNO, molecule

Particle level models: always count particles!



 $ONO_2^{-}$  ion

2017 3(e)

*	<ol> <li>point is earned for the correct choice.</li> </ol>
If $[HNO_2] = [NO_2^{-}]$ , $pH = pK_a$ , and the pH of the solution would be 3.40.	
Since $[HNO_2] > [NO_2^-]$ , as represented in the diagram, the solution has	
a pH less than 3.40.	1 point is earned for a
OR	valid justification.
$pH = pK_a + log \frac{[NO_2^-]}{[HNO_2]} \implies pH = 3.40 + log \frac{5}{10} \implies pH = 3.10$	

# One way to prepare a buffer is partially titrating a WA with a SB or a WB with a strong acid 2017 3(c)

- Nitrogen monoxide, NO(g), can undergo further reactions to produce acids, such as HNO<sub>2</sub>, a weak acid with a  $K_a$  of  $4.0 \times 10^{-4}$  and a p $K_a$  of 3.40.
- (c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M HNO<sub>2</sub>(aq) and 0.100 M NaOH(aq).
  - (i) Explain why the addition of 0.100 M NaOH(aq) to 0.100 M HNO<sub>2</sub>(aq) can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the NaOH(aq) to the HNO<sub>2</sub>(aq).

NaOH will neutralize some of the  $HNO_2$  to produce  $NO_2^-$ . The resulting solution contains a mixture of a weak acid and its conjugate base, which is a buffer solution.

 $HNO_2 + OH^- \rightarrow NO_2^- + H_2O$ 

1 point is earned for the recognition that the solution produced is a mixture of a weak acid and its conjugate base.

1 point is earned for the correct net ionic equation.

#### **YouTube Link to Presentation**

https://youtu.be/1c8eybhSmck