

Symbols HA = weak acid H^+ = strong acid
 A^- = conjugate base of weak acid (so, weak base) OH^- = strong base

BUFFERS

In some situations, a change in pH can cause extreme reactions to occur. For example, the pH of blood should be from 7.38-7.42. If it changes to 7 or 8, we would die. We must therefore have a mechanism to protect against even a slight change in pH. The chemical that does this is called a buffer. Buffers maintain pH, they do not make solutions neutral.

Buffer Components:

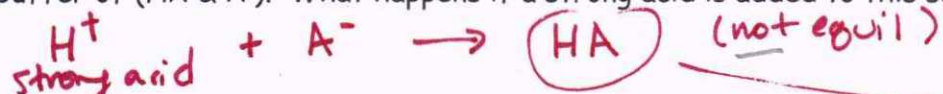
Buffers are made of 2 solutes that contain an acid/base conjugate pair (HA/A^-)

Ex. $(HC_2H_3O_2 \text{ \& \; } NaC_2H_3O_2)$ $(H_2CO_3 \text{ \& \; } HCO_3^-)$ $(NH_4^+ \text{ \& \; } NH_3)$
 * in blood

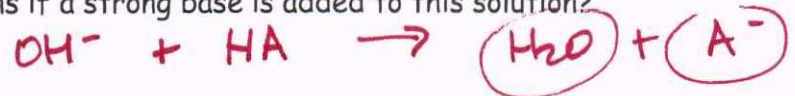
How Buffers Work:

A buffer must neutralize any strong acid or base added so that the original pH remains constant. One solute in the buffer will neutralize the acid, the other solute neutralizes the base.

Consider a buffer of $(HA \text{ \& \; } A^-)$. What happens if a strong acid is added to this solution?



What happens if a strong base is added to this solution?



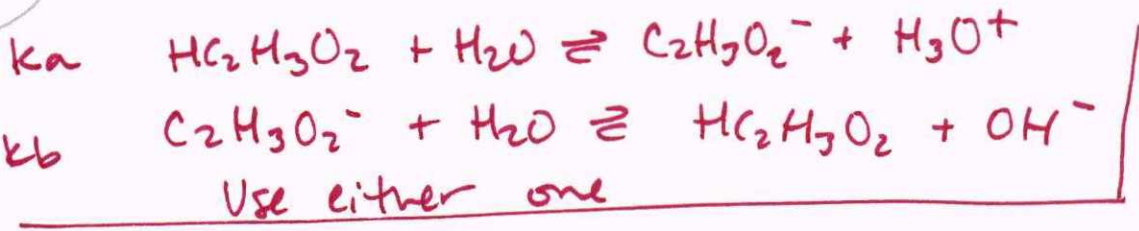
none of these species change the pH!

Calculating the pH of a Buffered Solution:

To calculate pH, write either the K_a or the K_b reactions that are occurring. Use the equation to determine the $[H^+]$ which can be used to calculate pH.

Ex. 1: A buffer solution contains 0.090 M acetic acid and 0.11 M sodium acetate. What is the pH?

Do #82



	HA	\rightleftharpoons	$C_2H_3O_2^-$	$+$	H^+
i	.090		.11		0
D	-x		+x		+x
e	.09-x		.11+x		x

$K_a = 1.8 \times 10^{-5} = \frac{(11+x)(x)}{.09-x}$

$x = 1.5 \times 10^{-5}$
 $= [H^+]$

$pH = 4.82$

The pH of a buffer depends on 1) K_a or K_b and 2) the ratio of $[HA] / [A^-]$.
 Diluting a buffer (does, does not) change its pH because it does not change K_a .

The basic K_a expression can be rearranged to another useful equation known as Henderson -

Hasselbalch Eqn. $[H^+] = K_a \frac{[HA]}{[A^-]}$

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

take -log of the eqn. \rightarrow $pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$
 or $pOH = pK_b + \log\left(\frac{A}{B}\right)$

According to the HH Eqn, when $[acid] = [base]$, $pH = pK_a$.

Simplifications (neglecting x) will always work for buffers, therefore the amount of acid or base ionized when a strong acid or base is added to a buffer can be neglected. Therefore, the initial concentrations can be plugged straight into the HH Eqn. in order to determine $[H^+]$ & pH .

Ex. 2: A buffer solution contains 0.090 M acetic acid and 0.11 M sodium acetate. What is the pH?
 (This is the same as Ex. 1. Solve this now using the HH Eqn.)

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

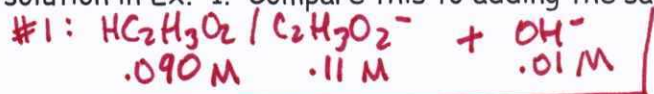
$$pH = -\log(1.8 \times 10^{-5}) + \log\left(\frac{.11}{.09}\right)$$

$$4.74 + .08715 = 4.83$$

Calculating ΔpH when a Strong Acid or Base is Added to a Buffer System:

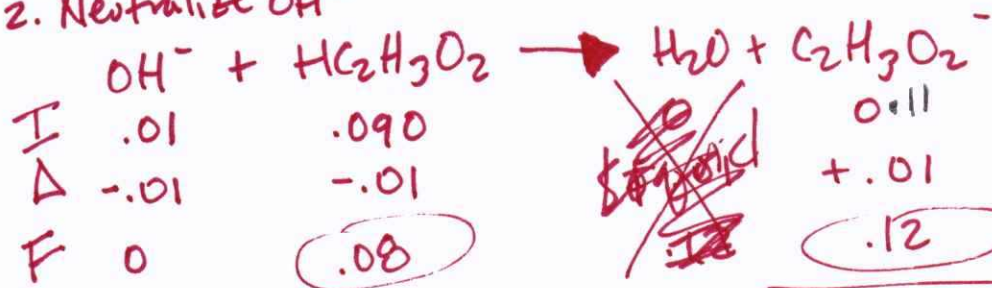
To determine changes in pH, you must first determine the original pH of the buffered solution. Then you must neutralize the strong base or acid that has been added. Last, to figure out the pH, you must determine the amount of $[H^+]$ that remains.

Ex. 3: Calculate the ΔpH that occurs when 0.010 moles of NaOH is added to 1.0 L of the buffered solution in Ex. 1. Compare this to adding the same amount of NaOH to pure water.



1. Original pH = 4.83

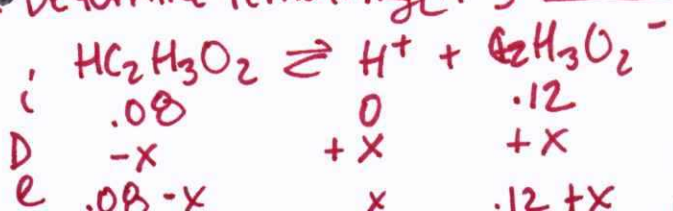
2. Neutralize OH^-



OR.
 3. Use HH Eqn.
 $pH = pK_a + \log\left(\frac{B}{A}\right)$
 $= -\log 1.8 \times 10^{-5} + \log\left(\frac{.12}{.08}\right)$
 $pH = 4.9$

NaOH in H_2O
 $[OH^-] = .01$ $pOH = 2$
 $pH = 12$

3. Determine remaining $[H^+]$



$$K_a = 1.8 \times 10^{-5} = \frac{x(x + .12)}{.08 - x}$$

$$x = 1.2 \times 10^{-5} M = [H^+]$$

$$pH = 4.9$$

Preparing a Buffer of a Given pH:

Buffers are made so that the ratio of HA / A⁻ is near 1. This makes the pH = pka

from HH Eqn.

1) Choose a weak acid with a pka near the needed pH. (pH = pka ± 1)

2) Adjust the ratio to get the exact desired pH.

of $[A^-]/[HA]$

Ex. 4: A solution buffered at pH = 5 is needed. Can we use HC₂H₃O₂/NaC₂H₃O₂ & in what ratio?

1) Check to see if pH = pka ± 1:

Ka = 1.8 x 10⁻⁵ pka = 4.7

so Yes

2) Adjust the ratio:

ka = $\frac{[H^+][A^-]}{[HA]}$ rearrange to solve for ratio $\frac{[A^-]}{[HA]}$

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

pH = 5
[H⁺] = 10⁻⁵

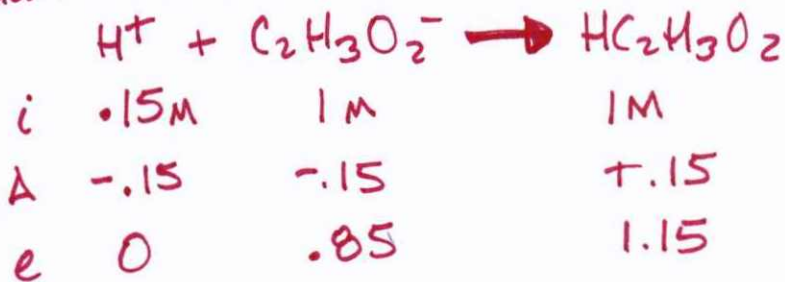
$\frac{1.8 \times 10^{-5}}{1 \times 10^{-5}} = \frac{1.8}{1}$ or $\frac{.18 \text{ M}}{.1 \text{ M}}$

Buffer Capacity:

There is a limit to the amount of strong base or acid that a buffer can neutralize. This limit is known as buffer capacity. Buffer capacity is determined by concentrations (or amounts) of HA & A⁻, NOT by the ratio.

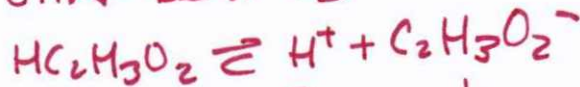
Ex. 5: A student prepared 1 L of a 1 M HC₂H₃O₂ and 1 M NaC₂H₃O₂ buffer for an experiment where 0.15 mol of H⁺ was to be generated. If there enough buffer capacity to neutralize the H⁺ without changing the pH by more than .1? — so calculate pH of buffer & pH w/ H⁺ added

Neutralize:



(1) pH of Buffer:

Either ka or kb



i	1	0	1
e	-x	+x	+x
	1-x	x	1+x

1.8 x 10⁻⁵ = x = [H⁺]

pH = 4.74

Calculate new H⁺ w/ ka (Use HH)

$pH = pka + \log\left(\frac{[B]}{[A]}\right)$
 $= -\log 1.8 \times 10^{-5} + \log\left(\frac{.85}{1.15}\right)$

pH = 4.61

ΔpH = .13

NO