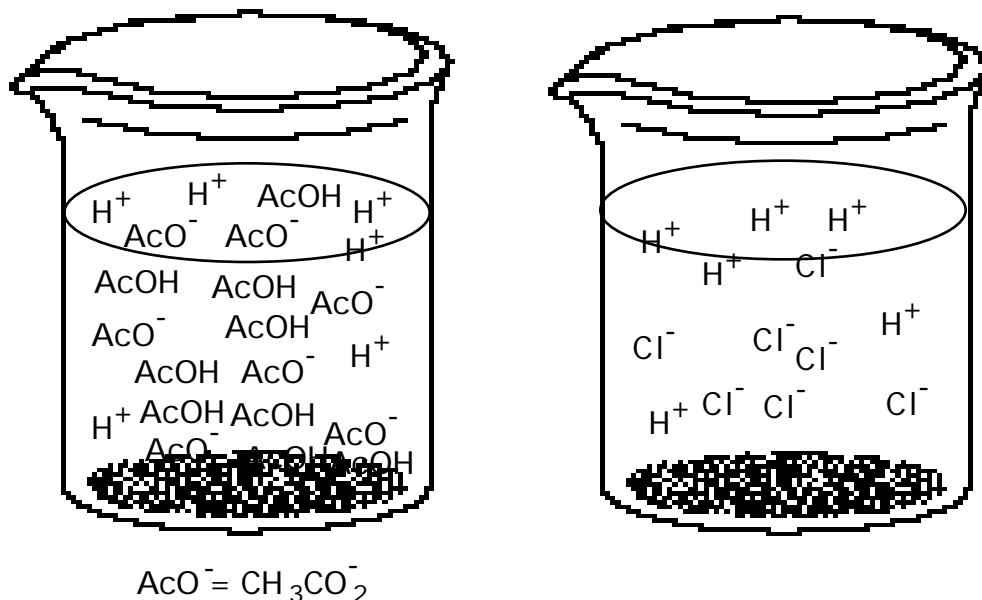


Compare 1 L of acetate buffer solution (0.50 mol of acetic acid and 0.50 mol sodium acetate) to 1 L of HCl solution



The acetate solution was made by dissolving 0.50 mol of acetic acid and 0.50 mol sodium acetate in 1 liter of water; at equilibrium $[\text{H}^+] = 1.8 \times 10^{-5} \text{ M}$.

The HCl solution was made by dissolving $1.8 \times 10^{-5} \text{ mol}$ of HCl in 1 liter of water.

Similarities

The pH of each of these solutions is the same; that is, the $[\text{H}^+]$ is the same in both beakers (go ahead and count).

Differences

The total amount of acid present is not the same.

$[\text{H}^+]$ is the same ($1.8 \times 10^{-5} \text{ M}$), but the acetate buffer contains additional acid in the form of undissociated acetic acid (0.50 M).

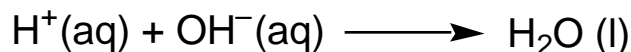
The amount of base present is not the same.

The HCl solution does not contain a base; Cl^- is the conjugate base, but the conjugate base of a strong acid does not act like a base.

The acetate buffer does contain a base; CH_3CO_2^- is the conjugate base, and the conjugate base of a weak acid is a weak base.

What happens when base is added to each flask. Say, 0.001 mol NaOH.

The following reaction occurs



So, the H^+ is consumed by the OH^- .

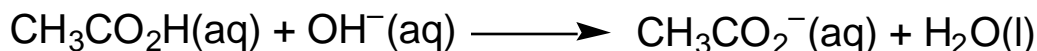
	H^+	OH^-	H_2O
start mol	0.000018	0.0010	
reaction	0.000018 -	0.0010 -	
	0.000018	0.000018	
after reaction	~0	9.82×10^{-4}	

Since it is a 1 L soln $[\text{OH}^-] = 9.82 \times 10^{-4}$ and find H^+ by using K_w

$$[\text{H}^+] = 10^{-14} / 9.82 \times 10^{-4} = 1.018 \times 10^{-11}$$

$$\text{pH} = 10.99$$

In the acetate flask the OH^- consumes the free H^+ and reacts with the H^+ still bound to the acetic acid



The concentration of acetic acid and acetate have both changed now

	$\text{CH}_3\text{C}(\text{O})\text{OH}$	OH^-	$\text{CH}_3\text{C}(\text{O})\text{O}^-$
start mol	0.50	0.0010	0.50
reaction	$0.50 - 0.0010$	$0.0010 - 0.0010$	$0.50 + 0.0010$
after reaction	0.499	~0	0.501

the amounts above are moles

The concentrations of the H^+ , CH_3CO_2^- , and $\text{CH}_3\text{CO}_2\text{H}$ are no longer equilibrium concentrations. The equilibrium will now react to the change.



Switch from limiting reagent to equilibrium problem...

	$\text{CH}_3\text{C}(\text{O})\text{OH}$	H^+	$\text{CH}_3\text{C}(\text{O})\text{O}^-$
I	0.499/1	~0	0.501/1.01
C	- x	+ x	+ x
E	0.499/1 - x	+ x	0.501/1.01 + x

$$1.8 \times 10^{-5} = \frac{(0.501 + x)x}{(0.499 - x)}$$

x is small...

$$1.8 \times 10^{-5} = \frac{(0.510)x}{(0.499)}$$

$$1.8 \times 10^{-5} = (0.510/0.499)x$$

$$x = 1.79 \times 10^{-5}$$

$$[\text{H}^+] = 1.79 \times 10^{-5} \quad \text{pH} = 4.75$$

In fact the $[\text{H}^+] = 1.79 \times 10^{-5}$ so $\text{pH} = 4.75$. The $[\text{H}^+]$ concentration only decreased by 0.0000001 even though 0.001 mole OH^- were added.

The weak acid (acetic acid) restored most of the lost protons.

What happens when more acid is added to each solution? Say 0.002 mol of HCl.

The HCl solution

The $[H^+] = 1.8 \times 10^{-5} \text{ mol} + 0.002 \text{ mol} = 0.002018 \text{ mol}$

$$\begin{aligned} \text{pH} &= -\log(0.002018) \\ &= 2.70 \end{aligned}$$

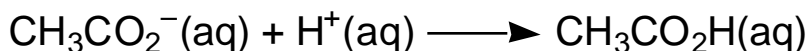
The acetate solution

Add HCl to the acetate buffer.



The $[H^+]$ increases, but once the $[H^+]$ increases the reaction is no longer at equilibrium. So, the equilibrium reacts to consume the extra protons. The acetate consumes the H^+ .

Treat this as a reaction of a strong acid with a weak base...



since $K = 1/1.8 \times 10^5$, this is a reaction that goes to completion.

	$\text{CH}_3\text{C}(\text{O})\text{O}^-$	H^+	$\text{CH}_3\text{C}(\text{O})\text{OH}$
start mol	0.50	0.0020	0.50
react	- 0.0020	- 0.0020	+ 0.0020
after rxn	0.498	~0	0.502

CH_3CO_2^- , a weak base, and $\text{CH}_3\text{CO}_2\text{H}$, a weak acid, are in solution.

Further, $[H^+]$ is listed as approximately zero. To find what the $[H^+]$ is an equilibrium problem must be solved.



	$\text{CH}_3\text{C}(\text{O})\text{OH}$	H^+	$\text{CH}_3\text{C}(\text{O})\text{O}^-$
init	0.502	~0	0.498
change	- x	+ x	+ x

equil 0.502 - x x 0.498 + x

$$1.8 \times 10^{-5} = \frac{(x)(0.498 + x)}{(0.502 - x)}$$

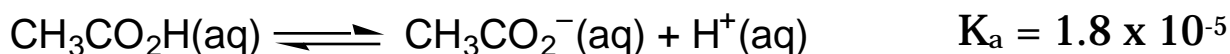
small x approx

$$x = 1.81 \times 10^{-5}$$

$$\text{pH} = 4.74$$

So, what makes a buffer? The presence of both a weak acid and the conjugate base.

Is a solution of acetic acid a buffer? NO. A solution acetic acid does not contain much base.



Acetic acid does not dissociate much so the amount of H^+ and CH_3CO_2^- is small.

Since the amount of acetate is small the solution cannot absorb any acid.

Is an acetate solution a buffer? No, there is nothing present to release protons.

Is a solution of NaCl and HCl a buffer?

NO. An acid and a conjugate base are present...yeah, but it is a strong acid, and the conjugate base is not a base.

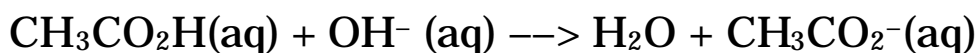


HCl dissociates 100% so there is no acid in reserve; that means, if base is added H⁺ is consumed, and there is no undissociated acid present to replace the H⁺ that have been consumed.

If H⁺ is added it remains free; Cl⁻ is such a weak base that it has no affinity for H⁺.

0.50 mol acetic acid are dissolved in 1 L of water. 0.25 mol NaOH are added. Is the resulting solution a buffer?

Yes! How is that a strong base and a weak acid is involved. Well if a strong base is added to the weak acid a reaction occurs.



	CH ₃ C(O)OH	OH	CH ₃ C(O)O ⁻
start mol	0.50	0.25	~0
reaction	- 0.25	- 0.25	+ 0.25
after rxn	0.25	~0	0.25

See, there is a solution of a weak acid and a weak base.

How do you make a buffer with a certain pH?

Well, pH is determined by [H⁺]

For an acid HA at equilibrium

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

or

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

if we start at an initial condition [HA]₀ and [A⁻]₀ then the [H⁺] = x

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

Since K_a is small the reaction is not going to proceed very far, especially since both reactants and products are already present. So, x is small.

So, $[HA] = [HA]_o - x \sim [HA]_o$ and $[A^-] = [A^-]_o + x \sim [A^-]_o$

so, $[H^+] = K_a ([HA]_o/[A^-]_o)$

furthermore, since it is concentration divided by concentration **the pH is determined by number of moles of acid divided by the number of moles of the conjugate base present in solution.**

let us take the $-\log$ of both sides

$$-\log[H^+] = -\log(K_a [HA]_o/[A^-]_o)$$

$$-\log[H^+] = -\log(K_a) + -\log([HA]_o/[A^-]_o)$$

$$pH = pK_a - \log([HA]_o/[A^-]_o)$$

or...

$$pH = pK_a + \log([A^-]_o/[HA]_o)$$

How would you make a buffer with a given pH...simple.

1. Pick the acid base system you want to use.
 - A buffer works best when there is an equal amount of acid and base present.
 - Pick an acid base system so that the pK_a is close to the pH

if $[A^-]/[HA] = 1$ then this relationship

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

simplifies to

$$\text{pH} = \text{pK}_a$$

if pK_a is close to the desired pH then $[\text{A}^-]/[\text{HA}]$ will not have to be far from 1

2. Use the Henderson-Hasselbalch equation or the K_a expression to find the ratio of acid to base required to give the desired pH.

If no special conditions have been stated then you have the answer.

For example

Prepare a buffer that has a pH of 3.50.

1. Check K_a / pK_a table for acid that has a K_a close to 3.50

I found HNO_2 has a $\text{pK}_a = 3.40$

2. Henderson-Hasselbalch equation

$$\text{pH} = \text{pK}_a + \log\left[\frac{[\text{NO}_2^-]}{[\text{HNO}_2]}\right]$$

$$3.50 = 3.40 + \log\left[\frac{[\text{NO}_2^-]}{[\text{HNO}_2]}\right]$$

$$0.10 = \log\left[\frac{[\text{NO}_2^-]}{[\text{HNO}_2]}\right]$$

$$1.26 = \frac{[\text{NO}_2^-]}{[\text{HNO}_2]}$$

So, I could use 1 mol HNO_2 and 1.26 mol NO_2^- (NaNO_2 if it is available).

If NaNO_2 is not available how would I make the solution?

I would start with 2.26 mol HNO_2 and add 1.26 mol NaOH .

Why? Because



So, 1.26 mol NaOH consumes 1.26 mol HNO₂ leaving 1 mol HNO₂ and 1.26 mol NaNO₂.

	HNO ₂	OH ⁻	NO ₂ ⁻
init	2.26 mol	1.26 mol	~0
rxn	- 1.26	- 1.26	+ 1.26
after rxn	1	~0	1.26

If any special conditions have been set forth you must now take them into account.

For example
concentration limits

limit concentration of 1 species

Prepare 1 L of the buffer above and the concentration of acid ([HNO₂]) must be 2.0 M.

so special condition says

$$1 \text{ L} \times \frac{2.0 \text{ mol HNO}_2}{1 \text{ L}} = 2.0 \text{ mol HNO}_2$$

you know the ratio of acid to base

$$\text{NO}_2^- / \text{HNO}_2 = 1.26$$

so amount of NO₂⁻

$$\text{NO}_2^- = 2.0 \cdot 1.26$$

$$\text{NO}_2^- = 2.52 \text{ mol}$$

limit total concentration

Prepare 500 mL of the buffer and the total concentration of acid and base must be 2.0 M.

so special condition says

$$0.50 \text{ L} \times \frac{2.0 \text{ mol (HNO}_2 + \text{Na}^+ + \text{NO}_2^-)}{1 \text{ L}} = 1.0 \text{ mol (HNO}_2 + \text{Na}^+ + \text{NO}_2^-)$$

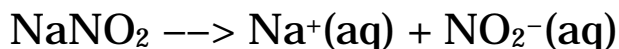
you know the ratio of acid to base

$$\text{NO}_2^- / \text{HNO}_2 = 1.26$$

or

$$1.26 \cdot \text{HNO}_2 = \text{NO}_2^-$$

and since



$$\text{Na}^+ = \text{NO}_2^-$$

substitute

$$1.0 \text{ mol} = \text{HNO}_2 + 1.26 \cdot \text{HNO}_2 + 1.26 \cdot \text{HNO}_2$$

$$1 = 3.52 \text{ HNO}_2$$

$$\text{HNO}_2 = 0.28 \text{ mol} \quad \text{and} \quad \text{NO}_2^- = 0.36 \text{ mol}$$

The special conditions are always the hard part here.

If you wanted to prepare an acetate buffer, pH = 4.69, you could prepare any of the following solutions

a 1.0 M acetic acid, 0.90 M sodium acetate solution

a 0.05 M acetic acid, 0.045 M sodium acetate solution

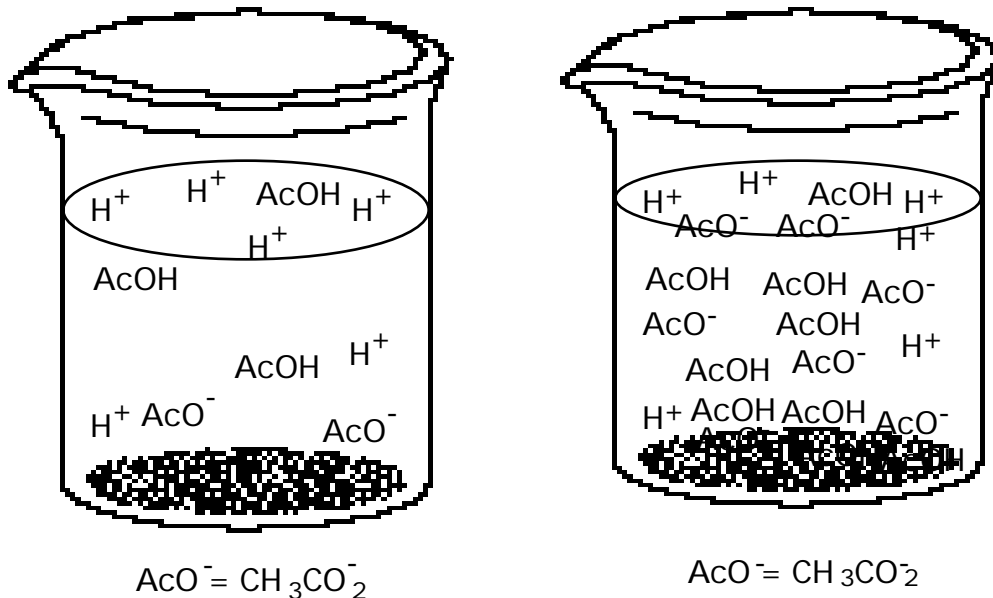
a 0.02 M acetic acid, 0.018 M sodium acetate solution

All these buffers have the same pH, but they are different...

They have different capacities.

The first solution will absorb more acid or base than the others, and it will have the smallest change in pH when each solution absorbs the same amount of acid or base.

Compare two acetate buffers



Both solutions contain the same $[\text{H}^+]$ because $[\text{H}^+]$ is controlled by ratio of acid to conjugate base, and both solutions are 3 acetates for every 2 acetic acids.

What is the pH of the solution?

$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]}$$

$$\text{pH} = 4.74 + \log(3/2)$$

$$\text{pH} = 4.74 + 0.176$$

$$\text{pH} = 4.92$$

The solution on the right has more acetate present so it can absorb more protons.

The solution on the right also has more acetic acid present so it can release more protons when a base is added.

The capacity of the solution on the right is higher.

Translation: the solution on the right can absorb more acid or base with a smaller amount of change in pH than the solution on the left.

The grand-daddy pain in the neck special case

Prepare 500 mL of a buffer with a pH of 3.50 which will absorb 0.010 mol H⁺ with a pH change of 0.02 pH units.

Dissect the problem...prepare buffer of certain pH translates to pick acid find appropriate acid base ratio...

So we pick HNO_2 because the $\text{pK}_a = 3.40$

determine ratio of acid to base

$$\text{pH} = \text{pK}_a + \log[\text{NO}_2^-]/[\text{HNO}_2]$$

$$3.50 = 3.40 + \log[\text{NO}_2^-]/[\text{HNO}_2]$$

$$0.10 = \log[\text{NO}_2^-]/[\text{HNO}_2]$$

$$1.26 = [\text{NO}_2^-]/[\text{HNO}_2]$$

Now the hard part...pH change of 0.02 when 0.01 mol H⁺ are added translates to pH can drop to 3.48 after the solution has reacted with 0.01 mol H⁺.

So, what does the solution look like after 0.01 mol H⁺ are added.

What happens when H⁺ is added?

NO₂⁻ reacts with H⁺ to make HNO₂

	HNO ₂	H ⁺	NO ₂ ⁻
init	HNO ₂	0.01	NO ₂ ⁻
reaction	+ 0.01	- 0.01	- 0.01
after rxn	HNO ₂ + 0.01	~0	NO ₂ ⁻ - 0.01

so after the acid has been added

$$\text{pH} = \text{pK}_a + \log(\text{NO}_2^-/\text{HNO}_2)$$

putting numbers in

$$3.48 = 3.50 + \log \frac{(\text{NO}_2^- - 0.01)}{(\text{HNO}_2 + 0.01)}$$

but since we know

$$1.26 = [\text{NO}_2^-]/[\text{HNO}_2] \quad \text{or} \quad 1.26 \cdot [\text{HNO}_2] = [\text{NO}_2^-]$$

$$3.48 = 3.50 + \log \frac{(1.26 \cdot \text{HNO}_2 - 0.01)}{(\text{HNO}_2 + 0.01)}$$

$$0.02 = \log \frac{(1.26 \cdot \text{HNO}_2 - 0.01)}{(\text{HNO}_2 + 0.01)}$$

$$1.047 = \frac{(1.26 \cdot \text{HNO}_2 - 0.01)}{(\text{HNO}_2 + 0.01)}$$

$$1.047 \cdot \text{HNO}_2 + 0.001047 = 1.26 \cdot \text{HNO}_2 - 0.01$$

$$-0.213 \text{ HNO}_2 = -0.011047$$

$$\text{HNO}_2 = 0.052 \text{ mol (0.0519)}$$

$$\text{NO}_2^- = 0.065 \text{ mol}$$

Remember when you do these problems if you add say 10 mL of a 0.2 M NaOH solution to 500 mL of a 1 M acetic acid 1 M acetate buffer solution the neutralization reaction is done in MOLES

0.002 mol NaOH reacts with 0.500 mol CH₃CO₂H leaving 0.498 mol

	CH ₃ CO ₂ H	NaOH	CH ₃ CO ₂ ⁻
start	0.50	0.0020	0.50
reaction	- 0.0020	- 0.0020	+ 0.0020
after rxn	0.498	~0	0.502

The molarity is used when doing the equilibrium part of the reaction; the volume is 0.50 + 0.010 = 0.51 L.

	CH ₃ CO ₂ H	H ⁺	CH ₃ CO ₂ ⁻
mol/L	0.498/0.51	~0	0.502/0.51
initial	0.976	~0	0.984
change	- x	+ x	+ x
equilibrium	0.976 - x	x	0.984 + x

$$1.8 \times 10^{-5} = \frac{x(0.984 + x)}{(0.976 - x)}$$

$$1.8 \times 10^{-5} = \frac{x(0.984)}{(0.976)}$$

$$1.8 \times 10^{-5} = \frac{x(0.984)}{(0.976)}$$

$$1.78 \times 10^{-5} = x$$

$$[H^+] = 1.78 \times 10^{-5}$$