

Buffers: General Ideas

In buffers you want solutions that don't change pH when a little H^+ or OH^- is added to them. You want any changes in $[\text{H}^+]$ to be buffered out. You accomplish this by making **a solution of a weak acid and the conjugate base (anion) of the weak acid**.

It's a pretty simple idea, if you have a weak acid, generically HA, then its equilibrium looks like:



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

You put in roughly equal amounts of the weak acid and, HA, its anion A^- (like you could add the same amounts of Acetic Acid, $\text{HC}_2\text{H}_3\text{O}_2$ and sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$) and you now have two molecules in the solution that are looking to grab up any extra OH^- 's (the acetic acid) or H^+ 's (the acetate ion) that happen to get in there.

Generally,

- The weak acid will react with OH^- 's: $\text{HA} + \text{OH}^- \longrightarrow \text{A}^- + \text{H}_2\text{O}$
- The acid anion will react with H^+ 's to form the weak acid: $\text{A}^- + \text{H}^+ \longrightarrow \text{HA}$

When you make a buffer, lots of HA and A^- are initially added therefore, little changes in their concentration because of the above reactions are considered to be negligible and it's just assumed that their concentrations are constant. If you look at the equilibrium of the weak acid you can see how this translates to a constant $[\text{H}^+]$

$$K_a = \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]} \xrightarrow{\text{do a little algebra}} [\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

So $[\text{H}^+]$ is pretty stable even if small amounts of OH^- or H^+ enter the solution.

That's how a buffer works

Now, you see how the K_a of the weak acid is directly proportional to the $[\text{H}^+]$ concentration in a particular buffer (depending on what your ratio of weak acid to acid anion is). So when you make a buffer, you say, "I want to make a buffered solution at pH 5.9," or something like that and you choose your weak acid-acid ion system to get that pH. The math for this is shown below and the important equation is called the **Henderson Hasselbach equation**:

$$\begin{array}{l} \text{take the "p" of} \\ \text{this equation} \end{array} \begin{array}{l} \nearrow [\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]} \\ \searrow -\log[\text{H}^+] = -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^-]} \end{array}$$

$$\text{Henderson Hasselbach equation: } \text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Buffers: How to Make Them

Now, you are often asked in questions, or maybe in a lab, to make a buffer for a solution in a specific pH range. There are about 10 weak acids to choose from. This is the procedure to follow:

Step 1. Knowing the target pH of the buffer allows you to choose the weak acid-acid anion pair. A general rule of thumb is to match the pK_a of the acid with the desired pH since in the Henderson Hasselbach equation the $\log[A^-]/[HA]$ term could be eliminated if $[A^-] = [HA]$ (remember $\log 1 = 0$). In the H-H equation this then just leaves you with $pH = pK_a$. You can then vary from the pH dictated by the pK_a by changing the concentration of the weak acid and its anion.

Making a buffer is like tuning-in something with a dial that makes big changes (choice of weak acid-acid anion pair and its pK_a) and a dial that makes fine tuning adjustments

(the ratio $[A^-]/[HA]$ --> can changes up to ± 1 from the pK_a) Anyway, here are the basic pairs to choose from:

Buffer pH	Weak Acid	Acid Anions	K_a	pK_a
4	Lactic acid, Hlac	Lac ⁻	1.4×10^{-4}	3.85
5	Acetic acid, HC ₂ H ₃ O ₂	C ₂ H ₃ O ₂ ⁻	1.8×10^{-5}	4.74
6	Carbonic acid, H ₂ CO ₃	HCO ₃ ⁻	4.4×10^{-7}	6.36
7	Dihydrogen Phosphate ion, H ₂ PO ₄ ⁻	HPO ₄ ²⁻	6.2×10^{-8}	7.21
8	Hypochlorous acid, HClO	ClO ⁻	2.8×10^{-8}	7.55
9	Ammonium ion, NH ₄ ⁺	NH ₃	5.6×10^{-10}	9.25
10	Hydrogen carbonate ion, HCO ₃ ⁻	CO ₃ ²⁻	4.7×10^{-11}	10.32

Step 2. Find the desired ratio $[A^-]/[HA]$.

We know from the equilibrium constant expression that: $\frac{[A^-]}{[HA]} = \frac{K_a}{[H^+]}$

and since we are given a target pH we know $[H^+]$: $[H^+] = 10^{-pH}$

So just plug that in and get a number for the ratio of the acid anion to the weak acid

$$\frac{[A^-]}{[HA]} = \frac{K_a}{10^{-pH}}$$

Step 3. So you'll either be given the moles of weak acid or acid anion or you could just choose an amount for one of them. In any case use the ratio to find the amount of (moles or mL of a molar solution) other one necessary to make your buffer.

Step 4. Convert to grams or liters if you have to specify things in terms of given molar solution.

That's it. You'll be asked to make a buffer for a certain pH and in the end you just specify what to put into the solution to make that buffer.

Buffers: How They React to the Addition of OH⁻ or H⁺

- Okay so the idea of a buffer is to have lots of species in solution that will react with any introduced OH⁻'s and H⁺'s and whose concentrations won't perceptibly change after they react with OH⁻ or H⁺.
- If you add enough H⁺ or OH⁻ it will perceptibly change the concentration of A⁻ (the acid anion) or HA (the weak acid), respectively, thus changing the ratio [A⁻]/[HA] (our fine tuning knob) which in turn changes the pH of the buffer solution.
- So what you're responsible to be able to do is calculate the new pH of a buffer if a strong acid (H⁺'s) or a strong base (OH⁻'s) is added to the solution.

This is what you do:

Step 1. In the original buffer you know:

$$\text{moles weak acid} = n_{\text{wa}}$$

$$\text{moles acid anion} = n_{\text{aa}}$$

Step 2. Look at what you add: who it uses up and who it forms

If you add H⁺: you use up acid anion: $\longrightarrow (n_{\text{aa}})_{\text{new}} = (n_{\text{aa}})_{\text{old}} - n_{\text{H}^+}$
 (A⁻ + H⁺ $\longrightarrow$ HA)

you form weak acid: $\longrightarrow (n_{\text{wa}})_{\text{new}} = (n_{\text{wa}})_{\text{old}} + n_{\text{H}^+}$

If you add OH⁻: use up weak acid: $(n_{\text{wa}})_{\text{new}} = (n_{\text{wa}})_{\text{old}} - n_{\text{OH}^-}$
 (HA + OH⁻ $\longrightarrow$ A⁻ + H₂O)

form acid anion: $(n_{\text{aa}})_{\text{new}} = (n_{\text{aa}})_{\text{old}} + n_{\text{OH}^-}$

Obviously, buffers have limits on the amount of H⁺ or OH⁻ they can absorb. The amount of H⁺ or OH⁻ a buffer can absorb before an appreciable pH change is called the **buffer capacity**.

Step 3. We can solve for the final composition using the methods previously introduced. We don't have to convert the final number of moles in the solution to molarity because the Henderson Hasselbach equation is a ratio of concentrations; the volume parts would just divide out anyway. So, the ratio of moles is the same as the ratio of molar concentrations.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Student Packet: 6.7: Buffers: AssessMe questions

- A buffer solution is formed by adding 0.500 mol of sodium acetate and 0.500 mol of acetic acid to 1.00 L H₂O. What is the pH of the solution at equilibrium?
($K_a = 1.80 \times 10^{-5}$)

A) 5.05 B) 4.74 C) 4.44 D) 2.38 E) I'm clueless
- The amount (in grams) of sodium acetate (MW = 82.0) to be added to 500.0 ml of 0.200 molar acetic acid ($K_a = 1.80 \times 10^{-5}$) in order to make a buffer with pH = 5.000 is

A) 69 B) 0.180 C) 14.8 D) 29.5 E) I'm clueless
- A strong monoprotic acid is being titrated with a 0.500 M NaOH solution. Which statement is true for this titration?

A) The pH at the equivalence point cannot be determined without knowing the identity of the acid.
 B) The pH at the equivalence point cannot be determined unless the concentration of the acid is known.
 C) The pH at the equivalence point depends on the identity of the acid and on the concentration of the acid.
 D) The pH at the equivalence point is always 7.0.
 E) I'm clueless
- Consider the titration of 100.0 ml of 0.500 M NaOH with 0.500 M HCl. After 50.0 ml of HCl has been added, the [H⁺] of the solution is:

A) 1.8×10^{-5} M B) 5.6×10^{-10} M
 C) 1.2×10^{-5} M D) None of these E) I'm clueless
- A solution has the following concentrations: [Cl⁻] = 1.5×10^{-1} M, [Br⁻] = 5.0×10^{-4} M, [CrO₄²⁻] = 1.9×10^{-2} M
 A solution of AgNO₃ (100% dissociated) is added to the above solution, drop by drop. Which silver salt will precipitate first?
 K_{sp} AgCl = 1.5×10^{-10} K_{sp} AgBr = 5.0×10^{-13} K_{sp} Ag₂CrO₄ = 1.9×10^{-12}

A) AgCl B) AgBr
 C) Ag₂CrO₄ D) AgCl and AgBr together E) I'm clueless
- Suppose that CaF₂ is to be used as a fluoridation agent in a municipal water system. What is the [F⁻] if extremely hard water ([Ca²⁺] = 0.070 M) is saturated with CaF₂?
 (K_{sp} CaF₂ = 1.7×10^{-10})

A) 1.3×10^{-5} M B) 2.5×10^{-5} M
 C) 5.0×10^{-5} M D) 1.0×10^{-4} M E) I'm clueless

Student Packet: 6.7: Buffers: ShowMe questions

- 1) A buffer is prepared in which the ratio of $\text{HCO}_3^- / \text{CO}_3^{2-}$ is 5.00. What is the pH of the buffer? (K_a for $\text{HCO}_3^- = 4.8 \times 10^{-11}$)

- 2) The ionization constant, K_a , for HF is 7.0×10^{-4} .
 - a) How many grams of KF must be added to 1.0 L of 1.0 M HF in order to prepare a buffer solution with a pH of 3.50? (assume no volume change when KF is added)

 - b) If 100.0 mL of 1.0 M KOH are added to one liter of the buffer solution in (a), what would be the resulting pH?

- 3) A buffer solution contains 0.40 moles of formic acid, HCOOH , and 0.60 moles of sodium formate, HCOONa , in 1.00 L of solution. (K_a of formic acid is 1.8×10^{-4})
 - a) Calculate the pH of this solution.

 - b) If 100 mL of this buffer solution is diluted to a volume of 1.00 L with pure water, does the pH change? Why?

- 4) Determine the pH of an HCN/KCN buffer containing 0.10 M HCN and 0.07 M KCN before and after the addition of 0.001 mol H^+ to one liter of buffer. (K_a of $\text{HCN} = 6.2 \times 10^{-10}$)

Student Packet: 6.7: Buffers: TestMe questions

- 1) How many moles of NH_4Cl must be added to 1.0 L of 1.0 M NH_3 solution to prepare a buffer solution with a pH of 9.00? ($K_b = 1.8 \times 10^{-5}$)
- A) 1.8 mol B) 0.55 mol C) 5.5×10^{-5} mol D) 1.8×10^4 mol E) 2.1 mol
- 2) Determine the amount (in grams) of sodium acetate (MW = 82.0) to be added to 500.0 mL of 0.200 molar acetic acid ($K_a = 1.80 \times 10^{-5}$) in order to make a buffer with pH = 5.000.
- A) 69 grams
B) 0.180 grams
C) 14.8 grams
D) 29.5 grams
E) None of the above
- 3) What volume of 0.500 M HNO_2 ($K_a = 4.0 \times 10^{-4}$) and 0.500 M NaNO_2 must be mixed to prepare 1.0 L of a solution buffered at pH 3.55?
- A) 500 mL of each solution
B) 703 mL 0.500 M HNO_2 , 297 mL 0.500 M NaNO_2
C) 413 mL 0.500 M HNO_2 , 587 mL 0.500 M NaNO_2
D) 297 mL 0.500 M HNO_2 , 703 mL 0.500 M NaNO_2
E) 587 mL 0.500 M HNO_2 , 413 mL 0.500 M NaNO_2
- 4) A buffer solution is formed by adding 0.500 mol of sodium acetate and 0.500 mol of acetic acid to 1.00 L H_2O . What is the pH of the solution at equilibrium? ($K_a = 1.80 \times 10^{-5}$)
- A) 5.05 B) 4.74 C) 4.44 D) 2.38 E) None of the above
- 5) A certain acid exists in a ratio of 2:3 for the protonated versus deprotonated forms in an aqueous solution. The pH of the solution is 4.20. What is the K_a of this acid?
- A) 4.02
B) 6.3×10^{-5}
C) 4.2×10^{-5}
D) 9.6×10^{-5}
E) None of the above