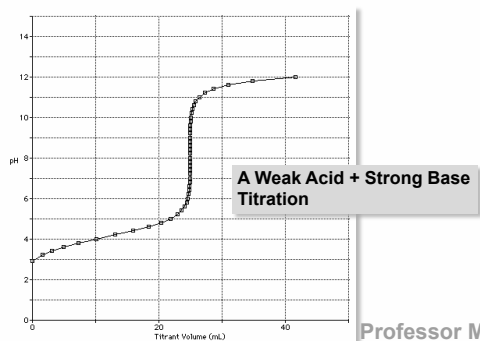


## ACID-BASE REACTIONS

Chapter 14  
("Part II")

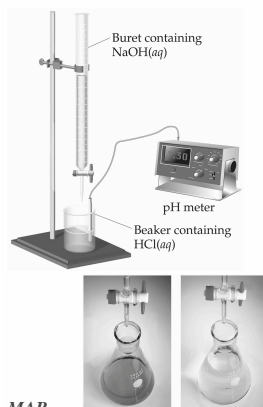


Last update:  
4/29/24

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Chemistry 223

Professor Michael Russell



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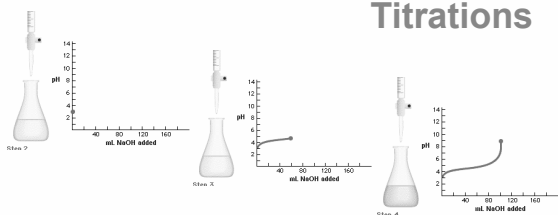
## Titration

In a titration a known concentration of base (*or acid*) is slowly added to a solution of acid (*or base*)

A pH meter or indicators are used to determine when the solution has reached the **equivalence point** (where moles of acid = moles of base)

**Goal:** to determine experimentally or calculate the pH at *any* point in a titration

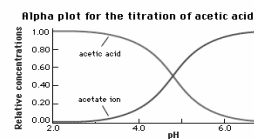
## Titration



**Adding NaOH from the buret to acetic acid:**  
Initially the pH increases very slowly, then rises dramatically at **equivalence point**  
pH rises, then levels off as equivalence point passed

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## Acid-Base Titrations



Notice how [HOAc] diminishes with NaOH, *but* [OAc<sup>-</sup>] increases with NaOH

Important to consider *conjugates* in titrations where weak acids or bases dominate

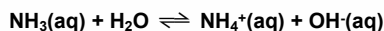
But first, *buffers* and the *common ion effect*

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## The Common Ion Effect

A special form of Le Chatelier's Principle...

**QUESTION:** What is the effect on the pH of adding NH<sub>4</sub>Cl to 0.25 M NH<sub>3</sub>(aq)?



Here we are adding an ion **COMMON** to the equilibrium with NH<sub>3</sub> (*i.e.* NH<sub>4</sub><sup>+</sup>)

Le Chatelier predicts that the equilibrium will shift to the \_\_\_\_\_.

The pH will go \_\_\_\_\_.

After all, NH<sub>4</sub><sup>+</sup> is an acid!

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## The Common Ion Effect

A special form of Le Chatelier's Principle...

**QUESTION:** What is the effect on the pH of adding NH<sub>4</sub>Cl to 0.25 M NH<sub>3</sub>(aq)?



Let us first calculate the pH of a 0.25 M NH<sub>3</sub> solution.

	[NH <sub>3</sub> ]	[NH <sub>4</sub> <sup>+</sup> ]	[OH <sup>-</sup> ]
initial			
change			
equilib			

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## The Common Ion Effect

*A special form of Le Chatelier's Principle...*

**QUESTION:** What is the effect on the pH of adding  $\text{NH}_4\text{Cl}$  to  $0.25 \text{ M NH}_3(\text{aq})$ ?



$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{0.25 - x}$$

Assuming  $x$  is  $\ll 0.25$ , we have

$$[\text{OH}^-] = x = [K_b(0.25)]^{1/2} = 0.0021 \text{ M}$$

This gives  $\text{pOH} = 2.67$

and so  $\text{pH} = 14.00 - 2.67 = 11.33$

$$\text{or: } \text{pH} = 14 + \log [K_b \cdot C_b]^{1/2} = 11.33$$

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## The Common Ion Effect

*A special form of Le Chatelier's Principle...*

**Problem:** What is the pH of a solution with  $0.10 \text{ M NH}_4\text{Cl}$  and  $0.25 \text{ M NH}_3(\text{aq})$ ?



We expect that the pH will decline on adding  $\text{NH}_4\text{Cl}$ . Let's test that!

	$[\text{NH}_3]$	$[\text{NH}_4^+]$	$[\text{OH}^-]$
initial			
change			
equilib			

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## The Common Ion Effect

*A special form of Le Chatelier's Principle...*

**Problem:** What is the pH of a solution with  $0.10 \text{ M NH}_4\text{Cl}$  and  $0.25 \text{ M NH}_3(\text{aq})$ ?



$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x(0.10 + x)}{0.25 - x}$$

Because equilibrium shifts left,  $x$  is MUCH less than  $0.0021 \text{ M}$ , the value *without*  $\text{NH}_4\text{Cl}$ .

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## The Common Ion Effect

*A special form of Le Chatelier's Principle...*

**Problem:** What is the pH of a solution with  $0.10 \text{ M NH}_4\text{Cl}$  and  $0.25 \text{ M NH}_3(\text{aq})$ ?



$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x(0.10 + x)}{0.25 - x}$$

$$[\text{OH}^-] = x = (0.25 / 0.10)K_b = 4.5 \times 10^{-5} \text{ M}$$

This gives  $\text{pOH} = 4.35$  and  $\text{pH} = 9.65$

**pH drops from 11.33 to 9.65 on adding a common ion ( $\text{NH}_4^+$ ).**

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## Buffer Solutions

The function of a buffer is to resist changes in the pH of a solution.

Buffers invoke a special case of the common ion effect.

Buffer Composition:

<u>Weak Acid</u>	+	<u>Conj. Base</u>
HOAc	+	OAc <sup>-</sup>
$\text{H}_2\text{PO}_4^-$	+	$\text{HPO}_4^{2-}$
<u>Weak Base</u>	+	<u>Conj. Acid</u>
$\text{NH}_3$	+	$\text{NH}_4^+$

*Buffers and Henderson-Hasselbalch Guide*

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## Buffer Solutions



HCl is added to pure water.

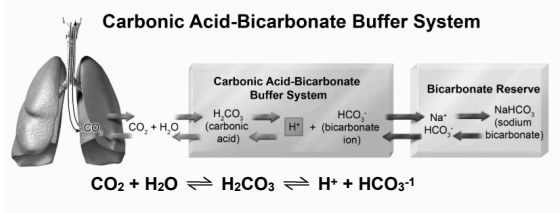


HCl is added to a solution of a weak acid  $\text{H}_2\text{PO}_4^-$  and its conjugate base  $\text{HPO}_4^{2-}$ .

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## Buffers in Our Bodies

The blood pH in our bodies is regulated by a carbonic acid / hydrogen carbonate ("bicarbonate") buffer system:



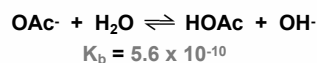
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Exhaling  $\text{CO}_2$  raises the pH of our blood!

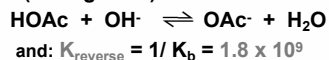
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## Buffer Solutions

Consider  $\text{HOAc}/\text{OAc}^-$  to see how buffers work  
The weak acid in buffers consumes strong base!  
We know:



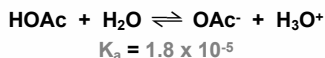
Therefore, the reverse reaction of the weak acid with added  $\text{OH}^-$  (strong base) would be:



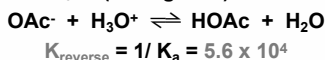
$K_{\text{reverse}}$  is VERY large, so  $\text{HOAc}$  completely consumes the  $\text{OH}^-$ !

## Buffer Solutions

Consider  $\text{HOAc}/\text{OAc}^-$  to see how buffers work  
Conjugate base in buffers consumes strong acid!



Therefore, the reverse reaction of the weak base with added  $\text{H}_3\text{O}^+$  (strong acid) would be:

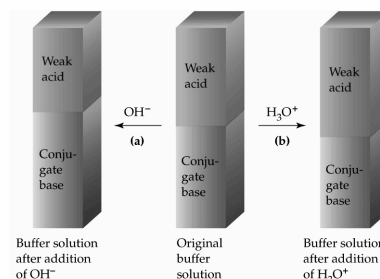


$K_{\text{reverse}}$  is VERY LARGE, so  $\text{OAc}^-$  completely consumes the  $\text{H}_3\text{O}^+$ !

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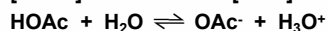
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## Buffer Solutions



## Buffer Solutions

**Problem:** What is the pH of a buffer that has  $[\text{HOAc}] = 0.700 \text{ M}$  and  $[\text{OAc}^-] = 0.600 \text{ M}$ ?



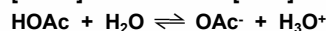
$$K_a = 1.8 \times 10^{-5}$$

	[HOAc]	[OAc <sup>-</sup> ]	[H <sub>3</sub> O <sup>+</sup> ]
initial			
change			
equilib			

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## Buffer Solutions

**Problem:** What is the pH of a buffer that has  $[\text{HOAc}] = 0.700 \text{ M}$  and  $[\text{OAc}^-] = 0.600 \text{ M}$ ?



$$K_a = 1.8 \times 10^{-5}$$

	[HOAc]	[OAc <sup>-</sup> ]	[H <sub>3</sub> O <sup>+</sup> ]
equilib	0.700 - x	0.600 + x	x

Assuming that  $x \ll 0.700$  and  $0.600$ , we have

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+](0.600)}{0.700}$$

$$[\text{H}_3\text{O}^+] = 1.8 \times 10^{-5} * (0.700 / 0.600) = 2.1 \times 10^{-5} \text{ and}$$

$$\text{pH} = 4.68$$

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## Buffer Solutions

Notice that the expression for calculating the  $H^+$  conc. of the buffer is:

$$[H_3O^+] = \frac{\text{Orig. conc. of HOAc}}{\text{Orig. conc. of OAc}^-} \cdot K_a$$

$$[H_3O^+] = \frac{[\text{Acid}]}{[\text{Conj. base}]} \cdot K_a \text{ or } [OH^-] = \frac{[\text{Base}]}{[\text{Conj. acid}]} \cdot K_b$$

Notice that  $[H_3O^+]$  or  $[OH^-]$  depend on  $K$  and the ratio of acid and base concentrations

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## Henderson-Hasselbalch Equation

$$[H_3O^+] = \frac{[\text{Acid}]}{[\text{Conj. base}]} \cdot K_a$$

Take the negative log of both sides of this equation:

$$pH = pK_a - \log \frac{[\text{Acid}]}{[\text{Conj. base}]}$$

The Henderson - Hasselbalch Eq!

$$pH = pK_a + \log \frac{[\text{Conj. base}]}{[\text{Acid}]}$$

The pH is determined largely by the  $pK_a$  of the acid and then adjusted by the ratio of acid and conjugate base. *Important equation!*

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## Henderson-Hasselbalch Equation

$$pH = pK_a + \log \frac{[\text{Conj. base}]}{[\text{Acid}]}$$

Note that the CONCENTRATIONS of the acid and conjugate base are not important.

It is the RATIO of the NUMBER OF MOLES that affects pH

Result: diluting a buffer solution does not change its pH

Result: You can use moles or molarity when using Henderson-Hasselbalch!

See: Buffers and Henderson-Hasselbalch Guide

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## Adding an Acid to a Buffer

Problem: What is the pH when 1.00 mL of 1.00 M HCl is added to

- 1.00 L of pure water (before HCl, pH = 7.00)
- 1.00 L of buffer that has  $[HOAc] = 0.700$  M and  $[OAc^-] = 0.600$  M (pH = 4.68)

Solution to Part (a)

pH of strong acid =  $-\log [H_3O^+] = -\log [HCl]$

$$M_1 \cdot V_1 = M_2 \cdot V_2$$

$$1.00 \text{ M} \cdot 1.00 \text{ mL} = M_2 \cdot 1001 \text{ mL}$$

$$M_2 = 9.99 \times 10^{-4} \text{ M} = [H_3O^+]$$

$$pH = 3.00$$

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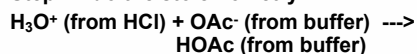
## Adding an Acid to a Buffer

What is the pH when 1.00 mL of 1.00 M HCl is added to

- 1.00 L of pure water (after HCl, pH = 3.00)
- 1.00 L of buffer that has  $[HOAc] = 0.700$  M and  $[OAc^-] = 0.600$  M (pH = 4.68)

Solution to Part (b)

Step 1 - do the stoichiometry



The reaction occurs completely because  $K$  is very large.

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## Adding an Acid to a Buffer

What is the pH when 1.00 mL of 1.00 M HCl is added to

- 1.00 L of pure water (after HCl, pH = 3.00)
- 1.00 L of buffer that has  $[HOAc] = 0.700$  M and  $[OAc^-] = 0.600$  M (pH = 4.68)

Solution to Part (b): Step 1-Stoichiometry

	$[H_3O^+]$	$[OAc^-]$	$[HOAc]$
Initial			
Change			
After rxn			

Now we need to calculate pH using our new buffer solution

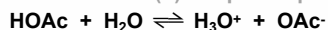
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### Adding an Acid to a Buffer

What is the pH when 1.00 mL of 1.00 M HCl is added to

- a) 1.00 L of pure water (after HCl, pH = 3.00)  
 b) 1.00 L of buffer that has [HOAc] = 0.700 M and [OAc<sup>-</sup>] = 0.600 M (pH = 4.68)

Solution to Part (b): Step 2 - Equilibrium



Initial  
Change  
Equilibrium

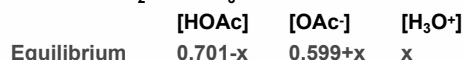
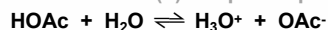
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### Adding an Acid to a Buffer

What is the pH when 1.00 mL of 1.00 M HCl is added to

- a) 1.00 L of pure water (after HCl, pH = 3.00)  
 b) 1.00 L of buffer that has [HOAc] = 0.700 M and [OAc<sup>-</sup>] = 0.600 M (pH = 4.68)

Solution to Part (b): Step 2 - Equilibrium



Because [H<sub>3</sub>O<sup>+</sup>] = 2.1 × 10<sup>-5</sup> M *BEFORE* adding HCl, we again neglect x relative to 0.701 and 0.599.

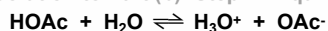
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### Adding an Acid to a Buffer

What is the pH when 1.00 mL of 1.00 M HCl is added to

- a) 1.00 L of pure water (after HCl, pH = 3.00)  
 b) 1.00 L of buffer that has [HOAc] = 0.700 M and [OAc<sup>-</sup>] = 0.600 M (pH = 4.68)

Solution to Part (b): Step 2 - Equilibrium



$$[\text{H}_3\text{O}^+] = \frac{[\text{HOAc}]}{[\text{OAc}^-]} \cdot K_a = \frac{0.701}{0.599} \cdot (1.8 \times 10^{-5})$$

$$[\text{H}_3\text{O}^+] = 2.1 \times 10^{-5} \text{ M} \rightarrow \text{pH} = 4.68$$

The pH has not changed on adding HCl to the buffer!

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### Adding an Acid to a Buffer

Use the Henderson-Hasselbalch equation to calculate the pH when 1.00 mL of 1.00 M HCl is added to 1.00 L of buffer that has [HOAc] = 0.700 M and [OAc<sup>-</sup>] = 0.600 M

We can use an *alternate* form of the H-H equation:

$$\text{pH} = \text{p}K_a + \log \left( \frac{\text{mol}_{\text{Conj base}} - \text{mol}_{\text{strong acid}}}{\text{mol}_{\text{weak acid}} + \text{mol}_{\text{strong acid}}} \right)$$

$$\text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.74$$

$$\text{pH} = 4.74 + \log \left( \frac{0.600 - 0.00100}{0.700 + 0.00100} \right) = 4.67$$

Answer in good agreement with "double ice" method (4.68)

See: [Buffers and Henderson-Hasselbalch Guide](#)

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## Adding Acids and Bases to Buffers

For adding strong acids to buffers:

$$\text{pH} = \text{p}K_a + \log \left( \frac{\text{mol}_{\text{Conj base}} - \text{mol}_{\text{strong acid}}}{\text{mol}_{\text{weak acid}} + \text{mol}_{\text{strong acid}}} \right)$$

For adding strong bases to buffers:

$$\text{pH} = \text{p}K_a + \log \left( \frac{\text{mol}_{\text{Conj base}} + \text{mol}_{\text{strong base}}}{\text{mol}_{\text{weak acid}} - \text{mol}_{\text{strong base}}} \right)$$

Very useful for calculating pH changes in buffers!  
 See: [Buffers and Henderson-Hasselbalch Guide](#)

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## Preparing a Buffer

You want to create a buffer solution with a pH = 4.30.

This means [H<sub>3</sub>O<sup>+</sup>] = 10<sup>-pH</sup> = 5.0 × 10<sup>-5</sup> M

It is best to choose an acid such that:

- \* [H<sub>3</sub>O<sup>+</sup>] ≈ K<sub>a</sub>, or
- \* pH ≈ pK<sub>a</sub>

You get the *exact* [H<sub>3</sub>O<sup>+</sup>] (or pH) by adjusting the *ratio* of weak acid to conjugate base.

For a pH = 4.30 buffer, we will look for a value of K<sub>a</sub> ≈ 5.0 × 10<sup>-5</sup> or a pK<sub>a</sub> ≈ 4.30



Henderson



Hasselbalch

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## Preparing a Buffer

You wish to create a buffer solution at pH = 4.30 (or  $[H_3O^+] = 5.0 \times 10^{-5} M$ .) Which of these buffer combinations should you select?

POSSIBLE BUFFERS	$K_a$	$pK_a$
$HSO_4^- / SO_4^{2-}$	$1.2 \times 10^{-2}$	1.92
HOAc / OAc <sup>-</sup>	$1.8 \times 10^{-5}$	4.74
HCN / CN <sup>-</sup>	$4.0 \times 10^{-10}$	9.40

Best choice is acetic acid / acetate - closest in  $[H_3O^+]$  to  $K_a$  or pH to  $pK_a$ !

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## Preparing a Buffer

You want to create a buffer solution at pH = 4.30 (or  $[H_3O^+] = 5.0 \times 10^{-5} M$ ) using HOAc and OAc<sup>-</sup>. Equal moles of acid (HOAc) and base (OAc<sup>-</sup>) create pH = 4.74 (=  $pK_a$ ). Find the ratio of acid to base needed to get the buffer to 4.30.

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]}, \text{ or rearranged:}$$

$$[H_3O^+] = 5.0 \times 10^{-5} = \frac{[HOAc]}{[OAc^-]} (1.8 \times 10^{-5})$$

$$\begin{aligned} \text{Solve for } [HOAc] / [OAc^-] \text{ ratio:} \\ = [H_3O^+] / K_a = 2.8 / 1 \end{aligned}$$

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## Preparing a Buffer

You want to create a buffer solution at pH = 4.30 (or  $[H_3O^+] = 5.0 \times 10^{-5} M$ ). Find the ratio of acid to base needed to get the buffer to 4.30.

$[HOAc] / [OAc^-]$  ratio = 2.8 / 1 (previous slide)

Therefore, if you use 0.10 mol of NaOAc and 0.28 mol of HOAc, you will have pH = 4.30.

$$pH = pK_a + \log \frac{[Conj. base]}{[Acid]}$$

Could have also used  
Henderson Hasselbalch:

$$4.30 = 4.74 + \log \frac{[Conj. base]}{[Acid]}$$

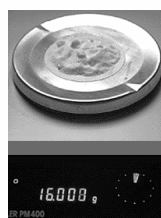
$$10^{-0.44} = 0.36 = \frac{[base]}{[acid]}, \text{ invert:}$$

$$\frac{[acid]}{[base]} = 2.8$$

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## Preparing a Buffer Solution



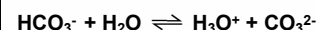
Buffer prepared from

8.4 g NaHCO<sub>3</sub>

weak acid

16.0 g Na<sub>2</sub>CO<sub>3</sub>

conjugate base



What is the pH?

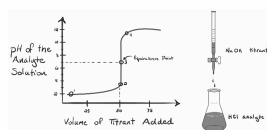
Check yourself! Answer: 10.50

## Titration Calculations

Allow us to calculate pH at any point in a titration

We will study four types of titrations:

- SA + SB (equivalence pH = 7)
- SB + SA (equivalence pH = 7)
- WA + SB (equivalence pH > 7)
- WB + SA (equivalence pH < 7)



Titration separated into **regions** each with their own pH formula

Buffers used in WA + SB and WB + SA

We will do examples of all four as practice in lab.

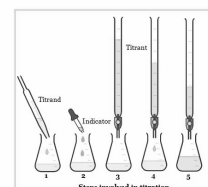
See [Titration Guide](#)

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## Titration Calculation Hints

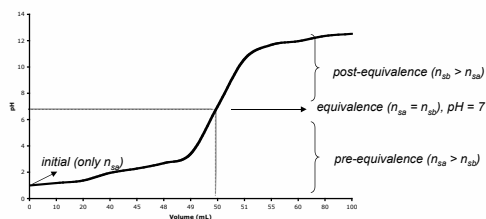
- Strong acids and strong bases **annihilate** their opposites
- Weak acids and bases produce their **conjugates**
- $K_a$  and  $K_b$  may be determined through titrations or half-equivalence pH values
- Remember:  $K_a * K_b = K_w = 1.00 * 10^{-14}$  (25 °C)
- Often helpful to find  $pK_a$  or  $pK_b$
- Remember:  $pK_a + pK_b = 14$
- Need to know **initial concentration and volume of titrant**



## Strong Acid + Strong Base

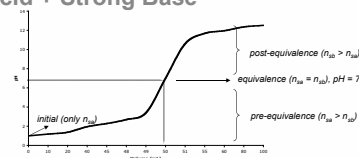


A strong acid + strong base titration



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## Strong Acid + Strong Base

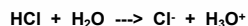


$$\begin{aligned} \text{Initial:} & \quad \text{pH} = -\log \left[ \frac{n_{\text{sa}}}{V_{\text{sa}}} \right] \\ \text{Pre-equivalence:} & \quad \text{pH} = -\log \left( \frac{n_{\text{sa}} - n_{\text{sb}}}{V_{\text{sa}} + V_{\text{sb}}} \right) \\ \text{Equivalence:} & \quad \text{pH} = 7 \text{ (neutral salt + water)} \\ \text{Post-equivalence:} & \quad \text{pH} = 14 + \log \left( \frac{n_{\text{sb}} - n_{\text{sa}}}{V_{\text{sb}} + V_{\text{sa}}} \right) \end{aligned}$$

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## Acid-Base Reactions

**QUESTION:** You titrate 50. mL of a 0.100 M solution of HCl with 0.100 M NaOH. What is the pH of the initial solution?



**SOLUTION:**

HCl is a strong acid

NaOH is a strong base

Hence, this is a strong acid + strong base titration

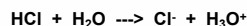
**Other common strong acids:** HNO<sub>3</sub>, HBr, HI, HClO<sub>4</sub>

**Other common strong bases:** KOH, LiOH

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## Acid-Base Reactions

**QUESTION:** You titrate 50. mL of a 0.100 M solution of HCl with 0.100 M NaOH. What is the pH of the initial solution?



**SOLUTION:**

$$\text{For strong acids, } \text{pH} = -\log[\text{H}_3\text{O}^+]$$

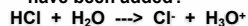
$$\text{pH} = -\log(0.100)$$

$$\text{pH} = 1.000$$

MAR

## Acid-Base Reactions

**QUESTION:** You titrate 50. mL of a 0.100 M solution of HCl with 0.100 M NaOH. What is the pH after 45 mL of NaOH have been added?



**SOLUTION:**

First, determine which region of a strong acid and strong base titration to use by comparing mol HCl to mol NaOH

$$n_{\text{sa}} = 0.050 \text{ L} \cdot 0.100 \text{ M} = 0.0050 \text{ mol HCl}$$

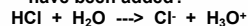
$$n_{\text{sb}} = 0.045 \text{ L} \cdot 0.100 \text{ M} = 0.0045 \text{ mol NaOH}$$

Since  $n_{\text{sa}} > n_{\text{sb}}$ , this pH will fall in the pre-equivalence region

MAR

## Acid-Base Reactions

**QUESTION:** You titrate 50. mL of a 0.100 M solution of HCl with 0.100 M NaOH. What is the pH after 45 mL of NaOH have been added?



From before:  $n_{\text{sa}} = 0.0050 \text{ mol}$ ,  $n_{\text{sb}} = 0.0045 \text{ mol}$

$$\text{pH} = -\log \left( \frac{n_{\text{sa}} - n_{\text{sb}}}{V_{\text{sa}} + V_{\text{sb}}} \right)$$

$$\text{pH} = -\log \left( \frac{0.0050 - 0.0045}{0.050 + 0.045} \right)$$

$$\text{pH} = 2.3$$

MAR

## Acid-Base Reactions

**QUESTION:** You titrate 50. mL of a 0.100 M solution of HCl with 0.100 M NaOH. What is the pH at the equivalence point?

At equivalence,  $\text{HCl} + \text{NaOH} \rightarrow \text{Na}^+ + \text{Cl}^- + \text{H}_2\text{O}$

Only species present at equivalence are  $\text{Na}^+$ ,  $\text{Cl}^-$  and water.

$\text{Na}^+$  and  $\text{Cl}^-$  are conjugates of strong bases and acids; hence, they have **no effect on the pH**

pH at equivalence point will be equal to 7 (neutral) due to presence of water

The volume required to get to equivalence:

$$0.0050 \text{ mol HCl} \cdot (\text{mol NaOH} / \text{mol HCl}) \cdot (L/0.100 \text{ mol NaOH}) = 0.050 \text{ L or } 50. \text{ mL}$$

MAR

## Acid-Base Reactions

**QUESTION:** You titrate 50. mL of a 0.100 M solution of HCl with 0.100 M NaOH. What is the pH after 55 mL of NaOH have been added?

**SOLUTION:** (from before,  $n_{\text{sb}} = 0.0050 \text{ mol}$ )

It took 50. mL of NaOH to reach equivalence; hence, we are now in the post-equivalence region

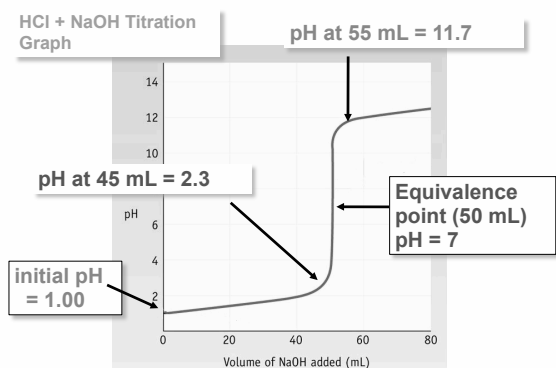
$$n_{\text{sb}} = 0.100 \text{ M} \cdot 0.055 \text{ L} = 0.0055 \text{ mol}$$

$$\text{pH} = 14 + \log \left( \frac{n_{\text{sb}} - n_{\text{sa}}}{V_{\text{sb}} + V_{\text{sa}}} \right)$$

$$\text{pH} = 14 + \log \left( \frac{0.0055 - 0.0050}{0.055 + 0.050} \right)$$

$$\text{pH} = 14 + (-2.3) = 11.7$$

MAR

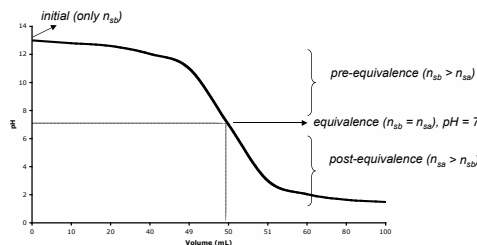


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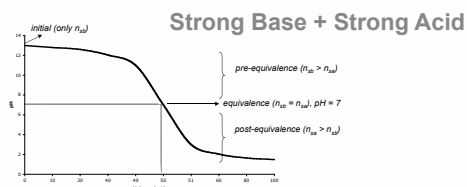
## Strong Base + Strong Acid

Notice similarities between SA + SB and SB + SA titrations!

A strong base + strong acid titration



MAR



**Initial:**  $\text{pH} = 14 + \log \left( \frac{n_{\text{sb}}}{V_{\text{sb}}} \right)$

**Pre-equivalence:**  $\text{pH} = 14 + \log \left( \frac{n_{\text{sb}} - n_{\text{sa}}}{V_{\text{sb}} + V_{\text{sa}}} \right)$

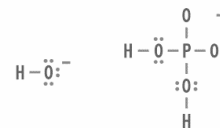
**Equivalence:**  $\text{pH} = 7$  (neutral salt + water)

**Post-equivalence:**  $\text{pH} = -\log \left( \frac{n_{\text{sa}} - n_{\text{sb}}}{V_{\text{sa}} + V_{\text{sb}}} \right)$

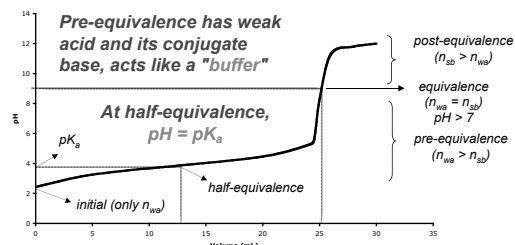
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## Weak Acid + Strong Base

Equivalence point dominated by conjugate base of weak acid



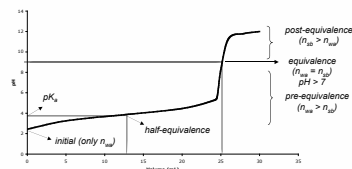
A weak acid + strong base titration



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## Weak Acid + Strong Base



Initial:

$$\text{pH} = -\log\sqrt{K_a C_{\text{wa}}}$$

$$\text{Pre-equivalence: } \text{pH} = \text{p}K_a + \log\left(\frac{n_{\text{sb}}}{n_{\text{wa}} - n_{\text{sb}}}\right)$$

$$\text{Equivalence: } \text{pH} = 14 + \log\sqrt{\left(\frac{K_w}{K_a}\right)\left(\frac{n_{\text{wa}}}{V_{\text{wa}} + V_{\text{sb}}}\right)}$$

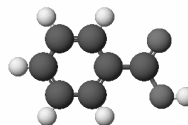
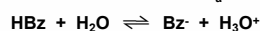
$$\text{Post-equivalence: } \text{pH} = 14 + \log\left(\frac{n_{\text{sb}} - n_{\text{wa}}}{V_{\text{sb}} + V_{\text{wa}}}\right)$$

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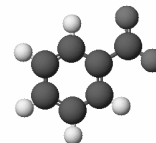
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## Acid-Base Reactions

**QUESTION:** You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the pH of the initial solution?  $K_a = 6.3 \times 10^{-5}$



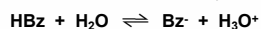
$\text{C}_6\text{H}_5\text{CO}_2\text{H} = \text{HBz}$   
Benzoic acid



Benzoate ion =  $\text{Bz}^-$

## Acid-Base Reactions

**QUESTION:** You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the pH of the initial solution?  $K_a = 6.3 \times 10^{-5}$



SOLUTION:

For weak acids,

$$\text{pH} = -\log\sqrt{K_a C_{\text{wa}}}$$

$$\text{pH} = -\log\sqrt{(6.3 \times 10^{-5})(0.025)}$$

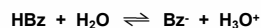
$$\text{pH} = 2.90$$

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## Acid-Base Reactions

**QUESTION:** You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the pH after 10. mL of NaOH have been added?  $K_a = 6.3 \times 10^{-5}$



SOLUTION:

First, determine which region of a weak acid (benzoic acid) and strong base (NaOH) titration to use by comparing mol HBz to mol NaOH

$$n_{\text{wa}} = 0.100 \text{ L} \times 0.025 \text{ M} = 0.0025 \text{ mol HBz}$$

$$n_{\text{sb}} = 0.010 \text{ L} \times 0.100 \text{ M} = 0.0010 \text{ mol NaOH}$$

Since  $n_{\text{wa}} > n_{\text{sb}}$ , this pH will fall in the pre-equivalence region. Note that because  $n_{\text{sb}}$  is converted to mol  $\text{Bz}^-$  (the conjugate base), this region acts like a buffer

## Acid-Base Reactions

**QUESTION:** You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the pH after 10. mL of NaOH have been added?  $K_a = 6.3 \times 10^{-5}$

From before:  $n_{\text{wa}} = 0.0025 \text{ mol}$ ,  $n_{\text{sb}} = 0.0010 \text{ mol}$

$$\text{p}K_a = -\log K_a = -\log(6.3 \times 10^{-5}) = 4.20$$

$$\text{pH} = \text{p}K_a + \log\left(\frac{n_{\text{sb}}}{n_{\text{wa}} - n_{\text{sb}}}\right) \quad \left\{ \begin{array}{l} \text{A version of the} \\ \text{Henderson-Hasselbalch} \\ \text{equation!} \end{array} \right.$$

$$\text{pH} = 4.20 + \log\left(\frac{0.0010}{0.0025 - 0.0010}\right)$$

$$\text{pH} = 4.20 - 0.176 = 4.02$$

MAR

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## Acid-Base Reactions

**QUESTION:** You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the pH after 12.5 mL of NaOH have been added?  $K_a = 6.3 \times 10^{-5}$

From before:  $n_{\text{wa}} = 0.0025 \text{ mol}$ ,  $\text{p}K_a = 4.20$

$$n_{\text{sb}} = 0.0125 \text{ L} \times 0.100 \text{ M} = 0.00125 \text{ mol NaOH}$$

Since  $n_{\text{wa}} > n_{\text{sb}}$ , this is the pre-equivalence region

$$\text{pH} = \text{p}K_a + \log\left(\frac{n_{\text{sb}}}{n_{\text{wa}} - n_{\text{sb}}}\right)$$

$$\text{pH} = 4.20 + \log\left(\frac{0.00125}{0.0025 - 0.00125}\right) = 4.20 + \log(1)$$

$$\text{pH} = 4.20 + 0 = 4.20$$

## Acid-Base Reactions

**QUESTION:** You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the pH after 12.5 mL of NaOH have been added?  $K_a = 6.3 \times 10^{-5}$

Before:  $n_{wa} = 0.0025$  mol,  $pK_a = 4.20$ ,  $n_{sb} = 0.00125$  mol

When  $n_{sb} = 1/2 n_{wa}$ , this is called the half-equivalence region  
 $pH = pK_a$  at the half-equivalence point

Useful method of finding  $K_a$  (and  $K_b$ ) values

Also, the volume of titrant (NaOH) at half equivalence is exactly half the volume necessary to reach equivalence

We will need  $(2 \times 12.5) = 25$  mL of NaOH to reach equivalence!

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## Acid-Base Reactions

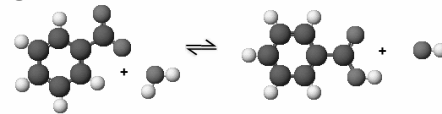
**QUESTION:** You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH to the equivalence point. What is the pH at the equivalence point?  $K_a = 6.3 \times 10^{-5}$

At equivalence,  $HBz + NaOH \rightarrow Na^+ + Bz^- + H_2O$

mol NaOH = mol HBz, or NaOH annihilates HBz

mol HBz = mol Bz<sup>-</sup> at equivalence, and pH dominated by conjugate base of weak acid

pH at equivalence point will be basic when titrating a weak acid with a strong base!



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## Acid-Base Reactions

**QUESTION:** You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH to the equivalence point. What is the pH at the equivalence point?  $K_a = 6.3 \times 10^{-5}$

$n_{wa} = 0.100 \text{ L} \times 0.025 \text{ M} = 0.0025$  mol HBz

0.0025 mol HBz = 0.0025 mol NaOH at equivalence

0.0025 mol NaOH \* (L / 0.100 mol) = 0.025 L =  $V_{sb}$

$$pH = 14 + \log \left( \frac{K_w}{K_a} \right) \left( \frac{n_{wa}}{V_{wa} + V_{sb}} \right)$$

$$pH = 14 + \log \left( \frac{10^{-14}}{6.3 \times 10^{-5}} \right) \left( \frac{0.0025}{0.100 + 0.025} \right)$$

$$pH = 14 + (-5.75) = 8.25$$

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## Acid-Base Reactions

**QUESTION:** You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the pH after 26.0 mL of NaOH have been added?

**SOLUTION:** (from before,  $n_{wa} = 0.0025$  mol)

It took 25 mL of NaOH to reach equivalence; hence, we are now in the post-equivalence region

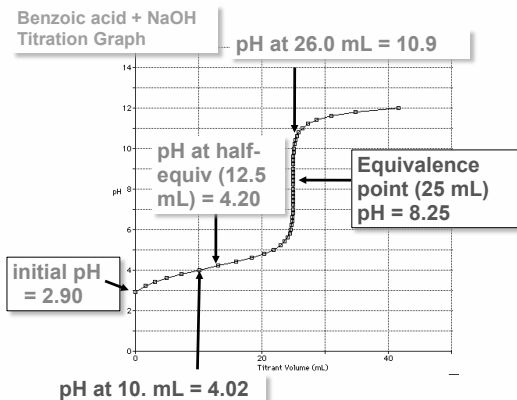
$n_{sb} = 0.100 \text{ M} \times 0.026 \text{ L} = 0.0026$  mol

$$pH = 14 + \log \left( \frac{n_{sb} - n_{wa}}{V_{sb} + V_{wa}} \right)$$

$$pH = 14 + \log \left( \frac{0.0026 - 0.0025}{0.026 + 0.100} \right)$$

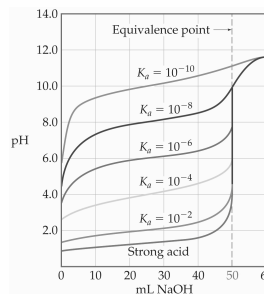
$$pH = 14 + (-3.10) = 10.9$$

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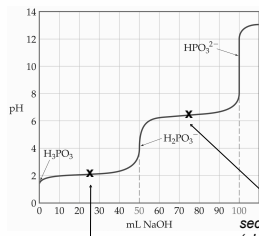
## Acid-Base Reactions



With weaker acids, the initial pH is higher and pH changes near the equivalence point are more subtle.

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## Polyprotic Acids



**Titration of polyprotic acids with bases have multiple equivalence points (and half equivalence points) for each dissociation.**

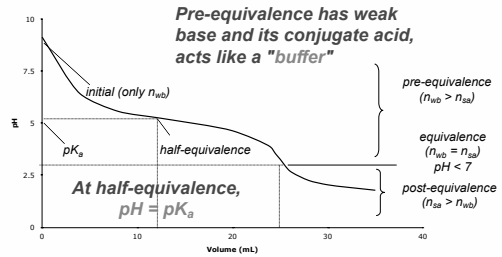
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## Weak Base + Strong Acid

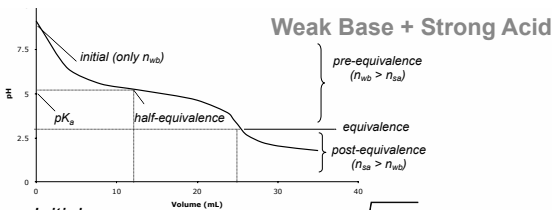
**Equivalence point dominated by conjugate acid of weak base**



A weak base + strong acid titration



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## Weak Base + Strong Acid

**Initial:** 
$$\text{pH} = 14 + \log \sqrt{K_b C_{wb}}$$

**Pre-equivalence:** 
$$\text{pH} = \text{p}K_a + \log \left( \frac{n_{wb} - n_{sa}}{n_{sa}} \right)$$

**Equivalence:** 
$$\text{pH} = -\log \sqrt{\frac{K_w}{K_b} \left( \frac{n_{wb}}{V_{wb} + V_{sa}} \right)}$$

**Post-equivalence:** 
$$\text{pH} = -\log \left( \frac{n_{sa} - n_{wb}}{V_{sa} + V_{wb}} \right)$$

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## pH Indicators

Indicator	pH 0	1	2	3	4	5	6	7	8	9	10	11	12
Methyl violet	Yellow												Violet
Thymol blue	Red			Yellow (acid range)						Blue (base range)			
Methyl orange	Red				Yellow-orange								
Broncesol green					Yellow				Blue				
Methyl red					Red				Yellow				
Chlorophenol red								Yellow		Red			
Bromthymol blue								Yellow		Blue			
Phenol red								Yellow		Red			
Phenolphthalein										Colorless		Red	
Thymolphthalein												Colorless	Blue
Alizarin yellow												Yellow	Violet

Equivalence point important in titration, can use an indicator to signify equivalence point

Indicator color change must reflect equivalence point to be useful!

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Focus on bromthymol blue for next slide

## Color Changes for Bromthymol Blue

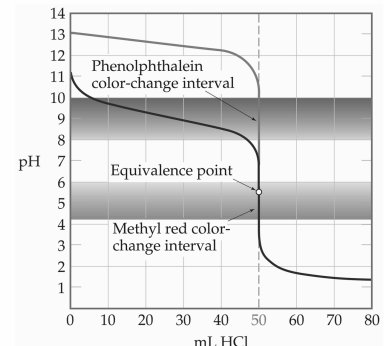


$\text{pH} < 6.0$      $\text{pH} = 6.0-7.5$      $\text{pH} > 7.5$

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## pH Indicators

**Which indicator to use?**  
**Phenolphthalein or Methyl Red?**  
 The pH at the equivalence point in this titration is < 7.  
**Methyl red is the indicator of choice here.**



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# End of Chapter 14 Part II



## How Strong Is That Acid?

Titration: One of Chemistry's Most Important Techniques. Enables You to Analyze Acids and Bases Quantitatively. An Illustration of Acids.

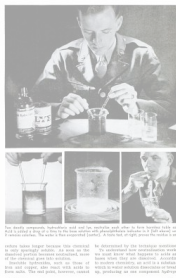
Neutralization reactions are a type of acid-base reaction. In a neutralization reaction, an acid reacts with a base to form a salt and water. The general equation for a neutralization reaction is:

$$\text{Acid} + \text{Base} \rightarrow \text{Salt} + \text{Water}$$

For example, hydrochloric acid (HCl) reacts with sodium hydroxide (NaOH) to form sodium chloride (NaCl) and water (H<sub>2</sub>O):

$$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$$

Neutralization reactions are important in many areas of chemistry, including analytical chemistry, environmental chemistry, and industrial chemistry. They are used to determine the concentration of an acid or base in a solution, to synthesize salts, and to neutralize acidic or basic waste.



- See:
- [Chapter Fourteen Part II Study Guide](#)
  - [Chapter Fourteen Part II Concept Guide](#)
  - [Types of Equilibrium Constants](#)
  - [Titration Guide](#)
  - [Buffers and Henderson-Hasselbalch Guide](#)
  - [Important Equations \(following this slide\)](#)
  - [End of Chapter Problems \(following this slide\)](#)

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## Important Equations, Constants, and Handouts from this Chapter:

### Titration (SA+SB, SB+SA, WA+SB, WB+SA) and Buffers chapter

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Conj. base}]}{[\text{Acid}]}$$

$$\text{pH} = \text{pK}_a + \log \left( \frac{\text{mol Conj base} - \text{mol strong acid}}{\text{mol weak acid} + \text{mol strong acid}} \right)$$

$$\text{pH} = \text{pK}_a + \log \left( \frac{\text{mol Conj base} + \text{mol strong base}}{\text{mol weak acid} - \text{mol strong base}} \right)$$

- Handouts:
- [Manipulating Equilibrium Constant Expressions](#)
  - [Types of Equilibrium Constants](#)
  - [Table of K<sub>a</sub> and K<sub>b</sub> values in Problem Set #2](#)
  - [Titration Guide](#)
  - [Buffers and Henderson-Hasselbalch Guide](#)

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Region	Equation
<b>Strong Acid + Strong Base:</b>	
Initial Region:	$\text{pH} \approx -\log(n_a / V_a)$
Pre-Equivalence Region:	$\text{pH} \approx -\log \left( \frac{n_a - n_b}{V_a + V_b} \right)$
Equivalence:	$\text{pH} = 7$
Post-Equivalence Region:	$\text{pH} \approx 14 + \log \left( \frac{n_b - n_a}{V_a + V_b} \right)$
<b>Strong Base + Strong Acid:</b>	
Initial Region:	$\text{pH} = 14 + \log(n_b / V_b)$
Pre-Equivalence Region:	$\text{pH} = 14 + \log \left( \frac{n_b - n_a}{V_a + V_b} \right)$
Equivalence:	$\text{pH} = 7$
Post-Equivalence Region:	$\text{pH} \approx -\log \left( \frac{n_a - n_b}{V_a + V_b} \right)$
<b>Weak Acid + Strong Base:</b>	
Initial Region:	$\text{pH} \approx -\log \left( \sqrt{K_a \frac{n_a}{V_a}} \right)$
Pre-Equivalence Region:	$\text{pH} = \text{pK}_a + \log \left( \frac{n_b}{n_a - n_b} \right)$
Half-Equivalence Region:	$\text{pH} = \text{pK}_a$
Equivalence:	$\text{pH} = 14 + \log \left( \frac{K_b}{K_a} \right) \left( \frac{n_a - n_b}{V_a + V_b} \right)$
Post-Equivalence Region:	$\text{pH} \approx 14 + \log \left( \frac{n_b - n_a}{V_a + V_b} \right)$
<b>Weak Base + Strong Acid:</b>	
Initial Region:	$\text{pH} = 14 + \log \left( \sqrt{K_b \frac{n_b}{V_b}} \right)$
Pre-Equivalence Region:	$\text{pH} = \text{pK}_b + \log \left( \frac{n_a}{n_b - n_a} \right)$
Half-Equivalence Region:	$\text{pH} = \text{pK}_b$
Equivalence:	$\text{pH} \approx -\log \left( \frac{K_a}{K_b} \right) \left( \frac{n_b - n_a}{V_a + V_b} \right)$
Post-Equivalence Region:	$\text{pH} \approx -\log \left( \frac{n_a - n_b}{V_a + V_b} \right)$

### End of Chapter Problems: Test Yourself

- See practice problem set #3 for additional titration and buffer examples
- Does the pH of the solution increase, decrease, or stay the same when you: a) Add solid ammonium chloride to a dilute aqueous solution of NH<sub>3</sub>; b) Add solid sodium acetate to a dilute aqueous solution of acetic acid; c) Add solid NaCl to a dilute aqueous solution of NaOH?
  - For each of the following cases, decide whether the pH is less than 7, equal to 7, or greater than 7: a) equal volumes of 0.10 M acetic acid, CH<sub>3</sub>CO<sub>2</sub>H, and 0.10 M KOH are mixed; b) 25 mL of 0.015 M NH<sub>3</sub> is mixed with 25 mL of 0.015 M HCl; c) 150 mL of 0.20 M HNO<sub>3</sub> is mixed with 75 mL of 0.40 M NaOH
  - What is the pH of a solution that consists of 0.20 M ammonia, NH<sub>3</sub>, and 0.20 M ammonium chloride, NH<sub>4</sub>Cl? (K<sub>a</sub> = 5.6 x 10<sup>-10</sup>)
  - What mass of sodium acetate, NaCH<sub>3</sub>CO<sub>2</sub>, must be added to 1.00 L of 0.10 M acetic acid to give a solution with a pH of 4.50? (K<sub>a</sub> = 1.8 x 10<sup>-5</sup>)
  - Phenol, C<sub>6</sub>H<sub>5</sub>OH, is a weak organic acid. Suppose 0.515 g of the compound is dissolved in exactly 125 mL of water. The resulting solution is titrated with 0.123 M NaOH:  $\text{C}_6\text{H}_5\text{OH}(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{C}_6\text{H}_5\text{O}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$  a) What is the pH of the original solution of phenol? b) What are the concentrations of all of the following ions at the equivalence point: Na<sup>+</sup>, H<sub>3</sub>O<sup>+</sup>, OH<sup>-</sup>, and C<sub>6</sub>H<sub>5</sub>O<sup>-</sup>? c) What is the pH of the solution at the equivalence point?

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### End of Chapter Problems: Answers

- a) pH decreases; b) pH increases; c) no change to pH
- a. pH > 7 b. pH < 7 c. pH = 7
- pH = 9.25
- 4.7 g
- a) pH = 5.62 b) [Na<sup>+</sup>] = 3.23 x 10<sup>-2</sup> mol/L, [H<sub>3</sub>O<sup>+</sup>] = 6.5 x 10<sup>-12</sup> mol/L, [OH<sup>-</sup>] = 1.5 x 10<sup>-3</sup> mol/L, and [C<sub>6</sub>H<sub>5</sub>O<sup>-</sup>] = 3.07 x 10<sup>-2</sup> mol/L c) pH = 11.19

See practice problem set #3 for additional titration and buffer examples

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