Buffers

(How do acids and bases react together?)

Critical Thinking Questions:

1. Complete and balance the reaction of acetic acid donating a hydrogen ion to water to make acetate and hydronium.

$$HC_2H_3O_2 \quad + \quad H_2O \rightleftharpoons$$

2. Draw lines connecting any conjugate acid-base pairs in the reaction in CTQ 1.

Model 1: Solutions ("systems") that may or may not be buffers

ID	System obtained by mixing 100 mL of each of the two listed solutions	Initial pH	pH after addition of 100 mL of 0.200 M NaOH	pH after addition of 100 mL of 0.200 M HCl
1	0.100 M $HC_2H_3O_2$ and 0.100 M $NaC_2H_3O_2$	4.73	4.91	4.55
2	0.100 M $HC_2H_3O_2$ and 0.100 M NaCl	2.88	4.16	1.71
3	0.100 M $HC_2H_3O_2$ and 0.050 M $NaC_2H_3O_2$	4.43	4.67	4.12
4	0.100 M HCN and 0.100 M NaCN	9.21	9.39	9.03

Critical Thinking Questions:

3. Compare the solutions in Model 1. List any systems (by ID number) that demonstrate large changes in pH (> 1 unit) when either acid or base is added.

4. List any systems that demonstrate small changes (<0.5 unit) in pH when either acid or base is added.

5. Work with your team to identify one or two characteristics that are shared by the solutions demonstrating small changes in pH but not by those demonstrating large changes in pH. Do not spend more than a minute or so on this task.

6. A **buffer** is a solution which is resistant to changes in pH when small amounts of acid or base are added. Based on this definition, which systems from Model 1 would make good buffers?

7. a. Use the molarity of acetic acid added to System (1) in Model 1 and the volume of the solution added (100 mL) to calculate the number of moles of acetic acid added to the system.

b. How many moles of acetate ion were added to this system? (Hint: Sodium acetate and acetate ion have the same molar concentration.)

8. Since System (1) contains both acetic acid and acetate ion, the equilibrium reaction you completed in CTQ 1 applies to this system. Suppose that some strong base (hydroxide ion) is added to this system. Write the two species from the reaction in CTQ 1 that could react with and *neutralize* the hydroxide. Work with your team to explain your choices.

9. Write a chemical equation for the reaction of hydroxide ion with acetic acid, producing acetate and water. Is hydroxide neutralized in this reaction? _____

10. As a team, explain why addition of strong base (hydroxide ion) to System (1) will not cause a great change in the pH of the solution, as long as the acetic acid is not used up.

11. What is the **one** species in CTQ 1 that could react with and neutralize any added hydronium ion?

12. Explain why addition of strong acid will not cause the pH of the solution in CTQ 1 to change much, as long as plenty of acetate is present.

13. Consider the following reaction:

$$HCl + H_2O \longrightarrow Cl^- + H_3O^+$$

a. Recalling that strong acids dissociate completely in water, draw a large 'X' through the species in the above reaction that will not be present in any significant amount.

b. Why is a forward arrow ($\longrightarrow$) used in this reaction instead of an equilibrium arrow ($\rightleftharpoons$)?

c. Work with your team to explain the following true statement: There is no species in the above reaction that can neutralize added hydronium ion.

14. Which would make a better buffer system: a strong acid and its conjugate base or a weak acid and its conjugate base? Explain.

15. Summarize the ingredients necessary for an effective buffer system.

16. How does the pH of a buffer system change when a small amount of acid is added?

17. How does the pH of a buffer system change when a small amount of base is added?

18. Which system in Model 1 is not an effective buffer?____ Considering your answer to CTQ 16, what does this system lack that causes it to be ineffective at buffering the pH?

19. What is the most important unanswered question about buffers remaining with your team?

Exercises:

1. Systems (1) and (3) in Model 1 contain the same conjugate acid-base pair. When the same small amounts of acid or base are added to each system, which one exhibits a slightly larger pH change? _____ Explain what difference in these systems leads to this slight decrease in buffering ability.

2. State if each system would be useful as a buffer or not. Then explain the reason(s) for your choice.
   a. A solution containing 0.08 M NaCN and 0.10 M HCN

   b. A solution containing 0.05 M NaOH in H_2O

   c. A solution containing 0.25 M HCl and 0.20 M NaCl

   d. A solution containing 0.05 M NH_4Cl and 0.10 M NH_3

   e. A solution containing 0.20 M KF and 0.15 M HF

3. Considering the solution in Exercise 2b.
   a. Write the three chemical species that would be present in significant amounts.

   b. Is there any species present that can neutralize added hydroxide? Explain.

4. Read the assigned pages in your textbook, and work the assigned problems.

Henderson-Hasselbalch Equation

(How do buffers prevent large pH changes?)

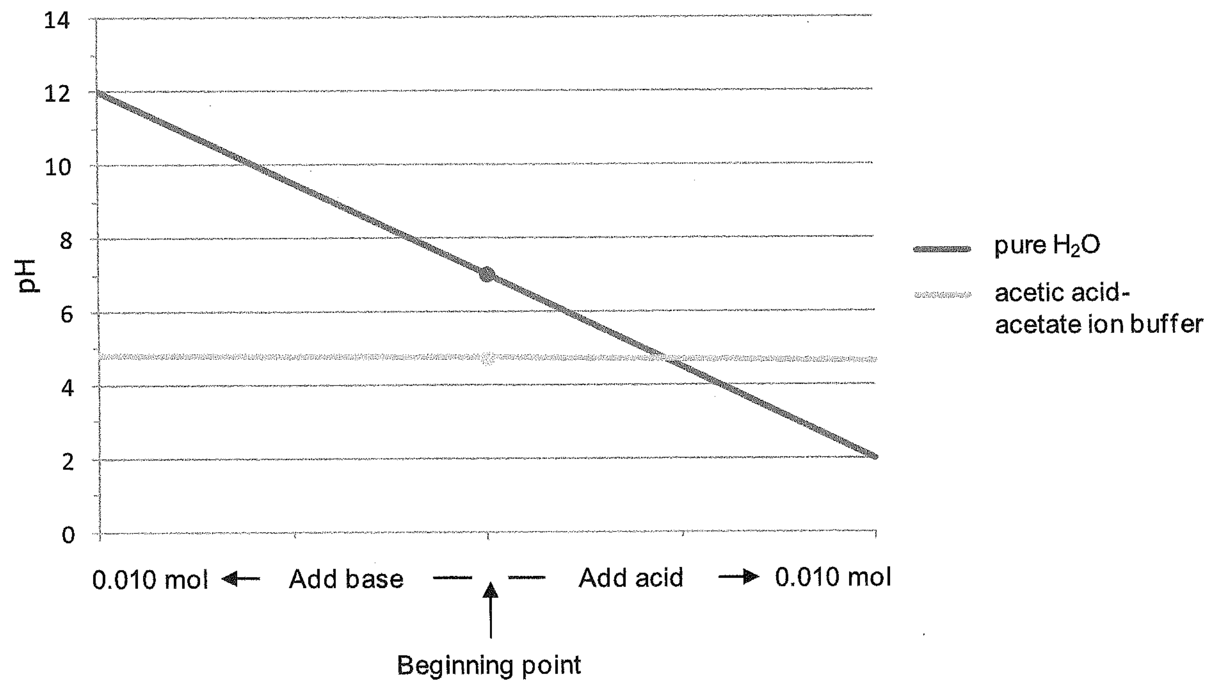
Model 1: pH of buffer systems

To calculate the pH of a buffer system, the *Henderson-Hasselbalch equation* is used.

$$pH = pKa + \log \frac{[A^-]}{[HA]}$$

Recall that HA represents any acid, and A^- represents the conjugate base.

Figure 1. Effect of acid and base addition to buffer and water.



Critical Thinking Questions:

1. The K_a value for acetic acid is 1.85×10^{-5}. What is the pK_a of the buffer system in Figure 1?

2. Using the equation in Model 1, calculate the initial pH of the acetate buffer system if $[CH_3COOH] = [CH_3COO^-] = 0.10$ M.

Manager: *Have your team work together to answer CTQ 3, parts a-c. Ensure that every team member understands each part before moving on.*

3. a. If 0.01 moles of strong acid are added to one liter of the acetic acid-acetate buffer from CTQ 2, what is the new concentration for total acid in the system [HA] (initial plus added amount)?

b. What is the new concentration of base, $[A^-]$? (Recall that some of the base will be used to neutralize the added acid.)

c. Using the Henderson-Hasselbalch equation, calculate the pH for this solution.

4. Using the Henderson-Hasselbalch equation, calculate the pH of the solution when 0.01 moles of base are added to one liter of the original solution. (Recall that some of the acid will be used to neutralize the added base.)

5. ***Manager:*** *Lead a team discussion comparing the changes in pH calculated for the buffer system in CTQs 3 and 4 to the same additions to water observed in Figure 1.* Record your observations.

6. How does your answer to CTQ 5 help your understanding of the purpose of buffers?

7. Phosphoric acid (H_3PO_4) has a K_a value of 7.1×10^{-3}.
   Manager: *Work with your team to first outline the necessary steps to solve the following problem.*
   a. What is the pH of the buffer solution with initial concentrations of 0.45 M H_3PO_4 and 0.28 M $H_2PO_4^-$?

   b. What is the new pH when 0.15 moles of base is added per liter of buffer solution?

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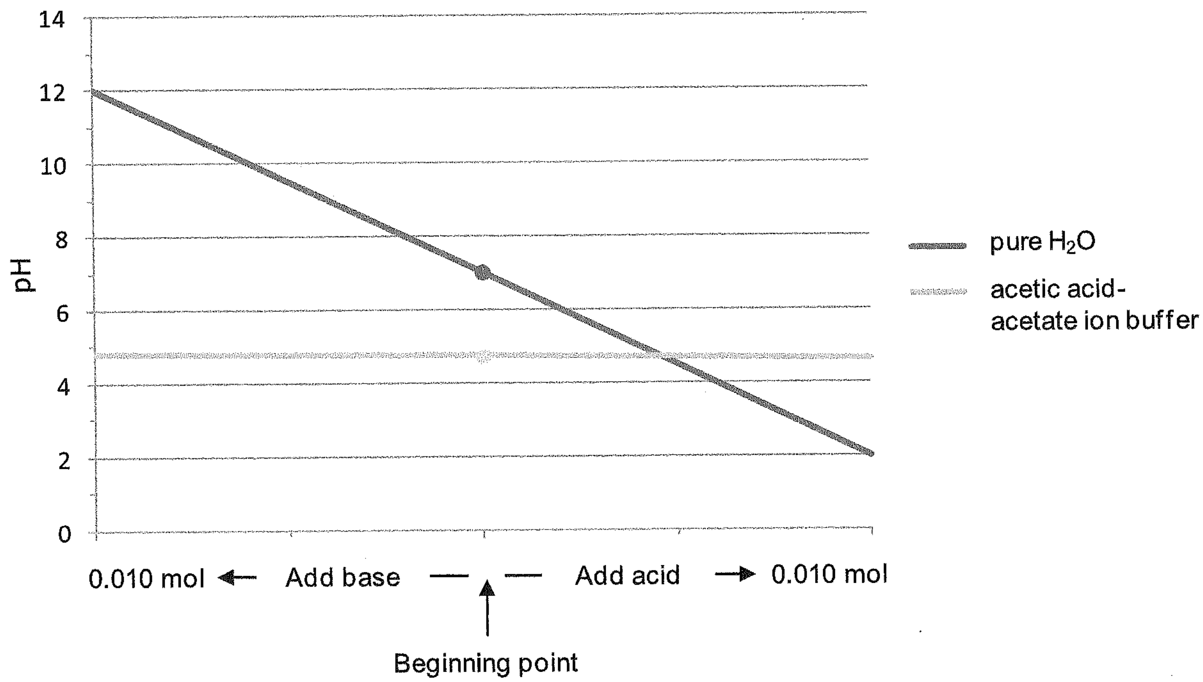

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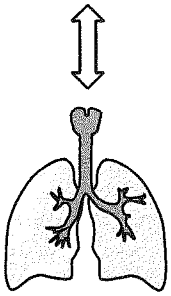
Model 2: Biological buffers

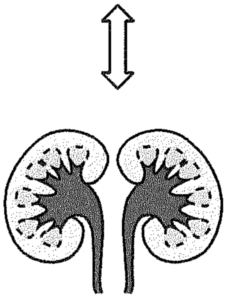
Buffers are vital for biological functions within the body. The carbonic acid–bicarbonate buffer maintains blood pH close to 7.4. Minor changes in pH can lead to coma and/or death. Carbonic acid (H_2CO_3) is unstable, causing the additional step in the following reaction. The lungs and kidneys help the system by removing excess CO_2 and acid, respectively.

Figure 2. Carbonic acid-bicarbonate buffer.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H_3O^+ + HCO_3^-$$



lungs



kidneys

(Note: For simplicity, H_2O was omitted as a reactant in the second step.)

Critical Thinking Questions:

8. Write a K_a expression for the reaction in Figure 2. In order to do this, you can ignore H_2CO_3, considering the reactants to be CO_2 and H_2O and the products to be H_3O^+ and HCO_3^-.

9. Rearrange the equation in CTQ 8 to solve for $[H_3O^+]$.

Manager: *Have your team work together for CTQ 10. Ensure that every team member understands before moving on.*

10. a. What is the relationship between $[H_3O^+]$ and pH? That is, how does pH change when $[H_3O^+]$ is increased?

    b. Consider your equation in CTQ 9. Work with your team to determine what would happen to $[H_3O^+]$ if the concentration of $[CO_2]$ increases? What would happen to the pH?

    c. Explain your answer to part (b) using Le Chatelier's Principle.

11. a. Write the Henderson-Hasselbalch equation for the second reaction in Figure 2.

b. Because the two reactions in Figure 2 share a compound, mathematically we can substitute [CO_2] for [H_2CO_3] in part (a). Rewrite the equation using this change.

12. a. The K_a for carbonic acid is 4.3×10^{-7}. What is the pH of a solution containing equal molar concentrations of HCO_3^- and CO_2?

b. Calculate the new pH if the concentration of CO_2 were twice that of HCO_3^-.

c. To maintain the usual pH of 7.4, would blood have equal molar concentrations of HCO_3^- and CO_2? If not, which would be higher? Work with your team to explain.

13. Some athletes consume sodium bicarbonate ($NaHCO_3$) before intense exercise to combat fatigue. Explain how this supplement (if effective) might help offset metabolic increases in CO_2 during exercise.

14. Work with your team to summarize how any increase or decrease in acid concentration can be minimized by the buffer system in the blood.

15. Give an example of how the Manager's role today helped ensure everyone understood the material.

16. What was one strength of your team today? Why was it beneficial for completion of the activity?

Exercises:

1. Formic acid (H_2COO) has a K_a of 1.8×10^{-4}. What is the pH of a buffer solution containing 0.32 M HCOOH and 0.14 M $HCOO^-$?

2. Nitrous acid (HNO_2) has a K_a of 4.5×10^{-4}. What is the pH of a system containing 0.100 M nitrous acid and 0.100 M nitrite (NO_2^-) when 0.020 moles of NaOH is added per liter?

3. Excessive exercise can lead to production of lactic acid by the muscles and release into the bloodstream. Explain how the carbonic acid-bicarbonate buffer system would work to handle the increase in acid concentration to minimize changes in pH.

4. Read the assigned pages in your textbook, and work the assigned problems.