N39 – Acid Base

Henderson-Hasselbalch
“He-Ha”

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Target: I can identify when a solution is a buffer and can perform calculations for buffered solutions.

Buffered Solutions

Buffer - A solution that resists a change in pH when either hydroxide ions or protons are added.

Buffered solutions contain either:

- **A weak acid and its matching salt**
- **A weak base and its matching salt**
- **A weak acid and ½ the amount of a strong base**
- **A weak base and ½ the amount of strong acid**

Buffered Solutions

Buffer - A solution that resists a change in pH when either hydroxide ions or protons are added.

Because those end up with leftover weak A/B and forming some conjugate ions (so you don't need to add a salt)!

Buffered solutions contain either:

- **A weak acid and its matching salt**
- **A weak base and its matching salt**
- ***A weak acid and ½ the amount of a strong base***
- ***A weak base and ½ the amount of strong acid***

Acid/Salt Buffering Pairs

The salt will contain the anion of the acid, and the cation of a strong base (NaOH, KOH)

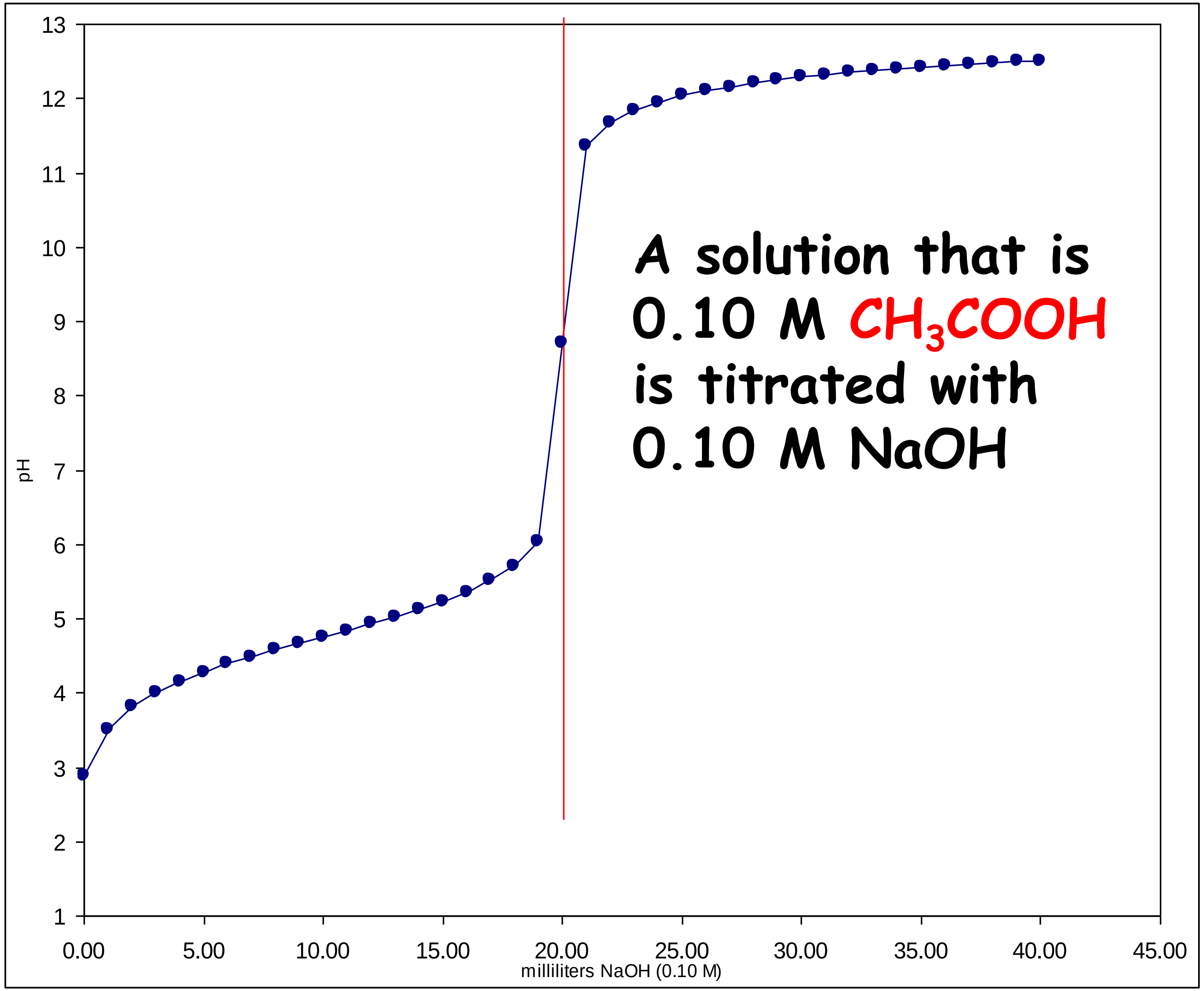
Weak Acid	Formula of the acid	Example of a salt of the weak acid
Hydrofluoric	**HF**	**KF** – Potassium fluoride
Formic	**HCOOH**	**KHCOO** – Potassium formate
Benzoic	C_6H_5COOH	NaC_6H_5COO – Sodium benzoate
Acetic	CH_3COOH	NaH_3COO – Sodium acetate
Carbonic	H_2CO_3 ($HHCO_3$)	$NaHCO_3$ - Sodium bicarbonate
Propanoic	$HC_3H_5O_2$	$NaC_3H_5O_2$ - Sodium propanoate
Hydrocyanic	**HCN**	**KCN** - potassium cyanide

Base/Salt Buffering Pairs

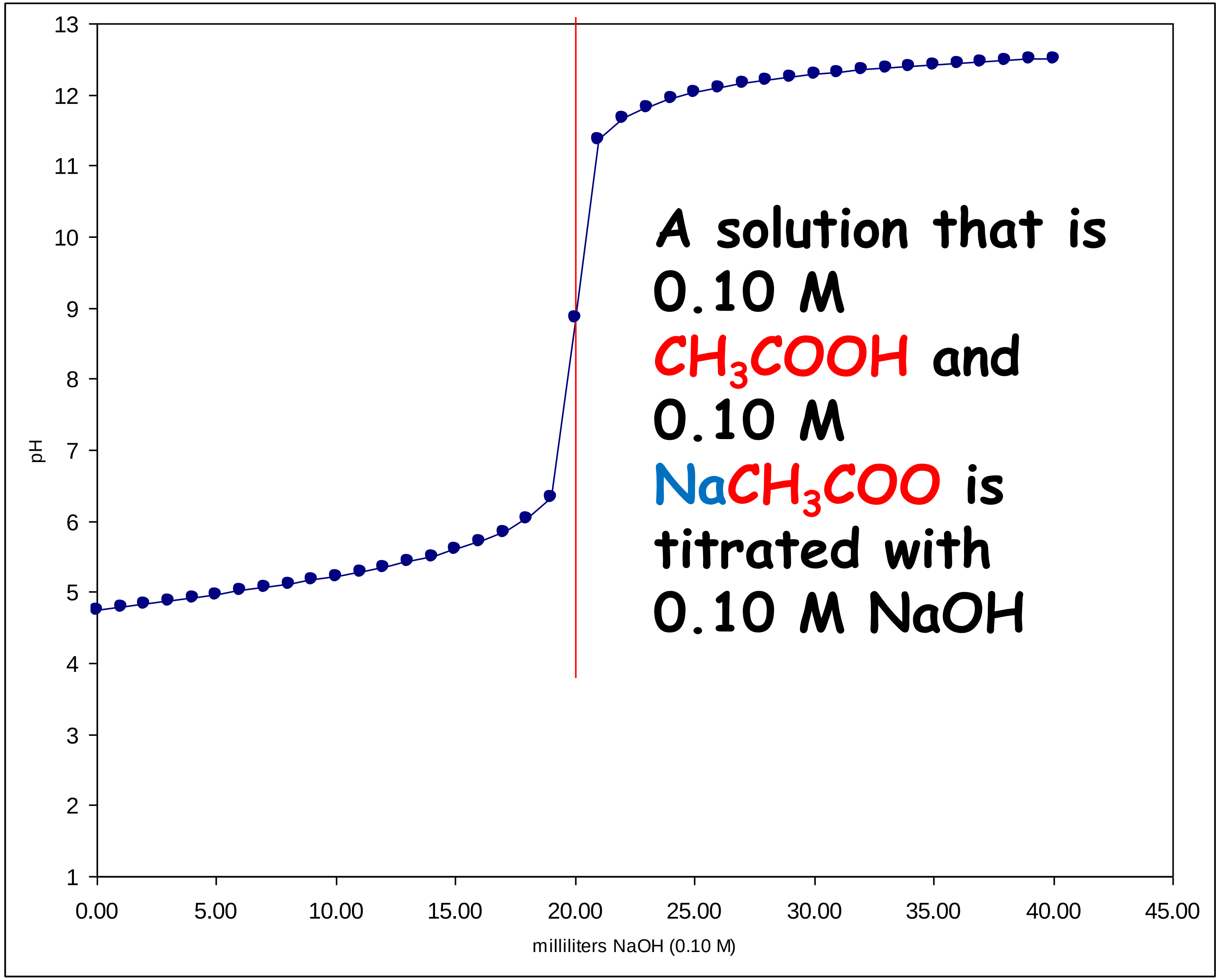
The salt will contain the cation of the base (base plus an extra hydrogen), and the anion of a strong acid (HCl, HNO_3)

Weak Base	Formula of the base	Formula of the cation of the base	Example of a salt of the weak acid
Ammonia	NH_3	NH_4^{+}	NH_4Cl - ammonium chloride
Methylamine	CH_3NH_2	$CH_3NH_3^{+}$	CH_3NH_3Cl – methylammonium chloride
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3^{+}$	$C_2H_5NH_3NO_3$ - ethylammonium nitrate
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3^{+}$	$C_6H_5NH_3Cl$ – aniline hydrochloride
Pyridine	C_5H_5N	$C_5H_5NH^{+}$	C_5H_5NHCl – pyridine hydrochloride

Titration of an Unbuffered Solution



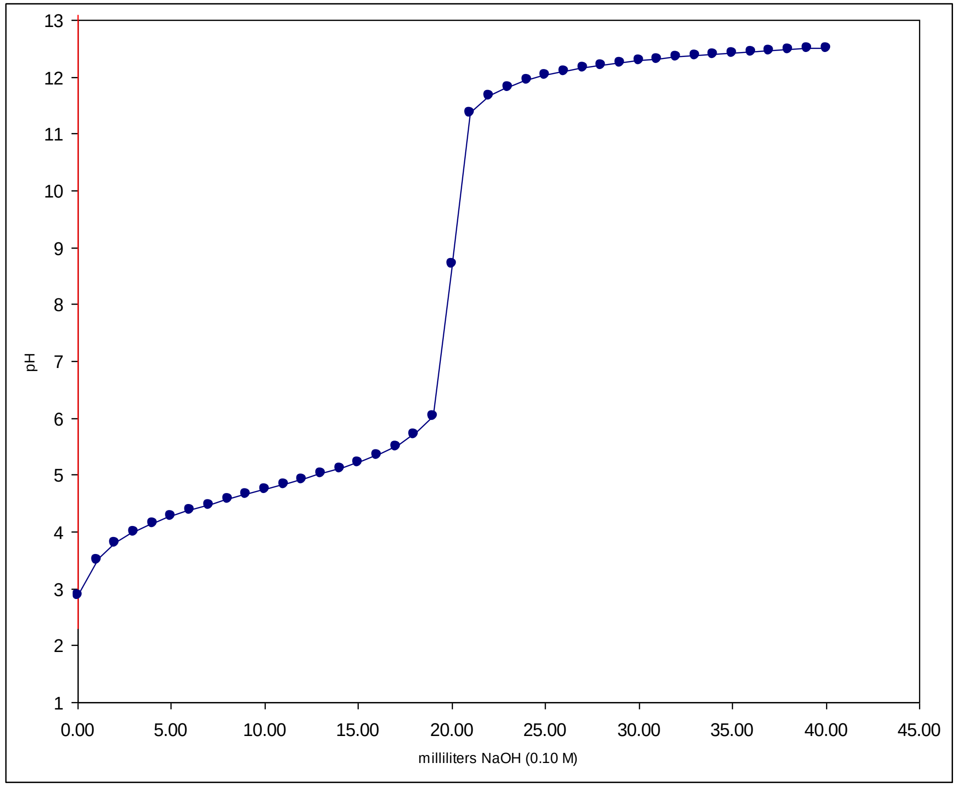
Titration of a Buffered Solution



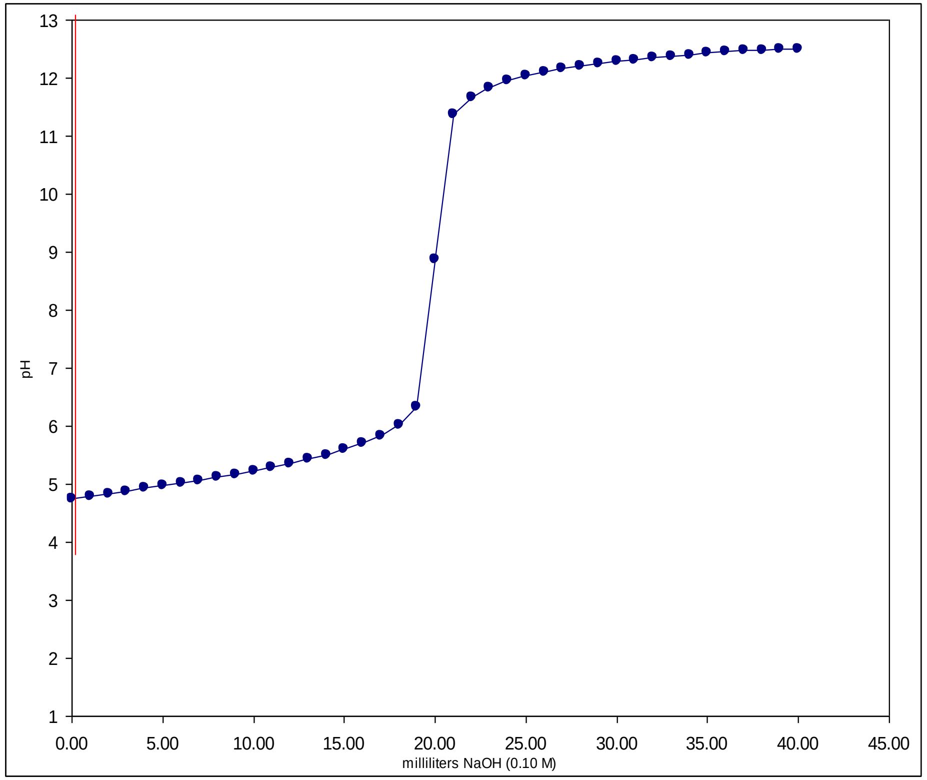
What do you notice about the shape of the curve?

Comparing Results

Unbuffered

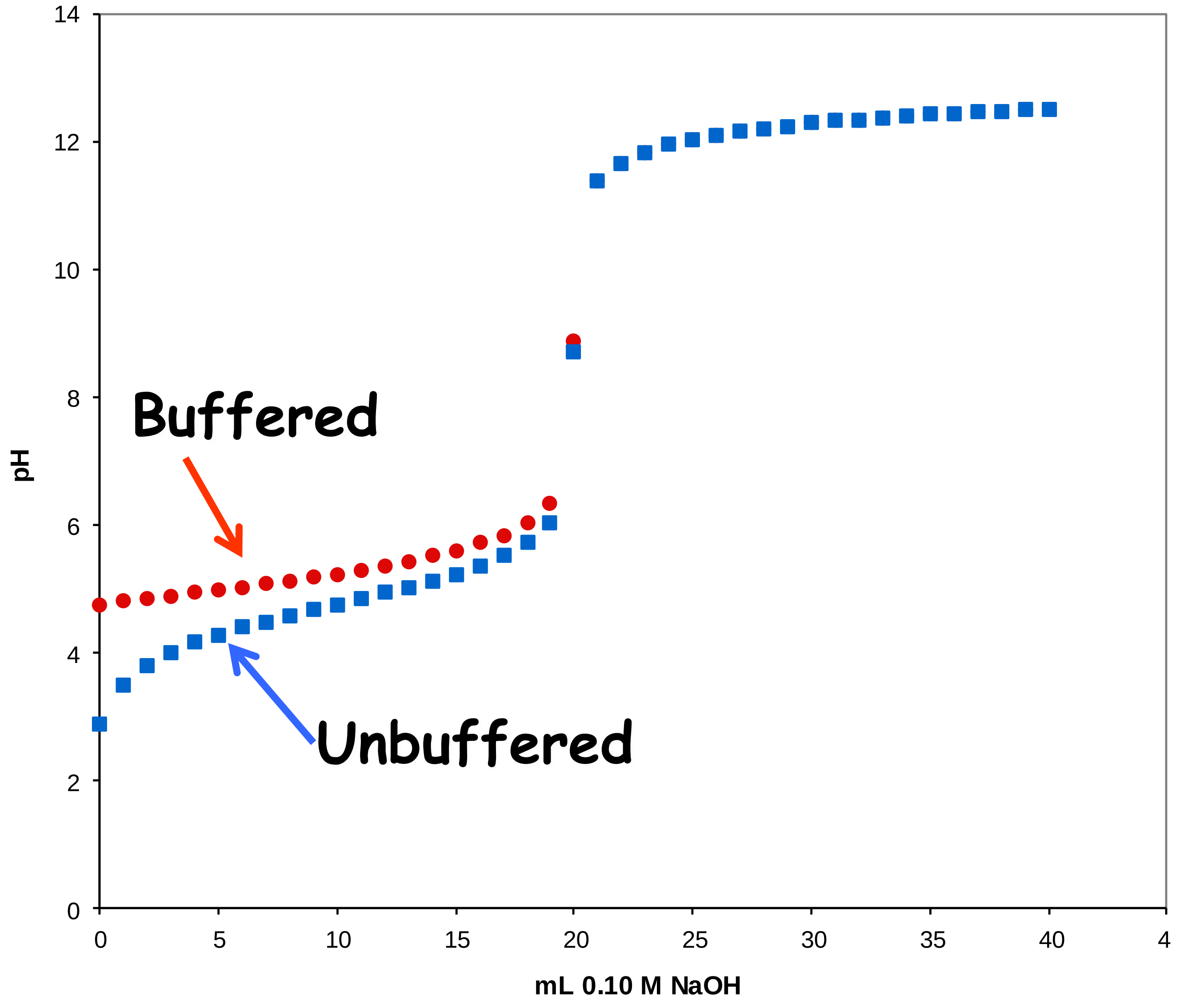


Buffered



- **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

Calculate the $[H^+]$ in a solution that is 0.10 M in NaF and 0.20 M in HF. ($K_a = 7.2 \times 10^{-4}$)

A. 7.2×10^{-4} M

B. 2.0 M

C. 1.4×10^{-3} M

D. 0.20 M

E. none of these

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

Calculate the $[H^+]$ in a solution that is 0.10 M in NaF and 0.20 M in HF. ($K_a = 7.2 \times 10^{-4}$)

Common Ion Effect!

- A. 7.2×10^{-4} M
- B. 2.0 M
- C. 1.4×10^{-3} M
- D. 0.20 M
- E. none of these

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

I	0.20	0	0.10
C			
E			
5%			

Calculate the $[H^+]$ in a solution that is 0.10 M in NaF and 0.20 M in HF. ($K_a = 7.2 \times 10^{-4}$)

Common Ion Effect!

A. 7.2×10^{-4} M

B. 2.0 M

C. 1.4×10^{-3} M

D. 0.20 M

E. none of these

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

I	0.20	0	0.10
C	-x	+x	+x
E			
5%			

Calculate the $[H^+]$ in a solution that is 0.10 M in NaF and 0.20 M in HF. ($K_a = 7.2 \times 10^{-4}$)

Common Ion Effect!

- **A** 7.2×10^{-4} M
- **B** 2.0 M
- **C** 1.4×10^{-3} M
- **D** 0.20 M
- **E** none of these

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

I	0.20	0	0.10
C	-x	+x	+x
E	0.20 – x	x	0.10 + x
5%			

Calculate the $[H^+]$ in a solution that is 0.10 M in NaF and 0.20 M in HF. ($K_a = 7.2 \times 10^{-4}$)

Common Ion Effect!

A. 7.2×10^{-4} M

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D. 0.20 M

E. none of these

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

I	0.20	0	0.10
C	-x	+x	+x
E	0.20 – x	x	0.10 + x
5%	0.20	x	0.10

Calculate the [H^+] in a solution that is 0.10 M in NaF and 0.20 M in HF. (K_a = 7.2 ×10^{-4})

A. 7.2 x 10^{-4} M

B. 2.0 M

C. 1.4 x 10^{-3} M

D. 0.20 M

E. none of these

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

$$Ka = \frac{[H^+][F^-]}{[HF]}$$

F^- present when you start because of the salt!

Calculate the $[H^+]$ in a solution that is 0.10 M in NaF and 0.20 M in HF. ($K_a = 7.2 \times 10^{-4}$)

- A. 7.2×10^{-4} M
- B. 2.0 M
- C. 1.4×10^{-3} M
- D. 0.20 M
- E. none of these

$$7.2 \, x \, 10^{-4} = \frac{[H^+][0.10]}{[0.20]};$$

$$[H^+] = 1.44 \, x \, 10^{-3} M$$

Calculate the $[H^+]$ in a solution that is 0.10 M in NaF and 0.20 M in HF. ($K_a = 7.2 \times 10^{-4}$)

- A) 7.2×10^{-4} M
- B) 2.0 M
- C) 1.4×10^{-3} M
- D) 0.20 M
- E) none of these

$$7.2\ x\ 10^{-4} = \frac{[H^+][0.10]}{[0.20]};$$

$$[H^+] = 1.44\ x\ 10^{-3} M$$

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
- B 0.70
- C 11.2
- D 3.14
- E none of these

$$[H^+] = 1.44\ x\ 10^{-3} M$$

$$pH = -log(1.44\ x\ 10^{-3} M)$$

$$pH = 2.84$$

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**
- B 0.70
- C 11.2
- D 3.14
- E none of these

$$[H^+] = 1.44\ x\ 10^{-3} M$$

$$pH = -log(1.44\ x\ 10^{-3} M)$$

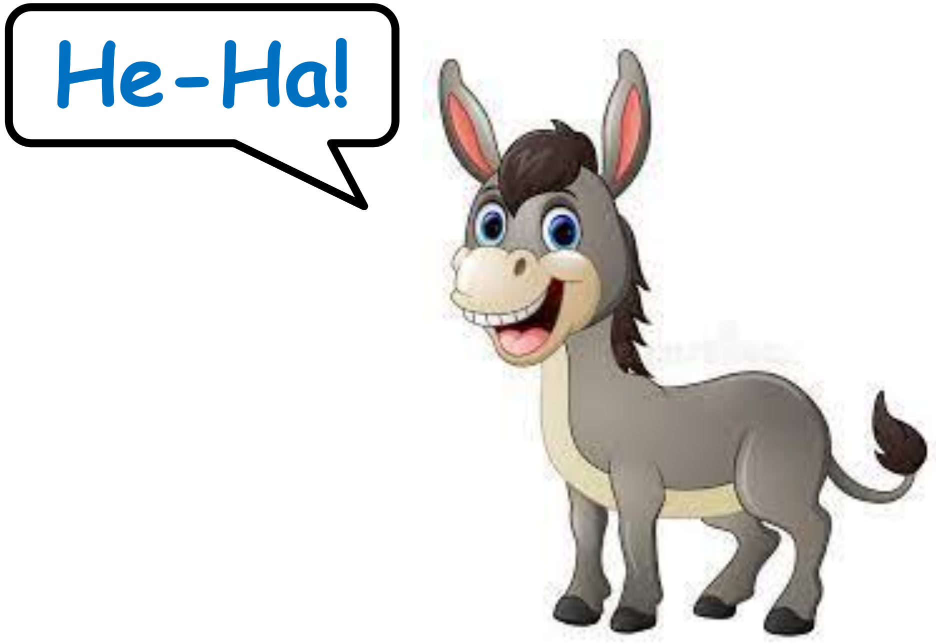
$$pH = 2.84$$

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

Other ways to think about He-Ha

Acid with a buffer:

$$pH = pKa + log\left(\frac{[salt]}{[Acid]}\right) = pK_a + log\left(\frac{\overset{salt}{[conj.Base]}}{[Acid]}\right)$$

Base with a buffer:

$$pOH = pKb + log\left(\frac{[salt]}{[Base]}\right) = pKb + log\left(\frac{\overset{salt}{[conj.Acid]}}{[Base]}\right)$$

Careful!

Check your formulas!

$$1.00\ M\ \ MgCl_2$$

$$= 2.00\ M\ Cl^-$$

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]

Calculate the $[H^+]$ in a solution that is 0.10 M in NaF and 0.20 M in HF. ($K_a = 7.2 \times 10^{-4}$)

- A. $7.2E^{-4}$ M
- B. 2.0 M
- C. $1.4E^{-3}$ M
- D. 0.20 M
- E. none of these

Calculate the $[H^+]$ in a solution that is 0.10 M in NaF and 0.20 M in HF. ($K_a = 7.2 \times 10^{-4}$)

- A. $7.2E^{-4}$ M
- B. 2.0 M
- C. $1.4E^{-3}$ M
- D. 0.20 M
- E. none of these

Acid solution with a salt added.

- HF = acid
- NaF = salt

The salt has the conjugate base of the acid.

- F^-

$$pH = pKa + Log\frac{[conj.Base\ Salt]}{[Acid]}$$

Calculate the $[H^+]$ in a solution that is 0.10 M in NaF and 0.20 M in HF. ($K_a = 7.2 \times 10^{-4}$)

A. $7.2E^{-4}$ M

B. 2.0 M

C. $1.4E^{-3}$ M

D. 0.20 M

E. none of these

$$pH = pKa + Log\frac{[conj.Base\ salt]}{[Acid]}$$

$$pH = -log[7.2E^{-4}] + log\frac{[0.1M]}{[0.2M]}$$

$$= 2.84$$

$[H^+] = 10^{-pH} = 10^{-2.84} = 0.00144M$

Calculate the $[H^+]$ in a solution that is 0.10 M in NaF and 0.20 M in HF. ($K_a = 7.2 \times 10^{-4}$)

A. $7.2E^{-4}$ M

B. 2.0 M

C. $1.4E^{-3}$ M

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E. none of these

$$pH = pKa + Log\frac{[conj. Base\ salt]}{[Acid]}$$

$$pH = -log[7.2E^{-4}] + log\frac{[0.1M]}{[0.2M]}$$

$$= 2.84$$

$[H^+] = 10^{-pH} = 10^{-2.84} = 0.00144M$

Buffer Capacity

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

If you keep the RATIO of salt to acid the same
but increase the QUANTITIES 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?

$$\frac{[\mathbf{0.05}]}{[\mathbf{0.10}]} \qquad \frac{[\mathbf{0.20}]}{[\mathbf{0.40}]}$$

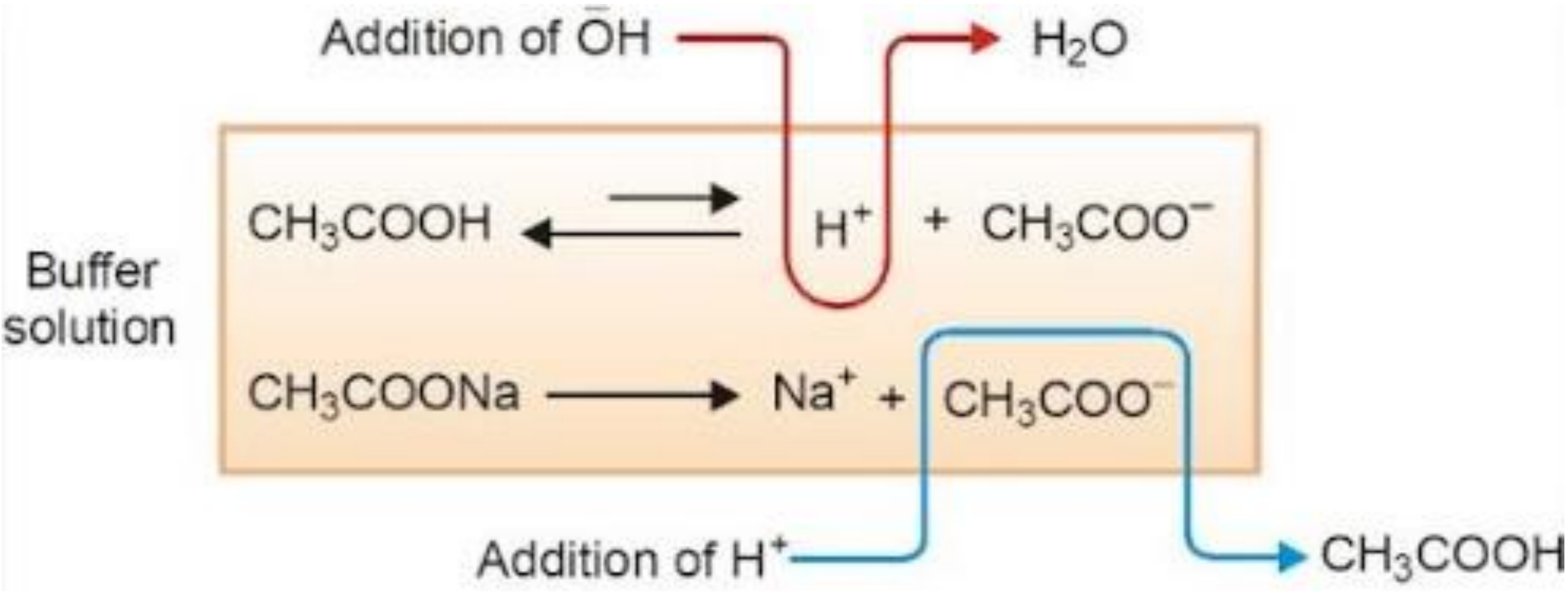
Max buffer capacity if you want it to work best for <u>BOTH</u> adding acid OR base, the "best" buffer would be a 1:1 ratio of salt to acid (or base)

$$\frac{[A^-]}{[HA]}$$

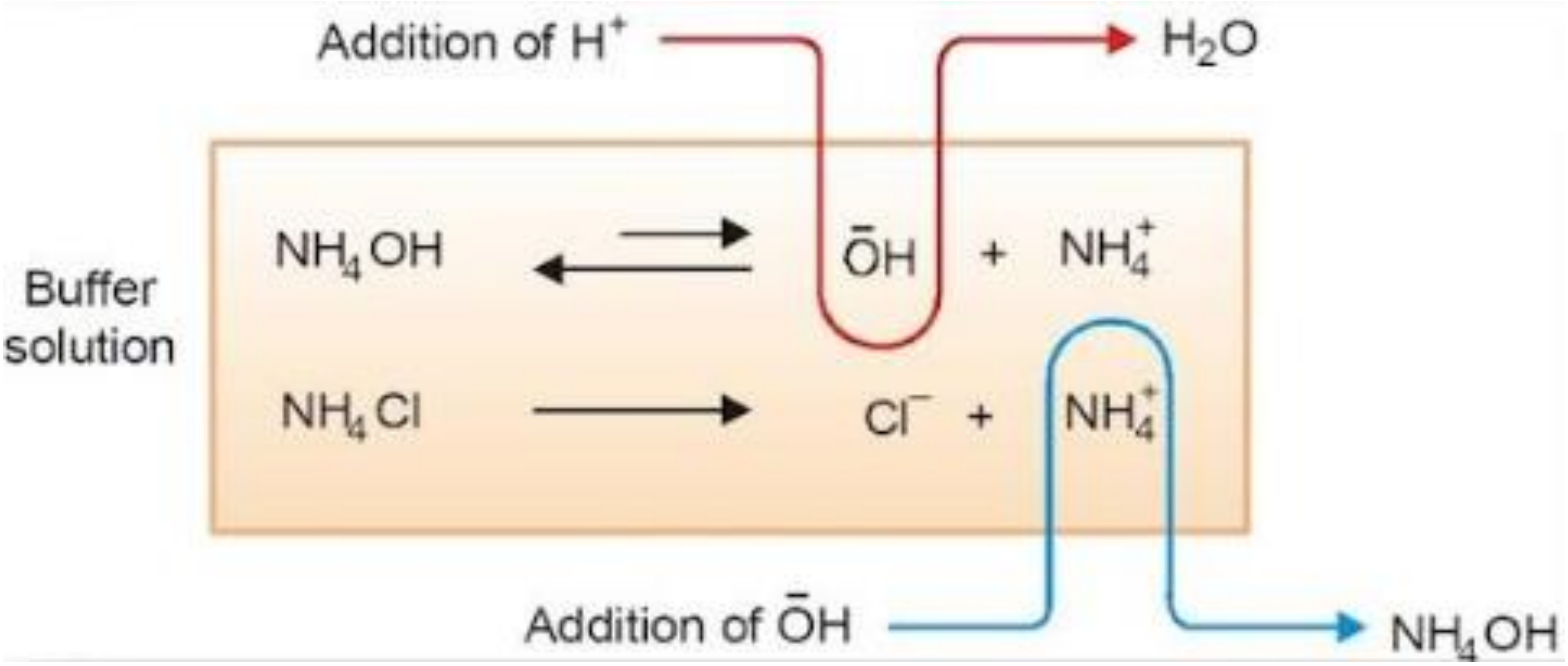
Will the pH of the buffered solution be the same or different if these were made with the same acid and the same salt? Why?

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



Suggestions…

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!

Suggestions…

Find your preferred method. They all have pros and cons.

Ice tables

Pro = familiar Con = takes forever, lots of steps

He-Ha

Pro = fast, on the AP eq. sheet Con = Have to recognize to use it, not always solving for pH

Rearranging Law of Mass Action

Pro = simple Con = Have to recognize to use it, extra step to get to pH or pOH

Suggestions…

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!

YES, 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.

Suggestions…

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You never know which info they will give you…

You want to be able to solve any variety of problems!

YES, 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.

Example - 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.

Suggestions…

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!

Example with Stoichiometry

- 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!**

Example with Stoichiometry

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

$$pH = pKa + Log \frac{[conj. Base\ salt]}{[Acid]}$$

$$pH = -log[1.77\ x\ 10^{-4}] + log \frac{[0.500\ M]}{[0.700\ M]}$$

$$= 3.61$$

Example with Stoichiometry

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

Example with Stoichiometry

(a) Calculate the pH of a 0.500 L buffer solution composed of 0.700 M formic acid (HCOOH , Ka = 1.77 x 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

$$HCOOH + NaOH \rightarrow H_2O + Na^+ + COOH^-$$

HCOOH: Weak Acid

NaOH: Strong Base

Na^+: Weak Conj. Acid

$COOH^-$: Conj. Base SALT

Weak Acid + corresponding Salt = BUFFER!

Example with Stoichiometry

(a) Calculate the pH of a 0.500 L buffer solution composed of 0.700 M formic acid (HCOOH , Ka = 1.77 x 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

$$HCOOH + NaOH \rightarrow H_2O + Na^+ + COOH^-$$

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

Example with Stoichiometry

(a) Calculate the pH of a 0.500 L buffer solution composed of 0.700 M formic acid (HCOOH , Ka = 1.77 x 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

$$HCOOH + NaOH \rightarrow H_2O + Na^+ + COOH^-$$

$$\frac{0.500\ \text{L HCOOH}}{} \Big| \frac{0.700\ \text{mol}}{1\ \text{L}}$$ **= 0.350 mol HCOOH** to start with

$$\frac{0.060\ \text{L}\ OH^-}{} \Big| \frac{1\ \text{mol}}{1\ \text{L}}$$ **= 0.060 mol OH^-** added

$$\frac{0.500\ \text{L}\ COOH^-}{} \Big| \frac{0.500\ \text{mol}}{1\ \text{L}}$$ **= 0.250 mol $COOH^-$** (and also mol Na^+) salt to start with

Example with Stoichiometry

(a) Calculate the pH of a 0.500 L buffer solution composed of 0.700 M formic acid (HCOOH , Ka = 1.77×10^{-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 table!

$$HCOOH + NaOH \rightarrow H_2O + Na^+ + COOH^-$$

HCOOH	NaOH	H_2O	Na^+	$COOH^-$
0.350 mol	0.060 mol	0	0.250 mol	0.250 mol

Example with Stoichiometry

(a) Calculate the pH of a 0.500 L buffer solution composed of 0.700 M formic acid (HCOOH , Ka = 1.77 x 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 table!

HCOOH + NaOH → H_2O + Na^+ **+ $COOH^-$**

0.350 mol	0.060 mol	0	0.250 mol	0.250 mol
-0.060	-0.060	+0.060	+0.060	+0.060

Example with Stoichiometry

(a) Calculate the pH of a 0.500 L buffer solution composed of 0.700 M formic acid (HCOOH , Ka = 1.77 x 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 table!

$$HCOOH + NaOH \rightarrow H_2O + Na^+ + COOH^-$$

HCOOH	NaOH	H_2O	Na^+	$COOH^-$
0.350 mol	0.060 mol	0	0.250 mol	0.250 mol
-0.060	-0.060	+0.060	+0.060	+0.060
0.290	0	0.060	0.310	**0.310**

BACK TO [ ] FOR THE HE-HA CALCULATIONS!

Example with Stoichiometry

Mole table!

$HCOOH$ + $NaOH$ →		H_2O +	Na^+ +	$COOH^-$
0.290	0	0.060	0.310	**0.310**

Back to [ ] !

$$pH = pKa + Log\frac{[conj.\,Base\ salt]}{[Acid]}$$

Yes, I know the volumes cancel out... but the eq. is a [ ] equation!

$$pH = -log[1.77\ x\ 10^{-4}] + log\frac{[0.310\ mol/(0.500\ L + 0.060\ L]}{[0.290\ mol/(0.500\ L + 0.060L)]}$$

$$= 3.78$$

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

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

H_3O^+ added, equilibrium position shifts to the left

$$CH_3COOH(aq) \leftarrow CH_3COO^-(aq) + H_3O^+$$

OH^- added, equilibrium position shifts to the right

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

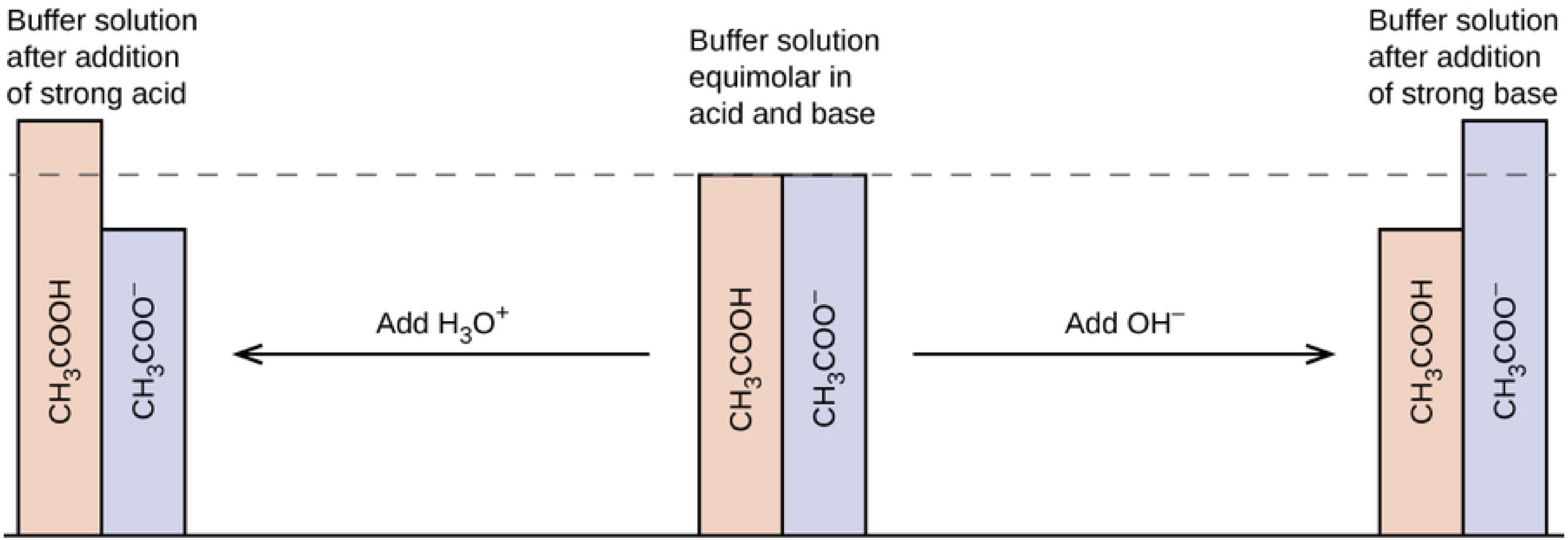

Figure 14.6.2: This diagram shows the buffer action of these reactions.

Crash Course Video

Buffers, the Acid Rain Slayer

https://youtu.be/8Fdt5WnYn1k?si=gaA6JxbNHhhIN-Nt

Bozeman Science Video

pH and Buffers

https://youtu.be/rIvEvwViJGk?si=CrPu5FtV0xLr8Amu

Professor Dave Video

Acid-Base Equilibria and Buffer Solutions

https://youtu.be/jdmHjFp_35I?si=jncpa2ZIOWpPH72Z

YouTube Link to Presentation

https://youtu.be/1c8eybhSmck