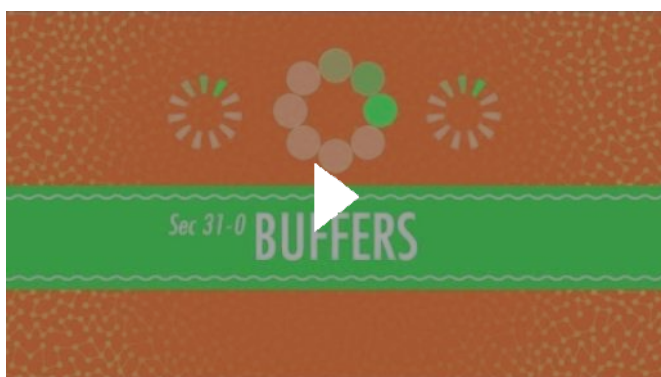


VI) Buffers

March 5, 2018 1:49 PM

[Buffers, the Acid Rain Slayer: Crash Course Chemistry #31](#)



4. Read Hebden p.161 (bottom) & 162 on Universal Indicators
 Do Hebden p.162 #108-112 and p.163 #116-119
5. The indicator thymol blue has two colour changes (see the acid-base indicator table). How is this possible?

VI) Buffers

What is a buffer? *a solution contains equal amounts of a weak acid & its conjugate weak base. It is an equilibrium solution that keeps the pH steady when an acid (or base) is added to the system.*
 => prevent large Δ in pH.

What composes a buffer?

- Large, equal concentrations
 - weak acid / conjugate base
- For example: acetic acid buffer \leftarrow 1.0L of 1.0M CH_3COOH
 1.0L of 1.0M NaCH_3COO *a spect ion*
 $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$
add NaCH_3COO cause a shift left \downarrow $[\text{H}_3\text{O}^+]$

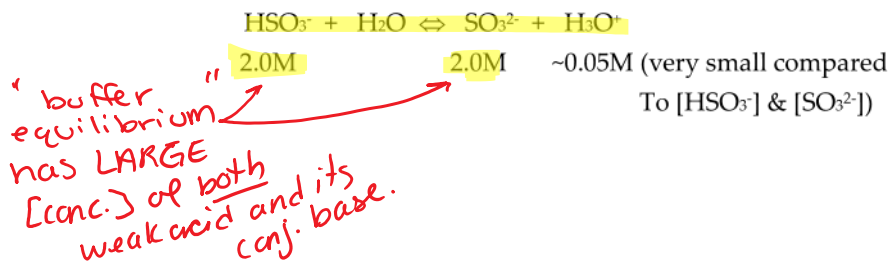
How would you make an $\text{HSO}_3^-/\text{SO}_3^{2-}$ 2.0M buffer solution?

- ① add 2.0M Na_2SO_3 to water to create an equilibrium
 $\text{Na}_2\text{SO}_3 \rightarrow \text{Na}^+ + \text{SO}_3^{2-}$ *w.B*
 $\text{SO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^- + \text{OH}^-$ *basic solution low conc.*
- ② add 2.0M NaHSO_3 to the 'basic solution' formed
 $\text{NaHSO}_3 \rightarrow \text{Na}^+ + \text{HSO}_3^-$
 $\text{HSO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_3^{2-}$ *u. low conc. HSO_3^-*
** by adding the w.a. we get \uparrow [conc.] of BOTH SO_3^{2-} and HSO_3^-*

Would you have a buffer if you simply add 2.0M NaHSO_3 to water? Why or why not?

(if we only did step ②)
 No, because you would have a \uparrow $[\text{HSO}_3^-]$ BUT, without adding more of the conjugate base SO_3^{2-} the equilibrium will not shift, and the $[\text{SO}_3^{2-}]$ will be very low. (b/c HSO_3^- dissoci. $< 5\%$)

Let's suppose you've made a $\text{HSO}_3^-/\text{SO}_3^{2-}$ 2.0M buffer:



How does a buffer work?

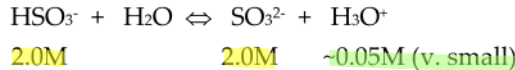
What determines pH in any solution?



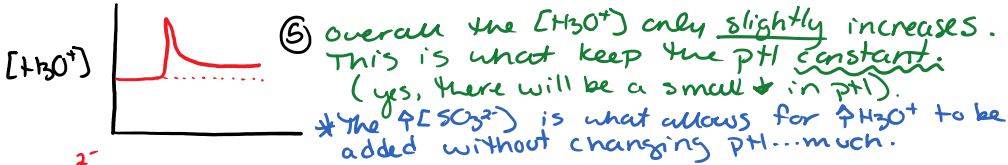
Therefore, if $[H_3O^+]$ and $[OH^-]$ can somehow be kept constant in the buffer solution, the pH will not drastically change.

Add ACID

What would happen if a small amount of HCl were added to the buffer solution? $HCl + H_2O \rightarrow Cl^- + H_3O^+$ (1) $\uparrow [H_3O^+]$ initially.



(4) causes $\uparrow [HSO_3^-]$, while $[SO_3^{2-}]$ and $[H_3O^+]$ decrease as they get used up. \leftarrow (3) equilibrium shift LEFT. (2) $\uparrow [H_3O^+]$ will \uparrow RVS rxn rate



$H_3O^+ + SO_3^{2-} \rightleftharpoons H_2O + HSO_3^-$
 run out of reactants for the RVS rxn.

You could keep adding HCl (which immediately becomes H_3O^+) and as long as there is sufficient SO_3^{2-} available in the solution, the H_3O^+ that forms due to HCl addition will react with SO_3^{2-} to form H_2O and HSO_3^- (a shift left in the equilibrium). Since most of the H_3O^+ reacts and is no longer present, the pH will not drastically change.

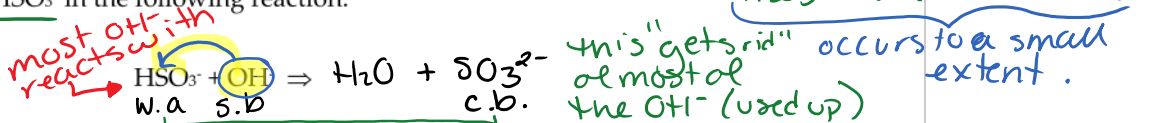
If HCl continues to be added, eventually SO_3^{2-} will be depleted enough so that H_3O^+ will no longer have anything to react with. What happens in this situation?

The buffer equilibrium will "break down", if SO_3^{2-} is used up. There is no longer any base present to react with H_3O^+ . At this point, any additional HCl added $\rightarrow Cl^- + H_3O^+$. $\uparrow [H_3O^+]$ causes a drastic \uparrow in pH.

Add Base

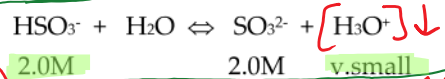
strong base (paired w group 1 or 2 cation)

If OH^- is added to our buffer solution, a small amount of it will react with the small amount of H_3O^+ present, but the majority will react with the weak acid HSO_3^- in the following reaction:



This is just like the original buffer equilibrium shifting to the right since HSO_3^- is turning into SO_3^{2-} :

(3) $[H_3O^+] \uparrow$ as a product of FWD rxn returns to original... almost



(1) initially $[H_3O^+] \downarrow$ as OH^- is added.

(2) shift RIGHT to counteract $\downarrow [H_3O^+]$ (FWD rxn is faster)

The critical idea here is that almost all of the OH^- being added reacts with

(returns to orig. almost)

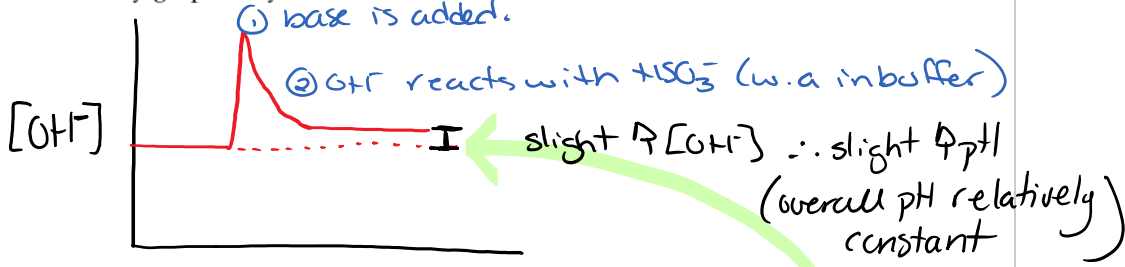
(2) shift RIGHT to counteract (Le Chatelier)
(FWD rxn is faster)

b/c of the R [HSO₃⁻]

The critical idea here is that almost all of the OH⁻ being added reacts with HSO₃⁻ to make water and SO₃²⁻, thereby 'getting rid' of OH⁻, so the pH of the solution will not rise drastically. It will, however, rise slightly.

↳ OH⁻ used up almost as soon as it is added.

Show why graphically:



Not quite all of the OH⁻ added will react, thus the pH will rise slightly.

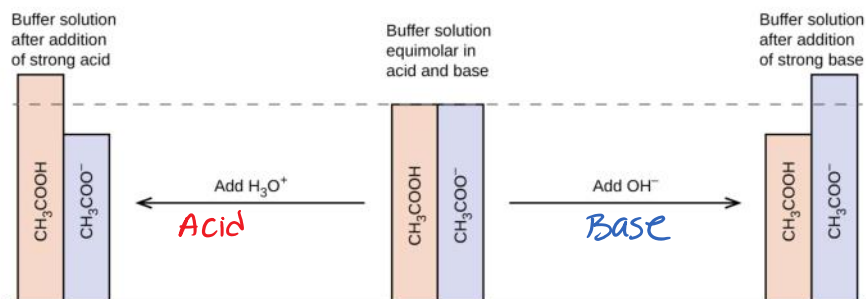
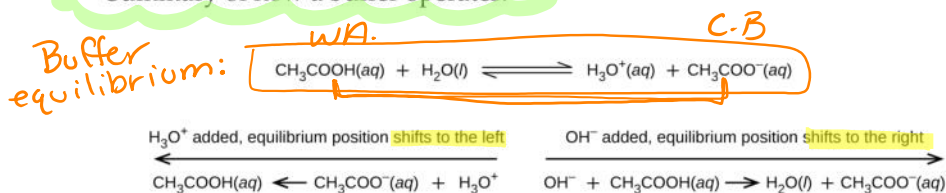
If too much OH⁻ is added, all of the HSO₃⁻ will eventually be used up and the buffer will collapse.

weak acid depleted through shift RIGHT (FWD rxn)

* The key to a functional buffer is the large, equal concentrations of a weak acid and its conjugate base.

The **weak conjugate base** (in our example SO_3^{2-}) is present **in large amounts** to **react with and deplete H_3O^+ added to the solution**. The **weak acid** (in our example HSO_3^-) is present **in large amounts** to **react with and deplete any OH^- added to the buffer**. Thus, the pH of the solution cannot drastically change as it is solely dependent on $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$.

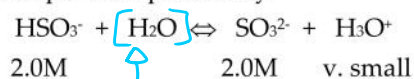
Summary of how a buffer operates:



Diluting a Buffer

Does diluting a buffer with water affect its performance?

Take the example used previously:

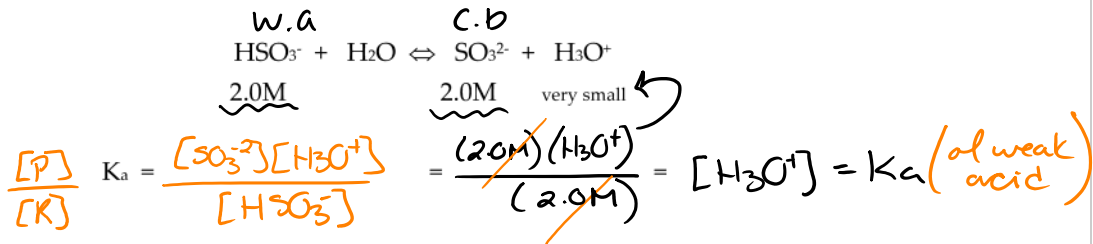


Adding water to the above equilibrium system will cause each concentration to decrease. Will it still work as a buffer? *depends on how much the [conc.] ↓, but yes. The buffer equilibrium will not last as long.*

Acidic and Basic Buffers

Each weak conjugate acid/base buffer system has a unique pH that it buffers.

The pH can be found by using the K_a of the weak acid. For example:



For the HSO_3^- : w. acid.

$$K_a = [\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}$$

Therefore, the pH of $\text{HSO}_3^-/\text{SO}_3^{2-}$ buffer system is $-\log(1.0 \times 10^{-7})$

$$= \underline{7.00}$$

Thus, the $\text{HSO}_3^-/\text{SO}_3^{2-}$ buffer system is called a neutral buffer.

$K_a > 1.0 \times 10^{-7} \therefore$ buffering pH < 7 **Acidic Buffer ***

Weak acids that have K_a values greater than 1.0×10^{-7} have buffering pHs less

than 7, thus they are called **acidic buffers**. Weak acids that have K_a values

less than 1.0×10^{-7} will have buffering pHs greater than 7, and are deemed

basic buffers.

$K_a < 1.0 \times 10^{-7} \therefore$ buffering pH > 7 **Basic Buffer**

Example: Find the buffering pH of an acetic acid / acetate buffer.



pH \rightarrow need $[\text{H}_3\text{O}^+] = K_a$

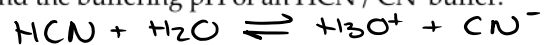
$$K_a = 1.8 \times 10^{-5} > 1.0 \times 10^{-7}$$

$$\therefore [\text{H}_3\text{O}^+] = 1.8 \times 10^{-5}$$

$$\text{buffering pH} = -\log(\underbrace{1.8 \times 10^{-5}}_{2 \text{ s.f.}}) = \underline{4.74} \quad \text{Acidic Buffer.}$$

\uparrow 2 d.p. ²⁷

Example: Find the buffering pH of an HCN / CN⁻ buffer.



$$K_a = 4.9 \times 10^{-10} = [\text{H}_3\text{O}^+]$$

$$\therefore \text{buffering pH} = -\log(4.9 \times 10^{-10}) = 9.31$$

BASIC
Buffer.

Assignment 7: Buffer Exercises

Read Hebden p.177-181 (stop after first paragraph on 181)

1. What composes a buffer and how would you make one?
2. Do Hebden p. 181 -182 #131-140
3. Read Hebden p. 182-183: *Buffers in Biological Systems*
What is the buffering pH in your blood?
What two buffering systems contribute to this?