

Making Buffers

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Purposes of the Experiment

Make a buffer with a desired pH. Demonstrate the buffering capacity of this buffer.

Background

Buffers are solutions containing a mixture of a weak acid (HA) and its conjugate base (A^-), or a weak base (B) and its conjugate acid (BH^+), that resist large changes in pH when base or acid is added to them. Buffers accomplish this by containing weak conjugate acids and bases that react with added reagents. For example, H_3O^+ added to a solution of a buffer made from HA and A^- , converts some of the base, A^- , into its conjugate acid HA. Some of the newly-formed HA does dissociate to yield a decrease in pH; however this change is minimized for two key reasons common to buffers.

First, HA is a weak acid, and it dissociates to a much lower degree than the H_3O^+ source that was originally added. The strong acid that was added is therefore effectively converted to a weak acid. Second, because the newly formed HA must dissociate in the presence of its conjugate base, A^- , the **common ion effect** further reduces the already small degree of HA dissociation to considerably smaller levels.

Buffer Equation

The two key points above are summarized in the following table, where [acid] and [base] represent the initial conjugate acid and base concentrations, respectively, immediately after complete reaction with added H_3O^+ , but before any HA dissociation.

	HA + H ₂ O	=	H ₃ O ⁺ + A ⁻
<i>initial</i>	[acid]		-0 [base]
<i>shift</i>	-x		+ x + x
<i>equil.</i>	[acid] - x		x [base] + x

The degree of HA dissociation (x) will be so small that [acid] - x ~ [acid] and that [base] + x ~ [base]. This approximation is always made for buffer solutions because of the two ideas expressed in the preceding section: (1) HA is a weak acid, and (2) the common ion effect further impedes its already slight dissociation. These ideas are summarized

algebraically in a rearranged HA acid dissociation K_a expression:

$$K_a = \frac{[H_3O^+][OH^-]}{[HA]}$$

$$K_a = \frac{[H_3O^+]([base] + x)}{[acid] - x} \approx \frac{[H_3O^+][base]}{[acid]}$$

or

$$pH = pK_a + \log \frac{[base]}{[acid]} \quad [1]$$

where $pK_a = -\log K_a$. Equation [1] is known as the Henderson-Hasselbalch equation.

Making a Buffer of a Desired pH

- choose the appropriate conjugate acid/base pair
- determine the target conjugate [base]/[acid] ratio
- determine amounts of conjugate acid/base required

• Choosing the appropriate acid/base pair

Commercial buffers are typically prepared with roughly equal acid and base absorbing capacity. Such a buffer is the most versatile and anticipates either base or acid absorbing applications. Equal base or acid absorbing capacity means that such a buffer has roughly equal amounts of conjugate acid and base present in solution. This idea can be expressed as

$$\frac{[base]}{[acid]} \approx 1 \quad [2]$$

so that equation [1] simplifies to

$$pH \sim pK_a \quad [3]$$

under these conditions (remember $\log 1 = 0$). Therefore, the appropriate conjugate acid/base pair to use to produce a buffer is where [acid] ~ [base]. Choose an acid whose pK_a is closest to the desired buffer pH. Buffers are usually made from acid/conjugate base systems that have $pK_a = \text{desired pH} \pm 1$. Once the acid is chosen, the appropriate conjugate base to use is necessarily also fixed.

• **Determine the target [base]/[acid] ratio**

It is nearly impossible to choose an acid whose pK_a is exactly equal to the desired pH. This problem is remedied by making fine adjustments in the [base] and [acid] used to make the buffer. Equation [1] indicates that adjustments in the pH of a buffer can be made by manipulating the [base]/[acid] ratio. In practice, after making a best choice of acid with pK_a closest to the desired buffer pH, one determines the target [base]/[acid] ratio that will yield exactly the desired pH. A HSO_3^-/SO_3^{2-} buffer will be worked as an example.

Because the pK_a of HSO_3^- is 7.21, the HSO_3^-/SO_3^{2-} conjugate acid/base pair is a potential buffer system when the desired pH is 7.00. Rewriting equation [1] including the appropriate known quantities one obtains

$$pH = 7.00 = 7.21 + \log \frac{[SO_3^{2-}]}{[HSO_3^-]}$$

and

$$7.00 - 7.21 = -0.21 = \log \frac{[SO_3^{2-}]}{[HSO_3^-]}$$

Therefore

$$10^{-0.21} = \frac{[SO_3^{2-}]}{[HSO_3^-]} = 0.62$$

The target ratio of $[SO_3^{2-}]/[HSO_3^-] = 0.62$ will give a buffer of $pH = 7.00$. A molar excess of HSO_3^- will be required. This particular $pH = 7.00$ buffer will have slightly greater base absorbing capacity because it contains more acid than conjugate base.

• **Determine amounts of conjugate acid/base required**

The target ratio represents only the relative amounts of conjugate base and acid in this buffer. Actual concentrations and moles to be used must be determined in order to physically prepare the buffer. As a basis for all further calculations assume that the buffer should have 0.10 M acid concentration. It is often the case that one of the conjugate partners is set at a desired level and the other is adjusted to match the target ratio. The corresponding conjugate base concentration can then be determined. Continuing with the HSO_3^-/SO_3^{2-} example

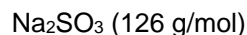
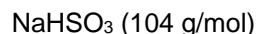
$$[HSO_3^-] = 0.10 \text{ M}$$

so that

$$[SO_3^{2-}] = (0.62)[HSO_3^-] = 0.62(0.10 \text{ M}) = 0.062 \text{ M}$$

This buffer must contain 0.10 M HSO_3^- and 0.062 M SO_3^{2-} to yield a buffer with $pH = 7.00$.

Suppose the materials to make the buffer are the sodium salts of the conjugate acid and base (molar masses are included).



Moles of acid and conjugate base require that a volume of desired buffer be known. Assume that 50 mL of buffer are to be made. Therefore

$$(0.050 \text{ L})(0.10 \text{ M } HSO_3^-) = 0.0050 \text{ mol } HSO_3^-$$

and

$$(0.050 \text{ L})(0.062 \text{ M } SO_3^{2-}) = 0.0031 \text{ mol } SO_3^{2-}$$

From these moles of acid and conjugate base the appropriate number of grams of salts can be determined (note 1:1 mole ratio of salt:anion).

$$(0.0050 \text{ mol } NaHSO_3)(104 \text{ g/mol}) = 0.52 \text{ g } NaHSO_3$$

$$(0.0031 \text{ mol } Na_2SO_3)(126 \text{ g/mol}) = 0.39 \text{ g } Na_2SO_3$$

50 mL of $pH = 7.00$ buffer can therefore be made by dissolving 0.52 g $NaHSO_3$ and 0.39 g Na_2SO_3 in enough water to yield 50 mL of solution.

Adding Acid or Base to a Buffer

Because the acid and conjugate base are in the same solution, Equation [1] can be rewritten as follows

$$\text{pH} = \text{pK}_a + \log \frac{\text{moles base}}{\text{moles acid}} \quad [4]$$

This form is especially useful for keeping track of the changes in the pH of a buffer as it responds to added reactants, for example, when weak base is converted to its conjugate acid by the addition of an H_3O^+ source.

As an example, consider the addition of 5 mL of 0.1M HCl to the above pH 7.00 $\text{HSO}_3^-/\text{SO}_3^{2-}$ buffer. This represents the addition of

$$(0.005 \text{ L})(0.1 \text{ M}) = 0.0005 \text{ mol H}^+$$

to the buffer. This added H^+ will convert the same amount of weak base, SO_3^{2-} , into its acid form, HSO_3^- . As a result of this reaction, the new amounts of conjugate acid and base in the buffer are

$$0.0031 \text{ mol} - 0.0005 \text{ mol} = 0.0026 \text{ mol SO}_3^{2-}$$

$$0.0050 \text{ mol} + 0.0005 \text{ mol} = 0.0055 \text{ mol HSO}_3^-$$

The new pH of the buffer can be determined simply by making the necessary adjustments in the $\text{SO}_3^{2-}/\text{HSO}_3^-$ ratio.

$$\begin{aligned} \text{new pH} &= 7.21 + \log \frac{0.0026 \text{ moles SO}_3^{2-}}{0.0055 \text{ moles HSO}_3^-} \\ &= 6.88 \end{aligned}$$

As a prelab comparison exercise you are asked to determine the resulting pH when 5 mL of 0.1 M HCl are added to 50 mL of pure water.

Experimental Procedure

I. Making a buffer of a desired pH

1. Your instructor will assign a target pH between the range of 4 to 10 for you to prepare.
2. Based on your assigned pH, determine which of the following acids in Table 1 would be best for preparing your buffer.

Table 1. Weak acids and dissociation constants

acid	K_a
acetic acid $\text{CH}_3\text{CO}_2\text{H}$	1.8×10^{-5}
dihydrogen phosphate ion H_2PO_4^-	6.2×10^{-8}
ammonium ion NH_4^+	5.6×10^{-10}

3. Determine the target ratio of [base]/[acid] needed to achieve the desired buffer pH.
4. Make your buffer so that [acid] = 0.10 M. Determine the necessary [base] based on your target ratio.
5. Determine the amounts (grams of solid or milliliters of solution) of the following reagents needed to prepare 50 mL of your buffer.

The following materials will be available. Pay close attention to compound formulas and molar masses in your calculations.

Table 2. Materials available for making buffers

Pure solids	g/mol
ammonium chloride	53.5
sodium acetate trihydrate $\text{NaCH}_3\text{CO}_2 \cdot 3\text{H}_2\text{O}$	136.1
sodium dihydrogenphosphate monohydrate $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	138.0
sodium hydrogenphosphate $\text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$	142.0
Aqueous solutions	
0.20 M acetic acid	
0.20 M ammonia	

6. Measure the appropriate amounts of reagents. Be certain to quantitatively transfer measured reagents, washing weighing boats and graduated cylinders as necessary. Dilute the mixture to 50 mL. Save this buffer solution for later tests.

II. Observing the buffering capacity of the buffer

You will add 0.5 M HCl incrementally to half of the buffer (one 25 mL portion) and 0.5 M NaOH to the other 25 mL portion.

A universal acid/base indicator will be used to visually monitor the change in pH as base or acid is added to your buffer solution. pH changes may also be monitored with a pH meter. Your instructor will tell you if you are also to use a pH meter to monitor these changes.

Adding HCl and NaOH to water

For comparison purposes, add 3-4 drops of indicator to two different 25 mL portions of distilled water. To one of the samples of water add one drop of 0.5 M HCl. To the other portion add one drop of 0.5 M NaOH. Compare the indicator color changes for these unbuffered solution to what you see when you add strong acid and base to your buffer in the next steps.

Adding HCl to the buffer

Obtain 10 mL of 0.5 M HCl(aq) in a graduated cylinder. To one 25 mL portion of your buffer add 3-4 drops of universal indicator solution. Using a dropper, add 1 mL increments of the HCl solution to your first portion of buffer. After each 1 mL addition allow time for complete reaction. Record the resulting solution color and pH. Repeat the process until all of the HCl has been added.

Adding NaOH to the buffer

Obtain 10 mL of 0.5 M NaOH(aq) in a graduated cylinder. To the second 25 mL portion of your buffer add 3-4 drops of universal indicator solution. Using a dropper, add 1 mL increments of the NaOH solution to your second portion of buffer. After each addition allow time for complete reaction. Record the resulting solution color and pH. Repeat the process until all of the NaOH has been added.

Dispose of the resulting solutions according to your instructor's directions.

Prelab Exercise

1. (a) Determine the pH of the solution that results from the addition of 5 mL of 0.1 M HCl to 50 mL of pure water.

(b) Compare the change in pH expected when the same amount of acid is instead added to the $\text{SO}_3^{2-}/\text{HSO}_3^-$ buffer described in the introduction.

2. Determine the moles of NaOH that could be absorbed by the $\text{SO}_3^{2-}/\text{HSO}_3^-$ buffer described in the introduction before the base absorbing capacity of this buffer is destroyed.

3. Consult an appropriate table of acid dissociation constants. For each of the following pH values, give the formula of an appropriate weak acid and its conjugate base that would be suitable for preparing a buffer of the desired pH.

(a) desired buffer pH = 3.5

(b) desired buffer pH = 7.3

(c) desired buffer pH = 10.0

Experimental Section

I. Making a buffer

Assigned target pH _____

(a) For this buffer, the conjugate acid and base formulas are:

Conjugate acid = _____ Conjugate base = _____

(b) Determine the appropriate target [base]/[acid] ratio required to meet your assigned target pH using your chosen conjugate acid/base pair. Show clear work.

target $\frac{[\text{base}]}{[\text{acid}]} =$ _____

(c) Determine the appropriate [base] if the [acid] = 0.1 M for your buffer. Show clear work.

required [base] = _____

(d) Determine the actual amounts of chemicals required to prepare 50 mL of your buffer. For stock chemicals that are solutions, determine the volume of stock solution required. For stock solids determine the mass of solid required. Show clear work.

Acid

_____ is required

Base

_____ is required

(e) Have the pH of your buffer checked by your instructor. Record your measured pH below.

very low (> to 0.2 under)	slightly low (up to 0.2 under)	Target pH	slightly high (up to 0.2 over)	very high (> 0.2 over)
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II. Observing the acid and base absorbing capacity of the buffer.

(a) Do you expect your buffer to have *greater acid* or *greater base* absorbing capacity? Defend your answer with appropriate reference to work on page 6.

(b) Record your observations for the addition of HCl and NaOH to your buffer using the following tables.

Total Volume HCl added (mL)	Buffer pH	Indicator Color
0		

Total Volume NaOH added (mL)	Buffer pH	Indicator Color
0		

(c) Do your data above indicate a greater acid or a greater base absorbing capacity for your buffer? Explain.

Post Laboratory Questions

1. Distilled water frequently contains dissolved CO_2 , making the pH different from the theoretical value for pure water. Would this cause the pH of your buffer to be slightly higher or slightly lower than the target pH? Explain.

(b) Based on your advice in (a), a researcher used this very buffer in a growth medium (including appropriate food and temperature control) for bacteria that proliferate at physiological pH. Despite this carefully prepared medium, however, bacterial growth was dismal. Explain.

2. (a) Was the pH of the buffer you prepared slightly higher or slightly lower than the target value?

4. Biochemists frequently use “phosphate” buffers in their work. Here, “phosphate” refers generally to the class of phosphate derived ions:



(b) The pH of a buffer can be adjusted by added small amounts of HCl or NaOH. Which of these should be added to your buffer to remedy the problem identified in (a)? Defend your choice.

(a) Which of these ions best represents the conjugate acid in a “phosphate” buffer at physiological pH? Explain.

3. Consider the HClO/ClO^- conjugate acid/base pair. Consult your text or other source for appropriate acid dissociation constants. The hypochlorite ion is the active ingredient in bleach, $\text{NaClO}(\text{aq})$.

(a) Explain why this acid/base pair would be a candidate for a buffer with $\text{pH} = 7.3$ (approximate physiological value).

(b) A buffer used in an experiment was described as “a 0.2 M phosphate buffer with $\text{pH} = 7.25$.” Based on the conjugate acid you identified in (a), determine the concentration of conjugate acid in this “0.2 M phosphate buffer.”