

# Buffers

## Skill Builder

### IDENTIFYING THE BUFFER SYSTEM

Remember that a buffer is a solution created from the combination of a conjugate weak acid/base pair in the same aqueous solution

#### Problem Solving Tips

- 1) The compounds must be related as a conjugate pair that differ by a single H<sup>+</sup>
- 2) Strong acids and bases will never be part of a buffer solution

### FINDING THE PH OF A BUFFER SYSTEM

Sometimes the problem asks for the pH and sometimes it asks for the [H<sup>+</sup>]. Since it's easy enough to convert between the two, NMSI suggests using this equation as your go-to buffer equation.

$$[H^+] = K_a \frac{[weak\ acid]}{[weak\ base]}$$

Alternatively, some people prefer to use Henderson-Hasselbach, which looks similar but involves logarithms.

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

#### Problem Solving Tips

- 1) Identify the acid and the base components of the buffer so that you can put them in the correct part of the equation
- 2) Use  $K_a \times K_b = K_w$  if needed to determine the  $K_a$  for the conjugate pair
- 3) Find the moles (or mmol) of the acid and base component and plug into the appropriate [ ].  
(You can also use molarity values after they have been adjusted for total volume, if you prefer)
- 4) Use  $pH = -\log [H^+]$  to find pH if needed

**INVADING THE BUFFER SYSTEM**

If a strong base or strong acid is added to a buffer system, we fondly call this an “invader” problem. While you will not be expected to calculate the pH of the system after an invasion, qualitative questions about reactions occurring and buffer capacity are fair game.

*Problem Solving Tips*

- 1) Make sure that all acid/base/invader quantities are in **moles or millimoles**.
- 2) Adjust the [weak acid] and [weak base] mole values for new values after buffer reacts with invader. To make it simple, remember if you “add acid” then “ADD to the acid” (and subtract from the base). Alternatively, some people prefer to set up a Before/Change/After table based on the reaction between the buffer component and the invader.

**BUILDING A BUFFER**

You may be asked to select a conjugate acid/base pair and understand the ratio of acid/base components in creating a buffer of a specified pH.

*Problem Solving Tips*

- 1) Choose the combination whose acidic component has a  $pK_a$  value closest to the target pH.
- 2) Remember buffers are also created when a strong A/B reacts with a weak A/B; each mole that reacts produces the conjugate salt and thereby creates a buffer system
- 3) A buffer’s capacity is determined by how many moles of its acidic and basic components are available to react.

**TITRATING IN THE BUFFER ZONE**

Any time a titration or mixture involves a strong/weak pair of acids and bases, a buffer will be created after the first drop hits the flask.

*Problem Solving Tips*

- 1) Recognize the buffer zone that occurs between the initial value and the equivalence point; it should be relatively horizontal.
- 2) The  $K_a$  of the acidic component of the buffer may be determined by the pH at the  $\frac{1}{2}$  equivalence point where the acid/base ratio is 1.

**REFERENCE TABLES**

Acid Name	Formula	$K_a$ Value
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	$1.8 \times 10^{-5}$
Acetylsalicylic acid	$\text{HC}_9\text{H}_7\text{O}_4$	$3.4 \times 10^{-4}$
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$	$6.3 \times 10^{-5}$
Bicarbonate ion	$\text{HCO}_3^-$	$4.7 \times 10^{-11}$
Carbonic acid	$\text{H}_2\text{CO}_3$	$4.4 \times 10^{-7}$
Formic acid	$\text{HCO}_2\text{H}$	$1.8 \times 10^{-4}$
Hydrocyanic acid	$\text{HCN}$	$6.2 \times 10^{-10}$
Hydrofluoric acid	$\text{HF}$	$7.2 \times 10^{-4}$
Hypochlorous acid	$\text{HClO}$	$2.9 \times 10^{-8}$
Lactic acid	$\text{HC}_3\text{H}_5\text{O}_3$	$1.4 \times 10^{-4}$
Propanoic Acid	$\text{HC}_3\text{H}_5\text{O}_2$	$1.3 \times 10^{-5}$

Base Name	Formula	$K_b$ value
Ammonia	$\text{NH}_3$	$1.8 \times 10^{-5}$
Methylamine	$\text{CH}_3\text{NH}_2$	$4.4 \times 10^{-4}$
Ethylamine	$\text{CH}_3\text{CH}_2\text{NH}_2$	$5.6 \times 10^{-4}$

**PRACTICE**

1. For each of the solutions below, first identify if it is a buffer or not and, if it is a buffer, identify the acid and base component of the buffer system.

a) equal volumes of equimolar solutions of  $\text{HClO}_2$  and  $\text{KClO}_2$  are mixed.

Buffer: YES NO

If yes, acid is \_\_\_\_\_ and base is \_\_\_\_\_.

b) 100 mL of 0.2 M  $\text{NH}_3$  and 125 mL of 0.1 M  $\text{NH}_4\text{Cl}$  are mixed.

Buffer: YES NO

If yes, acid is \_\_\_\_\_ and base is \_\_\_\_\_.

c) 50 mL of 0.1 M  $\text{HCl}$  and 25 mL of 0.2 M  $\text{NaCl}$  are mixed.

Buffer: YES NO

If yes, acid is \_\_\_\_\_ and base is \_\_\_\_\_.

d) equal volumes of 0.2 M  $\text{NaHSO}_4$  and 0.25 M  $\text{Na}_2\text{SO}_4$  are mixed.

Buffer: YES NO

If yes, acid is \_\_\_\_\_ and base is \_\_\_\_\_.

e) 100 mL of 0.25 M  $\text{HF}$  and 75 mL of 0.40 M  $\text{Li}_2\text{C}_2\text{O}_4$  are mixed.

Buffer: YES NO

If yes, acid is \_\_\_\_\_ and base is \_\_\_\_\_.

f) equal volumes of 0.1 M  $\text{CH}_3\text{NH}_2$  and 0.2 M  $\text{CH}_3\text{NH}_3\text{Br}$  are mixed.

Buffer: YES NO

If yes, acid is \_\_\_\_\_ and base is \_\_\_\_\_.

2. Find the pH of each of the following buffer solutions:

a) Find the pH of a 300 mL solution created by adding 4 moles of hypochlorous acid ( $\text{HClO}$ ) to 8 moles of sodium hypochlorite ( $\text{NaClO}$ ).

The acid is \_\_\_\_\_ and there are \_\_\_\_\_ mol or mmol

The base is \_\_\_\_\_ and there are \_\_\_\_\_ mol or mmol

b) Find the pH of a solution created by mixing 100 mL of 0.2 M lactic acid ( $\text{HC}_3\text{H}_5\text{O}_3$ ) and 2.5 g of sodium lactate ( $\text{NaC}_3\text{H}_5\text{O}_3$ ).

The acid is \_\_\_\_\_ and there are \_\_\_\_\_ mol or mmol

The base is \_\_\_\_\_ and there are \_\_\_\_\_ mol or mmol

c) Find the pH of a solution created by mixing 1.7 g of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) with 25 mL of 1.0 M ammonia ( $\text{NH}_3$ ).

The acid is \_\_\_\_\_ and there are \_\_\_\_\_ mol or mmol

The base is \_\_\_\_\_ and there are \_\_\_\_\_ mol or mmol

3. A buffer solution is created by mixing 200 mL of 0.2 M formic acid ( $\text{HCO}_2\text{H}$ ) with 30 mmol of potassium formate ( $\text{KHCO}_2$ ).

The acid is \_\_\_\_\_ and there are \_\_\_\_\_ mol or mmol

The base is \_\_\_\_\_ and there are \_\_\_\_\_ mol or mmol

a) Determine the pH of this solution.

b) Write the net ionic equation for the reaction that occurs when hydrochloric acid is added to the solution.

c) After the addition of 30 mL of 0.1 M HCl, \_\_\_\_\_ mmol of invader has been added.

\*d) Find the pH of the solution after the HCl was added.

4. A buffer solution is created by mixing 200 mL of 0.1 M benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ) with 4.5 g of sodium benzoate ( $\text{C}_6\text{H}_5\text{COONa}$ ).

The acid is \_\_\_\_\_ and there are \_\_\_\_\_ mol or mmol

The base is \_\_\_\_\_ and there are \_\_\_\_\_ mol or mmol

a) Determine the pH of this solution.

b) Write the net ionic equation for the reaction that occurs when sodium hydroxide is added to the solution.

c) After 0.01 moles of sodium hydroxide is added to the buffer \_\_\_\_\_ mmol of invader has been added

\*d) Find the pH of the solution after the sodium hydroxide was added.

5. A buffer solution is created by mixing 100 mL of 0.1 M sodium bicarbonate ( $\text{NaHCO}_3$ ) with 5.8 g of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ).

The acid is \_\_\_\_\_ and there are \_\_\_\_\_ mol or mmol

The base is \_\_\_\_\_ and there are \_\_\_\_\_ mol or mmol

a) Determine the pH of this solution.

b) Write the net ionic equation for the reaction that occurs when hydrobromic acid is added to the solution.

c) After 8 mL of 0.2 M HBr is added to the buffer \_\_\_\_\_ mmol of invader has been added.

\*d) Find the pH of the solution

6. Consider a buffer solution created by 500 mL of 0.1 M hydrocyanic acid (HCN) and 2.0 g of sodium cyanide (NaCN).

a) Determine the pH of the solution.

b) What volume of 0.5 M HCl could be added to this solution before the buffering capacity ended?

c) What mass of sodium hydroxide could be added to this solution before the buffering capacity ended?

7. Consider a buffer solution created by 500 mL of 0.2 M hydrocyanic acid and 4 g of sodium cyanide.
- Determine the pH of the solution.
  - Compare the pH of the original buffer solution in #6 and this buffer solution. Explain.
8. Which buffer solution, #6 or #7, has a greater capacity for handling added HCl? Why?
9. A buffer solution is created by mixing 2.8 g of sodium acetate ( $\text{NaC}_2\text{H}_3\text{O}_2$ ) with 200 mL of 0.1 M acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ).
- Determine the pH of this solution.
  - What effect will adding 50 mL of water to the buffer solution have on the pH? Explain.
10. Calculate the specified ratio of concentrations for each of the following to achieve the desired pH:
- hydrofluoric acid (HF) to fluoride ion ( $\text{F}^-$ ) in a buffer solution that has a pH of 3.2.
  - propanoate ion ( $\text{C}_3\text{H}_5\text{O}_2^-$ ) to propanoic acid ( $\text{HC}_3\text{H}_5\text{O}_2$ ) in a buffer solution that has a pH of 5.2.
  - hydrocyanic acid (HCN) to cyanide ion ( $\text{CN}^-$ ) in a buffer solution that has a pH of 9.1.



Lactic acid	Sodium lactate
Acetic acid	Sodium acetate
Sodium bicarbonate	Sodium carbonate
Ammonia	Ammonium chloride

11. Using the table above, choose the acid component and base component you would use to create a buffer solution of the given pH. (No quantities are necessary.) Then calculate the pK<sub>a</sub> for the acid component of your choice using the previously provided reference table.

a) pH = 3.8

Acid \_\_\_\_\_ Base \_\_\_\_\_ pK<sub>a</sub> \_\_\_\_\_

b) pH = 9.3

Acid \_\_\_\_\_ Base \_\_\_\_\_ pK<sub>a</sub> \_\_\_\_\_

c) pH = 10.4

Acid \_\_\_\_\_ Base \_\_\_\_\_ pK<sub>a</sub> \_\_\_\_\_

**Questions 12-14 refer to the following table of available chemicals.:**

0.1 M formic acid ( $\text{HCO}_2\text{H}$ )	sodium formate, $\text{NaHCO}_2$ (MW = 68.01g/mol )
0.2 M propanoic acid ( $\text{HC}_3\text{H}_5\text{O}_2$ )	sodium propanoate, $\text{NaC}_3\text{H}_5\text{O}_2$ (MW = 96.06 g/mol )
0.5 M carbonic acid ( $\text{H}_2\text{CO}_3$ )	sodium bicarbonate, $\text{NaHCO}_3$ (MW = 84.01 g/mol )
0.4 M ammonia ( $\text{NH}_3$ )	ammonium chloride, $\text{NH}_4\text{Cl}$ (MW = 53.49 g/mol)

12. Describe how to make 100 mL of a solution buffered at a pH of 4.3. Your description should include the identity of the acid and base component of your buffer as well as quantities of each chemical.

Choice of conjugate pair: \_\_\_\_\_

13. Describe how to make 200 mL of a solution buffered at a pH of 8.7. Your description should include the identity of the acid and base component of your buffer as well as quantities of each chemical.

Choice of conjugate pair: \_\_\_\_\_

14. Describe how to make 50 mL of a solution buffered at a pH of 6.9. Your description should include the identity of the acid and base component of your buffer as well as quantities of each chemical.

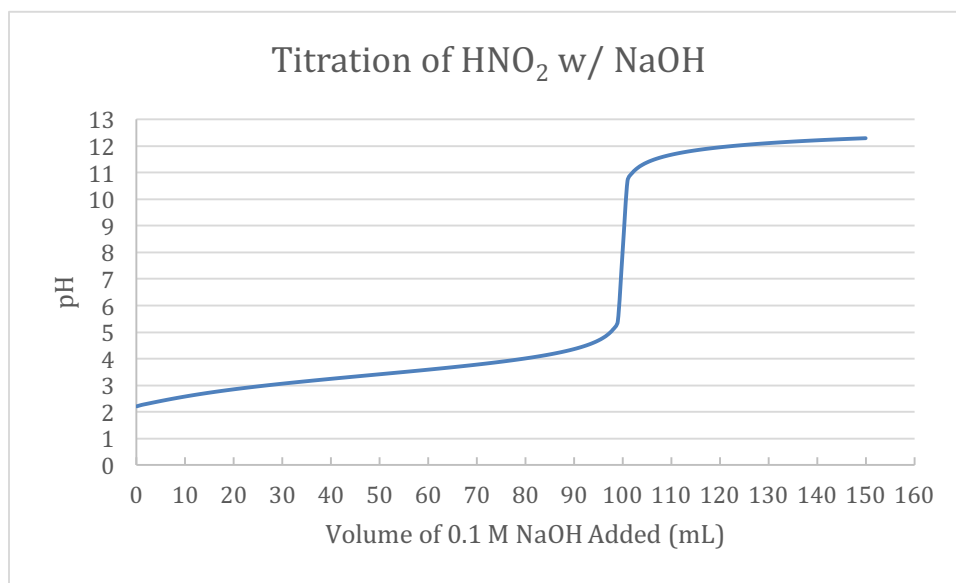
Choice of conjugate pair: \_\_\_\_\_

15. Suppose you have available 100 mL of 0.2 M acetic acid and 5 g of solid sodium hydroxide. Describe how to make 100 mL of a solution buffered at a pH of 4.9.

16. Suppose you have available 200 mL of 0.1 M acetylsalicylic acid and 10 g of solid potassium hydroxide. Describe how to make 200 mL of a solution buffered at a pH of 3.6.

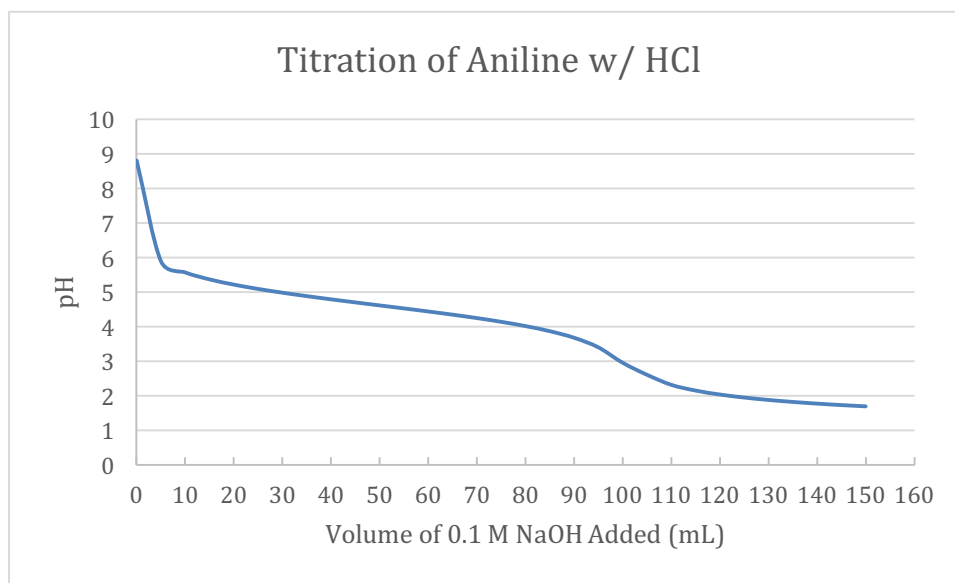
17. Suppose you have available 100 mL of 0.5 M methylamine and 100 mL of 0.5 M hydrochloric acid. Describe how to make a solution buffered at a pH of 10.2.

18. Consider the titration curve below that is created from adding 0.1 M NaOH to 100 mL of 0.1 M HNO<sub>2</sub>.



- a) Show the chemical reaction that occurs to result in a buffer solution when 20 mL of NaOH has been added.
- b) Using the curve, determine the  $K_a$  value of HNO<sub>2</sub>. Show the buffer calculation that relates to this determination.
- c) Using one color highlighter or pen, trace the values on the curve for which  $[\text{HNO}_2] > [\text{NO}_2^-]$ .
- d) Using another color highlighter or pen, trace the values on the curve for which  $[\text{NO}_2^-] > [\text{HNO}_2]$ .

19. Consider the titration curve that is created from adding 0.1 M HCl to 100 mL of 0.1 M aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ).



- Circle the region on the graph that represents a buffer solution present.
  - In the buffer region, using one color highlighter or pen, trace the values on the curve for which  $[\text{C}_6\text{H}_5\text{NH}_2] > [\text{C}_6\text{H}_5\text{NH}_3^+]$ .
  - In the buffer region, using one color highlighter or pen, trace the values on the curve for which  $[\text{C}_6\text{H}_5\text{NH}_2] < [\text{C}_6\text{H}_5\text{NH}_3^+]$ .
  - Estimate the value of  $K_b$  for aniline using the graph.
20. If the pH of a buffer solution of ethylamine ( $\text{CH}_3\text{CH}_2\text{NH}_2$ ) and ethylammonium nitrate ( $\text{CH}_3\text{CH}_2\text{NH}_3\text{NO}_3$ ) is 10.25, which component of the buffer, acid or base is present in higher quantity. Show your reasoning.
21. If the pH of a buffer solution of acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ) and sodium acetate ( $\text{NaC}_2\text{H}_3\text{O}_2$ ) is 5.5, which component of the buffer, acid or base is present in higher quantity. Show your reasoning.

**REFLECTION QUESTIONS**

1. When calculating the pH of a buffer system, what quantities do you need to have?
2. Why is it important to be working with moles or millimoles when dealing with an invader in a buffer?
3. When dealing with a buffer invader problem, what other chemistry problems are these similar to?
4. Why does the pH of a buffer system not change significantly when invaded by a small quantity of strong acid or base?
5. Why is it not necessary to use molarity values when calculating  $[H^+]$  for a buffer but molarity values must be used when dealing with a simple weak acid equilibrium expression?
6. Why does the  $pH = pK_a$  at the  $\frac{1}{2}$  equivalence point in the titration?
7. Look back at problems 2(b) and 2(c). What did you have to do differently in the problems?
8. When creating a buffer, what is the most important factor in the pH of the system?
9. When creating a buffer, what is the most important factor in the capacity of the system for handling invading acid or base?

## AP Problems

### 1993 Q1

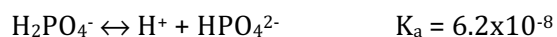


Methylamine,  $\text{CH}_3\text{NH}_2$ , is a weak base that reacts according to the equation above. The value of the ionization constant,  $K_b$ , is  $5.25 \times 10^{-4}$ . Methylamine forms salts such as methylammonium nitrate,  $(\text{CH}_3\text{NH}_3^+)(\text{NO}_3^-)$ .

- (b) Calculate the pH of a solution made by adding 0.0100 mole of a solid methylammonium nitrate to 120.0 milliliters of a 0.225-molar solution of methylamine. Assume that no volume change occurs.
- (c) How many moles of either NaOH or HCl (state clearly which you choose) should be added to the solution in (b) to produce a solution that has a pH of 11.00? Assume that no change in volume occurs.
- (d) A volume of 100. milliliters of distilled water is added to the solution in (c). How is the pH of the solution affected? Explain.

**1992 Q6**

The equations and constants for the dissociation of three different acids are given below.



- (a) From the systems above, identify the conjugate pair that is best for preparing a buffer with a pH of 7.2. Explain your choice.
- (b) Explain briefly how would you prepare the buffer solution described in (a) with the conjugate pair you have chosen.
- (c) If the concentrations of both the acid and the conjugate base you have chosen were doubled, how would the pH be affected? Explain how the capacity of the buffer is affected by this change in concentrations of acid and base.
- (d) Explain briefly how you could prepare the buffer solution in (a) if you had available the solid salt of only one member of the conjugate pair and solutions of a strong acid and a strong base.



**2015 Q3**

Potassium sorbate,  $\text{KC}_6\text{H}_7\text{O}_2$  (molar mass 150. g/mol) is commonly added to diet soft drinks as a preservative. A stock solution of  $\text{KC}_6\text{H}_7\text{O}_2(\text{aq})$  of known concentration must be prepared. A student titrates 45.00 mL of the stock solution with 1.25 M  $\text{HCl}(\text{aq})$  using both an indicator and a pH meter. The value of  $K_a$  for sorbic acid,  $\text{HC}_6\text{H}_7\text{O}_2$ , is  $1.7 \times 10^{-5}$ .

(a) Write the net ionic equation for the reaction between  $\text{KC}_6\text{H}_7\text{O}_2(\text{aq})$  and  $\text{HCl}(\text{aq})$ .

(d) Calculate the pH at the half-equivalence point.

(f) The pH of the soft drink is 3.37 after the addition of the  $\text{KC}_6\text{H}_7\text{O}_2(\text{aq})$ . Which species,  $\text{HC}_6\text{H}_7\text{O}_2$  or  $\text{C}_6\text{H}_7\text{O}_2^-$ , has a higher concentration in the soft drink? Justify your answer.