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The Buffer Zone: What is a buffer and in what pH range are they effective?

Learning objectives

Students will be able to:

Content
- Explain how the concentration of buffer components determines the pH of the solution.
- Explain the effects of additions of strong acids/bases to buffered and non-buffered solutions
- Determine the relationship between the pK_a of an acid and the optimal pH range of a buffer in order to select an appropriate buffer for a particular pH range.

Process
- Interpret tabulated information (Information Processing)
- Recognize and predict trends in data (Critical Thinking)
- Generalize problem solutions (Problem Solving and Critical Thinking)
- Include all group members (Teamwork)

Prior knowledge
- weak acid/base equilibrium calculations
- Equilibrium – common ion effect
- Conjugate acid/base pairs identity

Further Reading
- Buffers: D.C. Harris, *Quantitative Chemical Analysis*, 7th Edition, 2007 WH Freeman: USA, Section 9-5, p. 167-172.

- EDTA: D.C. Harris, *Quantitative Chemical Analysis*, 7th Edition, 2007 WH Freeman: USA, Sections 12-1 through 12-3, p. 228-237.

- Limitations of the Henderson-Hasselbalch Equation: Po, Henry N.; Senozan, N. M. *J. Chem. Educ*. **2001** *78* 1499.

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Consider this…

Table 1 shows the concentrations of acetic acid (CH_3COOH) and sodium acetate (CH_3COONa) for a series of solutions. Acetic acid is a weak acid with pK_a=4.76. Sodium acetate, a strong electrolyte, will completely dissociate in solution. Therefore, we refer to this component of the solution below as simply "acetate," (CH_3COO^-).

Table 1. The pH of solutions with certain concentrations of acetic acid and acetate. The right most two columns indicate the solution pH after 0.0005 moles of either HCl or NaOH is added to the acetic acid/acetate solution.

Solution	$[CH_3COOH]$	$[CH_3COO^-]$	Solution pH	pH after 0.0005 moles HCl added	pH after 0.0005 moles NaOH added
1	0.010	0.090	5.71	5.51	6.04
2	0.020	0.080	5.36	5.24	5.51
3	0.030	0.070		5.03	5.24
4	0.040	0.060	4.94		
5	0.050	0.050	4.76	4.67	4.85
6	0.060	0.040		4.49	4.67
7	0.070	0.030	4.39	4.28	4.49
8	0.080	0.020		4.01	4.28
9	0.090	0.010	3.81	3.48	4.01
10	0.000	0.000	7.00		

Key Questions

1. How does the pH of a solution change when the fraction of acetic acid present as acetic acid (CH_3COOH) increases?

2. How does the pH of a solution change when the fraction of acetic acid present as sodium acetate (CH_3COO^-) increases?

3. What are the concentrations of CH_3COOH and CH_3COO^- when the pH of the solution is equal to the pK_a for the acid?

4. As a group, summarize the relationship between pH and the relative amounts of *CH_3COOH and CH_3COO^-*. Include the significance of the pK_a in this relationship.

5. Formal concentration of a ***monoprotic weak acid*** is defined as F_{HA}=[HA]+[A^-]. As a group, divide solutions 1-9 in Table 1 among members and calculate the formal concentration of acetic acid and sodium acetate in each solution. Compare answers within the group. What do you notice about this value as the relative amounts of acetic acid and acetate vary?

A ***buffered solution*** (a "buffer") resists changes in pH when acids or bases are added or when dilution occurs. (*Harris, p. 167)*

A **buffer** solution contains a weak acid HA and its conjugate base A^-. The pH of a buffer solution can be calculated, in many cases, using the Henderson-Hasselbalch equation:

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

Note that the Henderson-Hasselbalch equation is derived on the basis of some significant assumptions. Chiefly among these assumptions is ignoring any dissociation of HA or hydrolysis of A^-. In other words, the concentrations of HA and A^- are assumed equal to their formal concentrations. The dissociation of water is also ignored. These approximations are valid for acids with pK_a values in the range of ~5-9, for concentrations greater than ~1 mM or less than ~1 M, or for situations in which the two components (HA or A^-) are close to the same concentration (i.e., within a factor of 100).

6. Assign each of the three empty pH cells in Table 1, column 4, to group members. Use the Henderson-Hasselbalch equation to calculate the pH value for these solutions. Have at least two students calculate each value to check for accuracy. Compare your answers and agree upon the correct values before proceeding.

7. Compare your group's answers to the other pH values listed in Table 1. Do your values follow the trends in the Table?

Consider this…

In general, when strong acid or base is added to solution, we expect that the pH of the solution will change. This occurs to a small extent in buffer solutions and a large extent in unbuffered solutions. The right most two columns in Table 1 show the resulting pH of the original solution *after either* strong acid (HCl) *or* strong base (NaOH) is added.

Key Questions

8. Examine the pH values listed in the column labeled "pH after 0.0005 moles HCl added." Does the solution pH increase or decrease after HCl was added? Explain.

9. Consider solution 10 in Table 1. Write a chemical reaction that explains what happens to the solution pH when HCl is added to solution 10.

10. As a starting point, you have 100.0 mL of deionized water (the [CH_3COOH] and [CH_3COO^-] are zero). Assume that addition of HCl or NaOH does not result in a substantial increase in volume. Divide the group in half and have one group consider addition of HCl and the other NaOH. Calculate the pH of the resulting solution after the addition of
    (a) 0.0005 moles of HCl.
    (b) 0.0005 moles of NaOH.

11. Compare solutions 5 and 10. How much does the pH of each solution change
    (a) when HCl is added
    (b) when NaOH is added

Enter your solution pHs in Table 1 and summarize your results here:

Solution	Change in pH when HCl is added	Change in pH when NaOH is added
5		
10		

12. What is the chemical reaction that describes the dissociation of acetic acid in water? Using this equilibrium reaction, explain why the pH of solution 5 doesn't change very much upon addition of
    (a) HCl.
    (b) NaOH.

13. In grammatically correct sentences using the data in Table 1, explain in your own words the effect of the addition of acid or base on the pH of a buffered solution. Compare your sentences in the group and reach a consensus.

14. Table 1 is missing two pH values for the addition of HCl and NaOH. As a group, design a calculation to determine each of the missing pH values. Consider that the added HCl or NaOH will react with the acetic acid or acetate in solution. Assume an initial volume of 100 mL and that the volume change on addition of HCl or NaOH is negligible. Carry out the calculation and add your values to the Table. Do your results follow the trends for those columns? Compare your strategy to that of another group.

15. Examine the set of solutions 1-9.
    - At what pH(s) of the buffer solution is the difference between the buffer solution pH (column 4) and the pH after addition of HCl (column 5) the smallest?
    - At what pH value(s) of the buffer solution is this difference the largest?

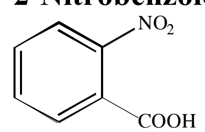
    The buffers in Table 1 show the most effective pH range for the acetic acid/acetate buffer.
    - Over what pH range is the acetic acid/acetate buffer the most effective?
    - Write the most effective pH range as an interval about the pK_a of acetic acid (i.e., pK_a ± ____). Note that one significant figure is sufficient in this expression.

16. Recall from question 15 that the acetic acid/acetate buffer is effective over a certain range around the pK_a. Beyond this range the amount of one of the species – acetic acid or acetate – begins to be sufficiently small that buffering is not effective.

Suppose you wanted to make a buffer of pH 8.0. Would the acetic acid/acetate pair be a good choice? Why or why not?

Consider this…
Table 2 shows the HA concentration for three different weak acids: acetic acid, carbonic acid (pK_1) and 2-nitrobenzoic acid. Each acid has a formal concentration of 0.100 M = F = [HA] + [A^-]. Note that the data are provided in 0.5 pH unit increments.

Table 2. The concentration of the acid (HA) form of a weak acid at various pHs.

pKa	**4.76**	**6.35**	**2.19**
	Acetic	**Carbonic**	**2-Nitrobenzoic**
	CH_3COOH	**H_2CO_3**	 **$O_2NC_6H_4COOH$**
pH	**[HA]**	**[HA]**	**[HA]**
1.0	0.10	0.10	0.09
1.5	0.10	0.10	0.08
2.0	0.10	0.10	0.06
2.5	0.10	0.10	0.03
3.0	0.10	0.10	0.01
3.5	0.09	0.10	0.00
4.0	0.09	0.10	0.00
4.5	0.06	0.10	0.00
5.0	0.04	0.10	0.00
5.5	0.02	0.09	0.00
6.0	0.01	0.07	0.00
6.5	0.00	0.04	0.00
7.0	0.00	0.02	0.00
7.5	0.00	0.01	0.00
8.0	0.00	0.00	0.00

Key Questions

17. Consider 2-nitrobenzoic acid in the last column.
    - At pH 2.0 what are the concentrations of 2-nitrobenzoic acid ($O_2NC_6H_4COOH$) and 2-nitrobenzoate ($O_2NC_6H_4COO^-$)?
    - At very low pHs which species 2-nitrobenzoic acid or 2-nitrobenzoate dominates?
    - At high pHs which species dominates?

18. Recall the effective range of a buffer (see questions 15 and 16). Over what pH range does acetic acid meet this definition? Over what ranges do carbonic and 2-nitrobenzoic acids meet this definition?

19. If you wanted to make a buffer that held the pH at ~6.5, which of these three acids and conjugate bases would you choose? Explain why your choice is the best choice for this pH. Discuss your reasoning with your group members and come to a consensus about which acid/base pair should be used to make the buffer.

20. List the acid/base concepts that you understand better as a result of doing this activity.

21. What strategies did your group use to ensure that everyone participated in the calculations in this activity?

Applications.

22. Joe makes a buffer solution for an experiment. He intends to have the pH set to 10.0. He uses acetic acid/acetate as the buffer system. Is the pH buffered in the desired range? How would you improve on Joe's experimental design?

23. In the laboratory you have a bottle of solid sodium acetate and a 0.100 M HCl solution. Could you make the buffer in solution 5 of Table 1? Explain, using chemical reactions, how you might do this or whether it is impossible to do so.

24. Write the K_a expression for a weak acid, HA, including activity coefficients. Derive the Henderson-Hasselbalch equation from this expression. Show how this equation simplifies to the familiar form when we assume that the ionic strength is low.

25. Suppose you want to make a buffer with a formal concentration of 0.28 M and a pH of 4.94. Calculate how you much acetic acid and sodium acetate you would use to make 1 L of this buffer.

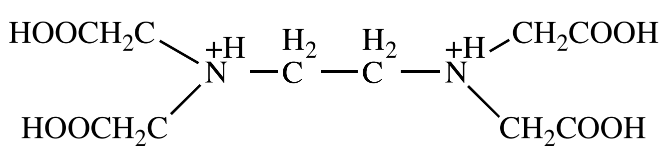
26. Many environmental systems, including lakes, are buffered by a carbonic acid/bicarbonate system. What pH range would you expect to find in a lake? Thoroughly explain your answer.

27. In southwestern PA, an area heavily influenced by acid rain/deposition due to industry in the Ohio River Valley, the pH of streams depends on the geological character of the watershed. Trout Run has a limestone base and has a pH of about 7.5 all year long. Bergstrom Run (about 2 miles away from Trout Run) has a sandstone base and a pH of about 3.5 in the spring after the snow melt. Explain why the two different streams have such different pHs when they both receive the same acid deposition.

28. In order to properly function, enzymes and other proteins must retain their structure. This structure is pH dependent because many of the amino acid side chains (R groups) contain acid or base functional groups. In the body, the pH is maintained by a complex variety of buffers, including the carbonic acid/bicarbonate buffer. Given that blood pH is maintained within a narrow range of 7.2-7.4, evaluate nature's choice of this particular buffer system.

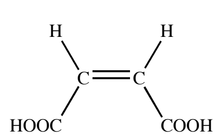
29. The hexaprotic acid ethylenediaminetetraacetic acid (EDTA) is widely used in complexation reactions with metal ions. It is frequently used for titrations of Ca^{2+} and Mg^{2+} ions in water as a measurement of water hardness. In order to observe typical titration behavior at the equivalence point, the pH of the solution must be buffered so that most of the EDTA exists in solution in the fully deprotonated form. Given the information about EDTA below, choose a pH value for optimal titration. Consult a table of acid dissociation constants to choose a buffer that can provide the necessary pH for titration.

n	pK_n
1	0.0
2	1.5
3	2.00
4	2.69
5	6.13
6	10.37

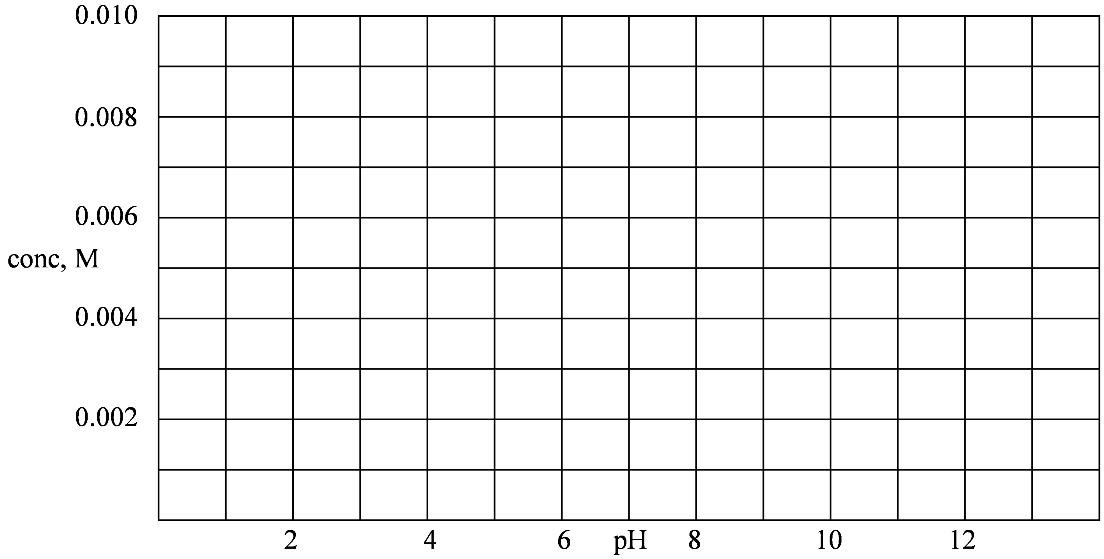


EDTA: H_6Y^{2+}

30. Consider *cis*-Butenedioic acid (Maleic Acid, pK_{a1}=1.92, pK_{a2}=6.27). Sketch the distribution graph for solution containing 0.01 M this weak acid. Label the lines with the respective species to tell them apart. Circle the regions on the graph where Maleic Acid would be a good buffer. Explain why it is in these pH regions that Maleic Acid is a good buffer.



Maleic Acid


0.010
0.008
0.006
conc, M
0.004
0.002
2
4
6
pH
8
10
12