

## Ch. 17 Applications of Aqueous Equilibria: Buffers and Titrations

What does a buffer do?

What does a buffer consist of?

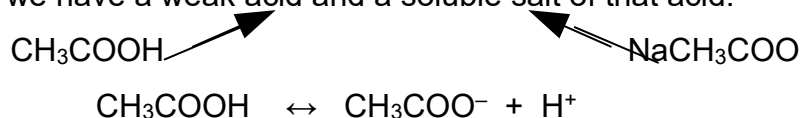
How do you make a buffer?

**Sec 1 The Common-Ion Effect:** The dissociation of a weak electrolyte decreases when a strong electrolyte that has an ion in common with the weak electrolyte – is added to the solution.

A. Examples include: 1) a solution containing a WA + soluble salt of the WA

2) a solution containing a WB + a soluble salt of the WB

Suppose we have a weak acid and a soluble salt of that acid.



Since NaCH<sub>3</sub>COO provides a high concentration of acetate ions (common ions), adding it to the solution...

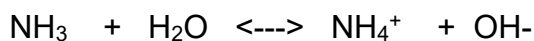
By Le Chatelier... (shifts the equilibrium far to the left)

The result is that... (H<sup>+</sup> concentration is drastically decreased)

COMMON ION EFFECT: (2 points)



B. How does this equilibrium reaction act as a buffer system?



answer: If an acid is added NH<sub>3</sub> will accept a proton, forming NH<sub>4</sub><sup>+</sup>. As ammonium increases, the equilibrium shifts to the left, forming more ammonia. If a base is added, the increase in hydroxide shifts the reaction to the left.

**Ex. #1:** Find the pH of a solution containing 0.085 M HNO<sub>2</sub> (K<sub>a</sub> = 4.5 × 10<sup>-4</sup>) and 0.10 M KNO<sub>2</sub>.

## Sec 2. Buffered Solutions (“buffers”) - p. 736

- A. contain a weak conjugate acid-base pair
- B. contain an acidic species and a basic species that do NOT consume each other through neutralization
- C. Buffer solutions resist changes in pH because they react with both hydronium and hydroxide ions.

Making an Acidic Buffer Solution

Making a Basic Buffer Solution

**Ex #2:** For a  $\text{CH}_3\text{COOH}$  and- $\text{CH}_3\text{COO}^-$  buffer, you could use...

For an  $\text{NH}_4^+$ -and- $\text{NH}_3$  buffer, you could use...

**Sec 3 Buffer Capacity:** the amount of acid or base the buffer can “neutralize” before the pH begins to change appreciably.

2 calculations needed:

- 1) *the pH of a solution where the buffer capacity has been exceeded;*
- 2) *choose among alternatives the best buffer system for a given pH.*

**Ex. #3:** Find the pH of a buffer that is 0.12 M lactic acid,  $\text{HC}_3\text{H}_5\text{O}_3$  ( $K_a = 1.4 \times 10^{-4}$ ) and 0.10 M sodium lactate. (answer: 3.8)

## BUFFER EFFECTIVENESS

- An effective buffer neutralizes moderate amounts of added acid or base.
- However, there is a limit to how much can be added before the pH changes significantly.
- The **buffer capacity** is the amount of acid or base a buffer can neutralize.
- The **buffer range** is the pH range in which the buffer can be effective.
- The effectiveness of a buffer depends on two factors: (1) the relative amounts of buffer acid and base, and (2) the absolute concentrations of buffer acid and base.

### Effectiveness of Buffers

- A buffer will be **most** effective when the ratio  $[\text{acid}]:[\text{base}] = 1$ .
  - Equal concentrations of acid and base
- A buffer will be effective when  $0.1 < [\text{base}]:[\text{acid}] < 10$ .
- A buffer will be most effective when the  $[\text{acid}]$  and the  $[\text{base}]$  are large.

### Buffer Range

- We have said that a buffer will be effective when  $0.1 < [\text{base}]:[\text{acid}] < 10$ .
- Substituting into the Henderson–Hasselbalch equation, we can calculate the maximum and minimum pH at which the buffer will be effective.

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

Lowest pH

$$\text{pH} = \text{p}K_a + \log(0.10)$$

$$\text{pH} = \text{p}K_a - 1$$

Highest pH

$$\text{pH} = \text{p}K_a + \log(10)$$

$$\text{pH} = \text{p}K_a + 1$$

Therefore, the effective pH range of a buffer is  $\text{p}K_a \pm 1$ .

When choosing an acid to make a buffer, choose one whose  $\text{p}K_a$  is closest to the pH of the buffer.

## Sec. 4 How Acid Buffers Work: Addition of Base

- Buffers work by applying LeChatelier's principle to WA equilibrium.
- Buffer solutions contain significant amounts of the weak acid molecules, HA.
- These molecules react with added base to neutralize it.



*dissociation ionization*  $K_a, K_b, pK_a, \text{ and } pK_b$  *conjugate acid base pairs*

**Acid association constant  $K_a$ :**  
 The equilibrium constant that measures the degree of dissociation for an acid under specific conditions. For an acid HA:  

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$
 *$[\text{H}_3\text{O}^+]$   $pK_a = -\log K_a$  smaller  $pK_a =$  stronger the acid*

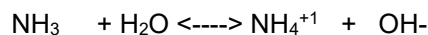
**Base dissociation constant  $K_b$ :**  
 The equilibrium constant that measures the degree of dissociation for a base under specific conditions. For a base BOH:  

$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]}$$

### 2 ways to solve the problem

What is the pH of a solution containing 2.00M ammonia and 3.00 M of ammonium chloride? Given:  $K_b = 1.81 \times 10^{-5}$

Way 1: Do ICE and the  $K_b$  expression:



$$K_b = \frac{[\text{NH}_4^{+1}][\text{OH}^-]}{[\text{NH}_3]} = 1.81 \times 10^{-5}$$

NH <sub>3</sub>	H <sub>2</sub> O	←----→	NH <sub>4</sub> <sup>+1</sup>	OH <sup>-</sup>
2.00	---		3.00	----
-x	---		x	+x
2.00-x	---		3.00+x	x

$$K_b = \frac{[\text{NH}_4^{+1}][\text{OH}^-]}{[\text{NH}_3]} = \frac{(3.00 + x)(x)}{(2.00 - x)} = 1.81 \times 10^{-5}$$

assume x small due to %5 rule:  $1.81 \times 10^{-5} = \frac{3.00(x)}{2.00}$

$$x = 1.21 \times 10^{-5} = [\text{OH}^-]$$

pOH = 4.918      pH = 9.082

Way 2: Henderson/Hasselbach equation: (for acids)  $\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$

OR

$$\text{(for bases)} \quad \text{pOH} = \text{pK}_b + \log \frac{[\text{HB}^+]}{[\text{B}]}$$

$$= 4.742 + \log \frac{3.00}{2.00}$$

= 4.918 then, don't forget to convert....

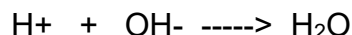
$$\text{pH} = 9.082$$

**Ex.#4:** A buffered solution of pH 4.74 contains 0.30 M  $\text{CH}_3\text{COOH}$  ( $K_a = 1.8 \times 10^{-5}$ ) and 0.30 M  $\text{NaCH}_3\text{COO}$ . Calculate the pH after 0.020 M NaOH is added. Ignore volume changes

## Titration

- In an **acid–base titration**, a solution of unknown concentration (**titrant**) is slowly added to a solution of known concentration until the reaction is complete.
- When the moles of acid are stoichiometrically equal to the moles of base, the titration has reached its **equivalence point**.
- An **indicator** is a chemical that changes color when the pH changes.

## Sec 5 Strong Acid – Strong Base Titrations



The reverse reaction of the autoionization of water is  $K = 1/K_w$

$$K = 1 / 1 \times 10^{-14}$$

This reaction is certainly complete;

**This type of titration is less an equilibrium problem than a stoich one.**

*\*Any indicator whose color*

*change begins and ends along the vertical line is okay.*

-- phenolphthalein (pH 8.3-10.0)

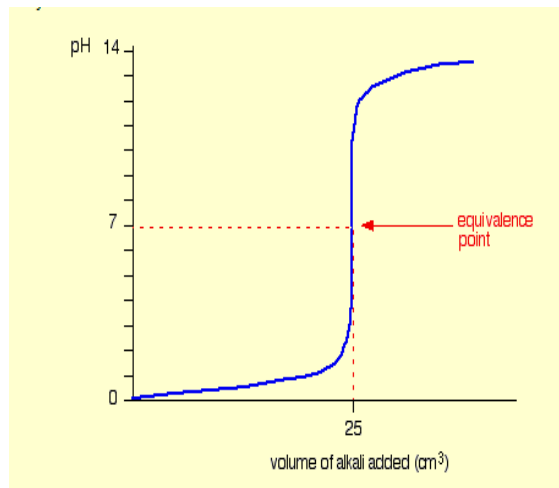
base =

acid =

-- methyl red (pH 4.2-6.0)

base =

acid =



ACID-BASE REACTIONS – TITRATION GRAPH HANDOUT or PRINTOUT

**What is the pH of a solution containing 25.00 mL of a 0.100 M HCl to which 10.00 mL of a 0.100 M solution of NaOH has been titrated?**

**Step 1: calculate the # of MOLES HCl and NaOH initially present**

$$0.100\text{mol/L} \times .02500 \text{ L} = 0.00250 \text{ moles HCl}$$

**\*MV = moles**

$$0.100 \text{ mol/L} \times .01000 \text{ L} = 0.00100 \text{ moles NaOH}$$

	HCl	+ NaOH	---->	NaCl	+ H <sub>2</sub> O
start	0.00250mol	0.00100 mol		0 mol	
change	-0.00100mol	-0.00100 mol		+0.00100mol	
after rxn	0.00150 mol	0 mol		.00100 mol	

**Step 2: Calculate the M of acid (or base) – both are STRONG!**

$$\text{HCl} = \frac{.00150 \text{ mol}}{.03500 \text{ L (total volume)}} = .0430 \text{ M}$$

$$[\text{H}_3\text{O}^+] = 4.30 \times 10^{-2} \text{M}$$

$$\text{pH} = -\log 4.30 \times 10^{-2} \text{ M} = 1.366$$

*\*\*\* After 25.00 mL of 0.100 M NaOH has been titrated (the equivalence pt), the pH is 7.00 because the NaOH exactly neutralizes the HCl.*

**Ex # 5:** Calculate the pH after the 4.00 mL of 0.2500 M HCl have been added to 50.00 mL of 0.1500 M NaOH. (ans: pH =13.1)

## What happens SB is added to a buffer?

Calculate the pH of the 0.250 M HCOOH/0.100 M HCOONa a buffer used after the addition of 10.0 mL of 6.00 M NaOH to the original buffered solution volume of 500.0 mL.

Strategy: 1) determine the moles of weak acid and base existing after the addition of the SB (stoichiometry part); 2) calculate the pH of the buffered solution after you have your new equilibrium concentration.  
(equilibrium part)

### 1) stoichiometry part

$$\text{mmoles HCOOH}_{\text{initial}} = 0.250 \text{ mmol/mL} \times 500.0 \text{ mL} = 125 \text{ mmol}$$

$$\text{mmoles HCOO}^{-}_{\text{initial}} = 0.100 \text{ mmol/mL} \times 500.0 \text{ mL} = 50.0 \text{ mmol}$$

$$\text{mmol OH}^{-}\text{-added} = 6.00 \text{ mmol/mL} \times 10.0 \text{ mL} = 60.0 \text{ mmol}$$

	HCOOH	+ OH <sup>-</sup>	---->	HCOO <sup>-</sup>
I (mmol)	125	60.0		50.0
F (mmol)	65.0	0		110

after addition of NaOH,

$$[\text{HCOOH}] = 65.0 \text{ mmol} / 510 \text{ mL} = 0.128 \text{ M}$$

(500+10)

equilibrium concentration

$$[\text{HCOO}^{-}] = 110 \text{ mmol} / 510 \text{ mL} = 0.216 \text{ M}$$

### 2) equilibrium part

The acid dissociation of HCOOH is the significant factor here.

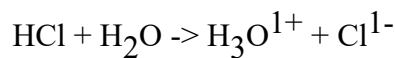
$$K_a = \frac{[\text{H}^{+}][\text{HCOO}^{-}]}{[\text{HCOOH}]}$$

$$1.8 \times 10^{-4} = \frac{[\text{H}^{+}][0.216]}{[0.128]} \Rightarrow [\text{H}^{+}] = 1.1 \times 10^{-4} \quad \text{pH} = 4.0 \quad (5\% \text{ rule holds})$$

**Identify Each Species.- CHEMISTRY 1<sup>st</sup>!**

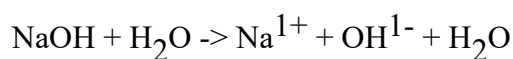
First identify each species and decide what it will do in water

1. **Is it a strong acid?** If yes, it will completely dissociate in water. Since it is the ions that do the chemistry, write them as ions. example:



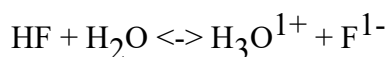
Since it is a strong acid it dissociates completely, you will not have any HCl.  $\text{Cl}^{1-}$  is not going to do anything in an acid base reaction. It is a spectator ion so leave it out. What you need is to figure out the  $[\text{H}_3\text{O}^{1+}]$  (ie: the concentration of hydronium ions). Remember concentration is moles over liters.

2. **Is it a strong base?** If yes it will completely dissociate in water. Since it is the ions that do the chemistry, write them as ions. example:



Since it is a strong base it dissociates completely. You will not have any NaOH.  $\text{Na}^{1+}$  is not going to do anything in an acid base reaction. It is a spectator ion so leave it out. What you need to do is figure out the  $[\text{OH}^{1-}]$  (ie: the concentration of hydroxide ions). Remember concentration is moles over liters.

3. **Is it a weak acid?** If yes it will partially dissociate in water. Now you need to pay attention to the equilibrium reactions. First write out the balanced equilibrium reaction. example:

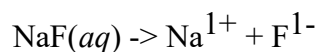


Then write out the equilibrium expression:

$$K_a = \frac{[\text{F}^{1-}] [\text{H}_3\text{O}^{1+}]}{[\text{HF}]}$$

You will need to use this expression to determine what concentration each species is at when the system is at equilibrium.

4. **Is it a salt?** What will it do in solution. FIRST, the salt will dissociate into ions. Just like NaCl in water dissociates and forms  $\text{Na}^{1+}$  and  $\text{Cl}^{1-}$ . Any other salt will do the same thing. You should be able to identify a salt by looking at the periodic table and thinking about trends in electronegativity. First let the salt dissociate. example:



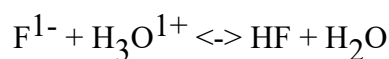
You need to do this so that you can decide what will happen in solution. Almost everyone in the class missed one or more problem because they failed to recognize a salt, and then see what it will do in solution. After you write the salt out as ions, look at the ions to see if you recognize any of them as a weak acid or a weak base. Or the conjugate acid or base. Anything with a  $K_a$  or  $K_b$ . After you recognize it as an acid or base, write the appropriate reaction.



This step can be a bit tricky. For the example here  $F^{1-}$  is the conjugate base of a weak acid. That means that it would like to gain a proton ( $H^{1+}$ ) from something. The reaction that you write depends upon what species are present. The idea here is to think about what the strongest acid is. If only the salt is present, the strongest acid is water.



But, If any acid is present you can write a different reaction.



Notice that this is like the acid dissociation of HF shown above. Since HF is a weak acid,  $F^{1-}$  is also a weak base. That means you need to use an equilibrium expression to solve for the concentration of each species. We will deal with the equilibrium expressions below.

### **Write out a list of all species present.**

After you identify all the species present and write out appropriate reactions, write out a list of all the species present, ignoring equilibrium reactions and species at first.

1. If you have a strong acid, write down [ $H_3O^{1+}$ ]
2. If you have a strong base, write down [ $OH^{1-}$ ]
3. If you have a weak acid, write down [HA]
4. If you have a conjugate base (from a salt), write down [ $A^{1-}$ ]

### **Deal with the strong acid and base.**

THESE WILL REACT TO COMPLETION WITH THE AVAILABLE SPECIES.

1. A strong acid will react with a strong base.
  - a. Determine which is the limiting reagent.
  - b. Find the final concentration of the excess reagent.
  - c. The final concentration of the excess reagent will determine the pH. DONE.
2. A strong acid will react with a conjugate base.
  - a. The reaction will go to completion.
  - b. Determine which is the limiting reagent.
  - c. If conjugate base is limiting, there is excess strong acid. This determines the pH. DONE.
  - d. If the strong acid is limiting, there will be excess conjugate base and the pH is determined for the buffer (produced from the conjugate base and the weak acid)
3. A strong base will react with a weak acid.
  - a. The reaction will go to completion
  - b. Determine the limiting reagent.
  - c. If the weak acid is limiting, there is excess strong base. This determines the pH. DONE
  - d. If the strong base is limiting, there will be excess weak acid and the pH is determined for the buffer (produced from the conjugate base and the weak acid).