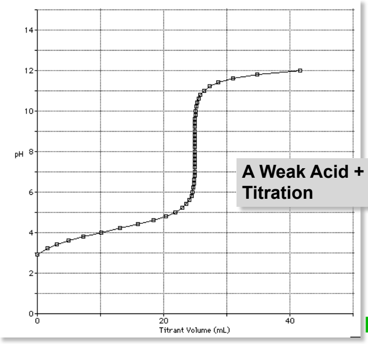
ACID-BASE REACTIONS

Chapter 14
("Part II")



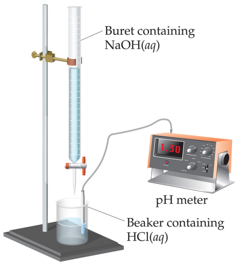
A Weak Acid + Strong Base Titration

Last update: 4/29/24

Chemistry 223
Professor Michael Russell

MAR

Titrations



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

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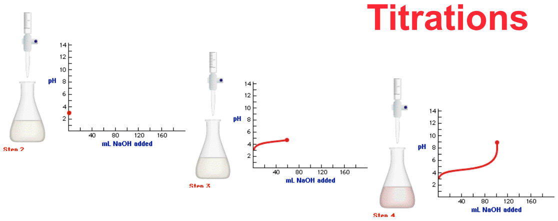
Titrations



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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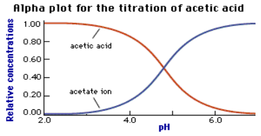
Acid-Base Titrations



Notice how [HOAc] diminishes with NaOH, *but* [OAc$^-$] 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_4Cl to 0.25 M $NH_3(aq)$?

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Here we are adding an ion COMMON to the equilibrium with NH_3 (*i.e.* NH_4^+)

Le Chatelier predicts that the equilibrium will shift to the ____________.

The pH will go _____________.

After all, NH_4^+ 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_4Cl to 0.25 M $NH_3(aq)$?

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Let us first calculate the pH of a 0.25 M NH_3 solution.

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
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 NH_4Cl to 0.25 M $NH_3(aq)$?

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = 1.8 \text{ x } 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.25 - x}$$

Assuming x is << 0.25, we have

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

This gives pOH = 2.67

and so pH = 14.00 - 2.67 = 11.33

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

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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 M NH_4Cl *and* 0.25 M $NH_3(aq)$?

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

We expect that the pH will decline on adding NH_4Cl. Let's test that!

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
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 M NH_4Cl *and* 0.25 M $NH_3(aq)$?

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = 1.8 \text{ x } 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x(0.10 + x)}{0.25 - x}$$

Because equilibrium shifts left, x is MUCH less than 0.0021 M, the value *without* NH_4Cl.

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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 M NH_4Cl *and* 0.25 M $NH_3(aq)$?

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = 1.8 \text{ x } 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x(0.10 + x)}{0.25 - x}$$

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

This gives pOH = 4.35 and pH = 9.65

pH drops from 11.33 to 9.65 on adding a common ion (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^-
$H_2PO_4^-$	+	HPO_4^{2-}
<u>Weak Base</u>	+	<u>Conj. Acid</u>
NH_3	+	NH_4^+

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Buffers and Henderson-Hasselbalch Guide

Buffer Solutions

HCl is added to pure water.

HCl is added to a solution of a weak acid $H_2PO_4^-$ and its conjugate base HPO_4^{2-}.

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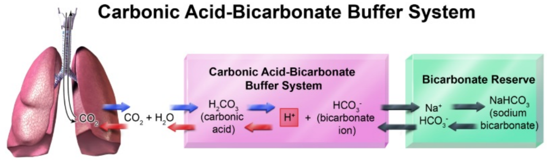
Buffers in Our Bodies

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



$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^{-1}$$

Exhaling CO_2 raises the pH of our blood!

Buffer Solutions

Consider $HOAc/OAc^-$ to see how buffers work

The weak acid in buffers consumes strong base!

We know:

$$OAc^- + H_2O \rightleftharpoons HOAc + OH^-$$

$$K_b = 5.6 \times 10^{-10}$$

Therefore, the *reverse* reaction of the *weak acid* with added OH^- (strong base) would be:

$$HOAc + OH^- \rightleftharpoons OAc^- + H_2O$$

and: $K_{reverse} = 1/\ K_b = 1.8 \times 10^9$

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

Buffer Solutions

Consider $HOAc/OAc^-$ to see how buffers work

Conjugate base in buffers consumes strong acid!

$$HOAc + H_2O \rightleftharpoons OAc^- + H_3O^+$$

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

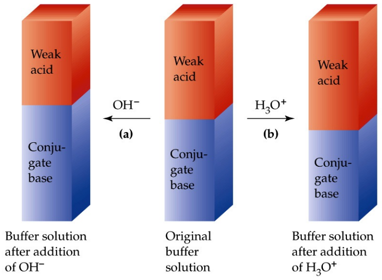
Therefore, the *reverse* reaction of the weak base with added H_3O^+ (strong acid) would be:

$$OAc^- + H_3O^+ \rightleftharpoons HOAc + H_2O$$

$$K_{reverse} = 1/\ K_a = 5.6 \times 10^4$$

$K_{reverse}$ is VERY LARGE, so OAc^- completely consumes the H_3O^+!

Buffer Solutions



Buffer Solutions

Problem: What is the pH of a buffer that has [HOAc] = 0.700 M and [OAc^-] = 0.600 M?

$$HOAc + H_2O \rightleftharpoons OAc^- + H_3O^+$$

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

	[HOAc]	[OAc^-]	[H_3O^+]
initial			
change			
equilib			

Buffer Solutions

Problem: What is the pH of a buffer that has [HOAc] = 0.700 M and [OAc^-] = 0.600 M?

$$HOAc + H_2O \rightleftharpoons OAc^- + H_3O^+$$

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

	[HOAc]	[OAc^-]	[H_3O^+]
equilib	0.700 - x	0.600 + x	x

Assuming that x << 0.700 and 0.600, we have

$$K_a = 1.8 \times 10^{-5} = \frac{[H_3O^+](0.600)}{0.700}$$

$[H_3O^+] = 1.8 \times 10^{-5} * (0.700 / 0.600) = 2.1 \times 10^{-5}$ *and*

pH = 4.68

Buffer Solutions

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

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

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

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

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Henderson-Hasselbalch Equation

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

Take the negative log of both sides of this equation:

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

The Henderson - Hasselbalch Eq!

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

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

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

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

a) 1.00 L of pure water (before HCl, pH = 7.00)

b) 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]**

$$M_1 \bullet V_1 = M_2 \bullet V_2$$

$$1.00\ M * 1.00\ mL = M_2 \bullet 1001\ mL$$

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

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

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-] = 0.600 M (pH = 4.68)

Solution to Part (b)

Step 1 - do the stoichiometry

H_3O^+ (from HCl) + OAc^- (from buffer) ---> HOAc (from buffer)

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

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-] = 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-] = 0.600 M (pH = 4.68)

Solution to Part (b): Step 2 - Equilibrium

$$HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^-$$

	[HOAc]	[OAc-]	$[H_3O^+]$
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-] = 0.600 M (pH = 4.68)

Solution to Part (b): Step 2 - Equilibrium

$$HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^-$$

	[HOAc]	[OAc-]	$[H_3O^+]$
Equilibrium	0.701-x	0.599+x	x

Because $[H_3O^+] = 2.1 \times 10^{-5}$ 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-] = 0.600 M (pH = 4.68)

Solution to Part (b): Step 2 - Equilibrium

$$HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^-$$

$$[H_3O^+] = \frac{[HOAc]}{[OAc^-]} \bullet K_a = \frac{0.701}{0.599} \bullet (1.8 \times 10^{-5})$$

$[H_3O^+] = 2.1 \times 10^{-5}$ M ------> 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-] = 0.600 M

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

$$pH = pK_a + \log \frac{(mol_{Conj\ base} - mol_{strong\ acid})}{(mol_{weak\ acid} + mol_{strong\ acid})}$$

$pK_a = - \log (1.80 * 10^{-5}) = 4.74$

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

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:

$$pH = pK_a + \log \frac{(mol_{Conj\ base} - mol_{strong\ acid})}{(mol_{weak\ acid} + mol_{strong\ acid})}$$

For adding strong bases to buffers:

$$pH = pK_a + \log \frac{(mol_{Conj\ base} + mol_{strong\ base})}{(mol_{weak\ acid} - mol_{strong\ base})}$$

Very useful for calculating pH changes in buffers!

See: Buffers and Henderson-Hasselbalch Guide

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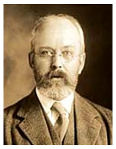
Preparing a Buffer



Henderson

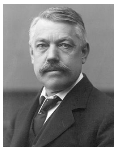
You want to create a buffer solution with a pH = 4.30.

This means $[H_3O^+] = 10^{-pH} = 5.0 \times 10^{-5}$ M

It is best to choose an acid such that:

- *** $[H_3O^+] \approx K_a$, *or***
- *** pH ≈ pK_a**

Hasselbalch



You get the *exact* $[H_3O^+]$ (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 $K_a \approx 5.0 \times 10^{-5}$ or a $pK_a \approx 4.30$

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Preparing a Buffer

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

POSSIBLE BUFFERS	**K_a**	**pK_a**
HSO_4^- / SO_4^{2-}	**1.2 x 10^{-2}**	**1.92**
HOAc / OAc^-	**1.8 x 10^{-5}**	**4.74**
HCN / CN^-	**4.0 x 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 x 10^{-5} M)* using HOAc and OAc^{-1}.

Equal moles of acid (HOAc) and base (OAc^{-1}) create pH = 4.74 (= pK_a). Find the ratio of acid to base needed to get the buffer to 4.30.

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

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

Solve for [HOAc] / $[OAc^-]$ ratio:

= $[H_3O^+]$ / K_a = 2.8 / 1

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Preparing a Buffer

You want to create a buffer solution at pH = 4.30 (or $[H_3O^+]$ = 5.0 x 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.**

Could have also used Henderson Hasselbalch:

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

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

$$10^{-0.44} = 0.36 {*} \,{}^{[base]}\!/_{[acid]}, \textit{ invert}:$$

$$^{[acid]}\!/_{[base]} = 2.8$$

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Preparing a Buffer Solution

Buffer prepared from

8.4 g $NaHCO_3$

weak acid

16.0 g Na_2CO_3

conjugate base

$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$

What is the pH?

Check yourself! Answer: 10.50

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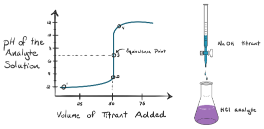
Titration Calculations

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)**



Titrations 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 <u>Titration Guide</u>

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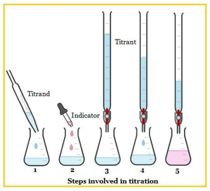
Titration Calculation Hints

- **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



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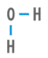
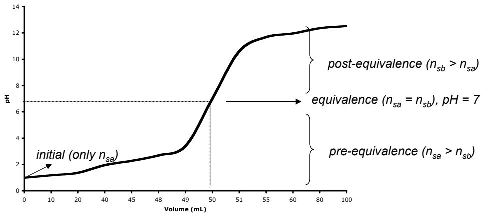
Strong Acid + Strong Base



A strong acid + strong base titration



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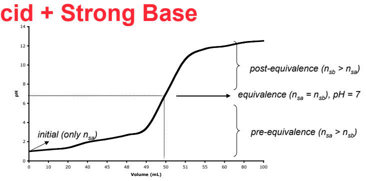
Strong Acid + Strong Base



Initial: $\mathrm{pH} = -\log[n_{sa} / V_{sa}]$

Pre-equivalence: $\mathrm{pH} = -\log\left(\dfrac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)$

Equivalence: pH = 7 (neutral salt + water)

Post-equivalence: $\mathrm{pH} = 14 + \log\left(\dfrac{n_{sb} - n_{sa}}{V_{sb} + V_{sa}}\right)$

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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?**

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

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_3, HBr, HI, $HClO_4$**

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?**

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

SOLUTION:

For strong acids,

$$\mathrm{pH} = -\log[H_3O^+]$$

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

$$\mathrm{pH} = 1.000$$

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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 after 45 mL of NaOH have been added?**

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

SOLUTION:

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

n_{sa} = 0.050 L * 0.100 M = 0.0050 mol HCl

n_{sb} = 0.045 L * 0.100 M = 0.0045 mol NaOH

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

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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 after 45 mL of NaOH have been added?**

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

From before: **n_{sa} = 0.0050 mol, n_{sb} = 0.0045 mol**

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

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

$$\mathrm{pH} = 2.3$$

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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 at the equivalence point?

***At equivalence,* HCl + NaOH ---> Na⁺ + Cl⁻ + H_2O**

Only species present at equivalence are Na^+, Cl^- and water.

Na^+ and 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 mol HCl * (mol NaOH / mol HCl) * (L/0.100 mol NaOH) = 0.050 L *or* 50. mL

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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 after 55 mL of NaOH have been added?

SOLUTION: *(from before, n_{sa} = 0.0050 mol)*

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

n_{sb} = 0.100 M * 0.055 L = 0.0055 mol

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

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

pH = 14 + (-2.3) = **11.7**

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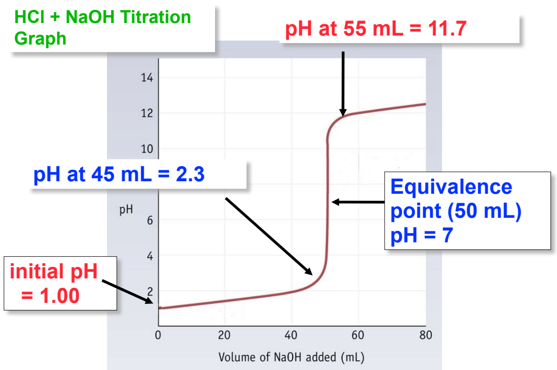
HCl + NaOH Titration Graph



pH at 55 mL = 11.7

pH at 45 mL = 2.3

Equivalence point (50 mL) pH = 7

initial pH = 1.00

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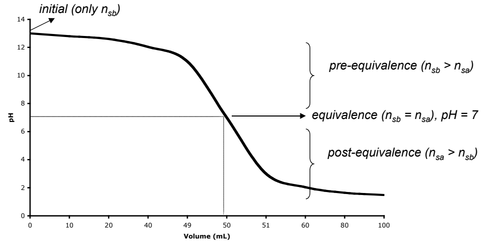
Strong Base + Strong Acid

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

A strong base + strong acid titration



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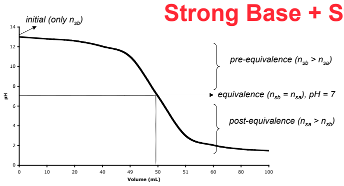
Strong Base + Strong Acid



Initial: pH = 14 + log [n_{sb} / V_{sb}]

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

Equivalence: pH = 7 (neutral salt + water)

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

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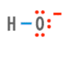
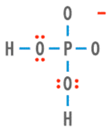
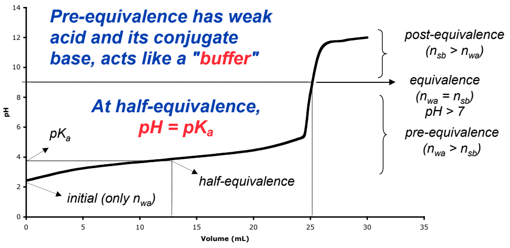
Weak Acid + Strong Base

Equivalence point dominated by conjugate base of weak acid





A weak acid + strong base titration



Pre-equivalence has weak acid and its conjugate base, acts like a "buffer"

At half-equivalence, pH = pK_a

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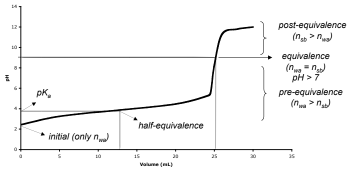
Weak Acid + Strong Base



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

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

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

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

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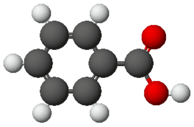
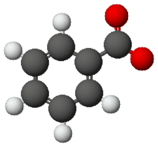
Acid-Base Reactions

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 x 10^{-5}

HBz + H_2O ⇌ Bz^- + H_3O^+



$C_6H_5CO_2H$ = HBz
Benzoic acid



Benzoate ion = Bz^-

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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 x 10^{-5}

HBz + H_2O ⇌ Bz^- + H_3O^+

SOLUTION:

For weak acids,

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

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

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 x 10^{-5}

HBz + H_2O ⇌ Bz^- + H_3O^+

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_{wa} = 0.100 L * 0.025 M = 0.0025 mol HBz

n_{sb} = 0.010 L * 0.100 M = 0.0010 mol NaOH

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

***Note that* because n_{sb} is converted to mol Bz^- (the conjugate base), this region acts like a buffer**

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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 x 10^{-5}

***From before:* n_{wa} = 0.0025 mol, n_{sb} = 0.0010 mol**

pK_a = -log K_a = - log (6.3*10^{-5}) = 4.20

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

A version of the Henderson-Hasselbalch equation!

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

pH = 4.20 - 0.176 = **4.02**

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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 x 10^{-5}

***From before:* n_{wa} = 0.0025 mol, pK_a = 4.20**

n_{sb} = 0.0125 L * 0.100 M = 0.00125 mol NaOH

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

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

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

pH = 4.20 + 0 = **4.20**

MAR

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*12.5) = 25 mL of NaOH to reach equivalence!

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Acid-Base Reactions

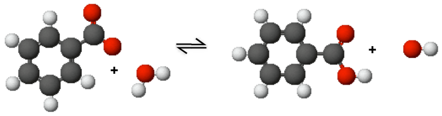
QUESTION: You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH to the equivalence point. What is the pH at the equivalence point? $K_a = 6.3 \times 10^{-5}$

At equivalence, HBz + NaOH ---> Na^+ + Bz^- + H_2O

mol NaOH = mol HBz, or *NaOH annihilates HBz*

mol HBz = mol Bz^- 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 L * 0.025 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}

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

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

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 M * 0.026 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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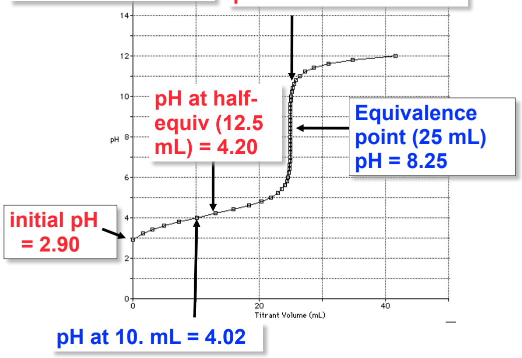
Benzoic acid + NaOH Titration Graph



pH at 26.0 mL = 10.9

pH at half-equiv (12.5 mL) = 4.20

Equivalence point (25 mL) pH = 8.25

initial pH = 2.90

pH at 10. mL = 4.02

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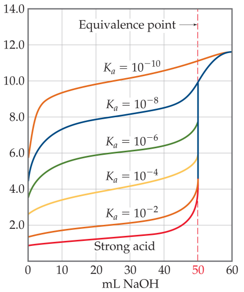
Acid-Base Reactions



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

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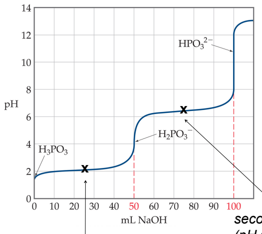
Polyprotic Acids



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

second half equivalence (pH = pKa for $H_2PO_3^{-1}$)

first half equivalence (pH = pKa for H_3PO_3)

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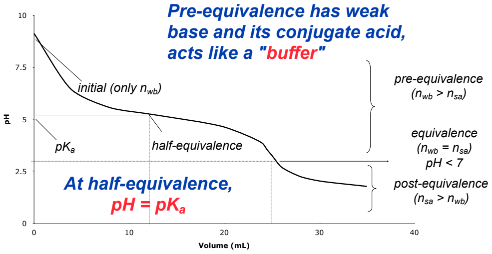
Weak Base + Strong Acid

Equivalence point dominated by conjugate acid of weak base

A weak base + strong acid titration



Pre-equivalence has weak base and its conjugate acid, acts like a "buffer"

At half-equivalence, pH = pK_a

pre-equivalence ($n_{wb} > n_{sa}$)

equivalence ($n_{wb} = n_{sa}$) pH < 7

post-equivalence ($n_{sa} > n_{wb}$)

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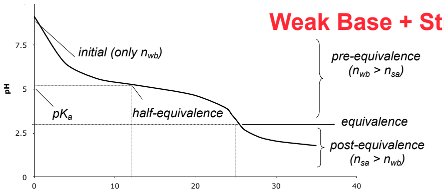
Weak Base + Strong Acid



pre-equivalence ($n_{wb} > n_{sa}$)

equivalence

post-equivalence ($n_{sa} > n_{wb}$)

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

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

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

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

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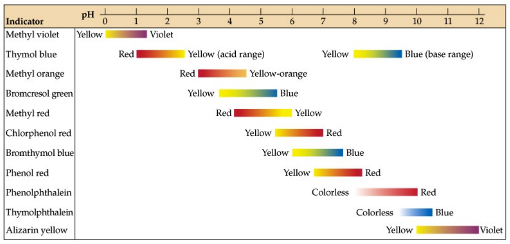
pH Indicators



Indicator		
Methyl violet	Yellow	Violet
Thymol blue	Red	Yellow (acid range)
	Yellow	Blue (base range)
Methyl orange	Red	Yellow-orange
Bromcresol green	Yellow	Blue
Methyl red	Red	Yellow
Chlorphenol 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!

Focus on bromthymol blue for next slide

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Color Changes for Bromthymol Blue

pH < 6.0 ***pH = 6.0-7.5*** ***pH > 7.5***

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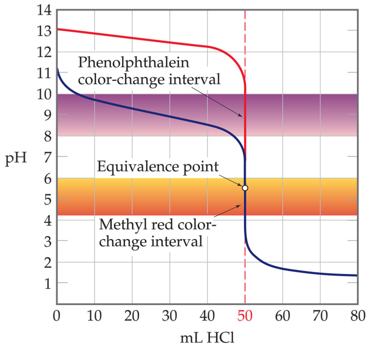
pH Indicators

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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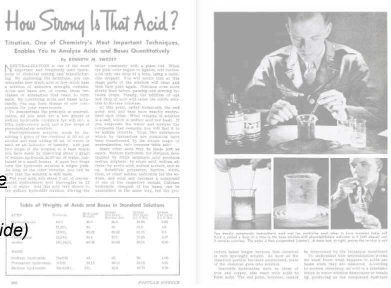
End of Chapter 14 Part II

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)*



How Strong Is That Acid?

Titration, One of Chemistry's Most Important Techniques, Enables You to Analyze Acids and Bases Quantitatively

By KENNETH M. SWEZEY

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Important Equations, Constants, and Handouts from this Chapter:

Titrations (SA+SB, SB+SA, WA+SB, WB+SA) *and* **Buffers** *chapter*

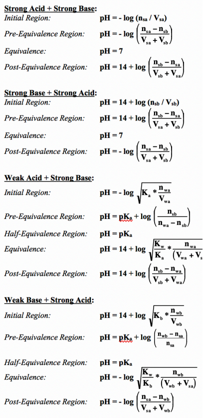
$$\mathbf{pH = pK_a + \log\frac{[Conj.\ base]}{[Acid]}}$$

$$pH = pK_a + \log\frac{(mol_{Conj\ base} - mol_{strong\ acid})}{(mol_{weak\ acid} + mol_{strong\ acid})}$$

$$pH = pK_a + \log\frac{(mol_{Conj\ base} + mol_{strong\ base})}{(mol_{weak\ acid} - mol_{strong\ base})}$$

Handouts:

- *[Manipulating Equilibrium Constant Expressions](#)*
- *[Types of Equilibrium Constants](#)*
- *Table of K_a and K_b values in Problem Set #2*
- *Titration Guide*
- *Buffers and Henderson-Hasselbalch Guide*



Strong Acid + Strong Base:
Initial Region: $pH = -\log(n_{sa} / V_{sa})$
Pre-Equivalence Region: $pH = -\log\left(\frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)$
Equivalence: $pH = 7$
Post-Equivalence Region: $pH = 14 + \log\left(\frac{n_{sb} - n_{sa}}{V_{sb} + V_{sa}}\right)$

Strong Base + Strong Acid:
Initial Region: $pH = 14 + \log(n_{sb} / V_{sb})$
Pre-Equivalence Region: $pH = 14 + \log\left(\frac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}}\right)$
Equivalence: $pH = 7$
Post-Equivalence Region: $pH = -\log\left(\frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)$

Weak Acid + Strong Base:
Initial Region: $pH = -\log\sqrt{K_a * \frac{n_{wa}}{V_{wa}}}$
Pre-Equivalence Region: $pH = pK_a + \log\left(\frac{n_{sb}}{n_{wa} - n_{sb}}\right)$
Half-Equivalence Region: $pH = pK_a$
Equivalence: $pH = 14 + \log\sqrt{\frac{K_w}{K_a} * \frac{n_{wa}}{(V_{wa} + V_s}}$
Post-Equivalence Region: $pH = 14 + \log\left(\frac{n_{sb} - n_{wa}}{V_{sb} + V_{wa}}\right)$

Weak Base + Strong Acid:
Initial Region: $pH = 14 + \log\sqrt{K_b * \frac{n_{wb}}{V_{wb}}}$
Pre-Equivalence Region: $pH = pK_a + \log\left(\frac{n_{wb} - n_{sa}}{n_{sa}}\right)$
Half-Equivalence Region: $pH = pK_a$
Equivalence: $pH = -\log\sqrt{\frac{K_w}{K_b} * \frac{n_{wb}}{(V_{wb} + V_{sa})}}$
Post-Equivalence Region: $pH = -\log\left(\frac{n_{sa} - n_{wb}}{V_{sa} + V_{wb}}\right)$

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End of Chapter Problems: *Test Yourself*

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

1. 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_3; b) Add solid sodium acetate to a dilute aqueous solution of acetic acid; c) Add solid NaCl to a dilute aqueous solution of NaOH?
2. 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_3CO_2H, and 0.10 M KOH are mixed; b) 25 mL of 0.015 M NH_3 is mixed with 25 mL of 0.015 M HCl; c) 150 mL of 0.20 M HNO_3 is mixed with 75 mL of 0.40 M NaOH
3. What is the pH of a solution that consists of 0.20 M ammonia, NH_3, and 0.20 M ammonium chloride, NH_4Cl? ($K_a = 5.6 \times 10^{-10}$)
4. What mass of sodium acetate, $NaCH_3CO_2$, must be added to 1.00 L of 0.10 M acetic acid to give a solution with a pH of 4.50? ($K_a = 1.8 \times 10^{-5}$)
5. Phenol, C_6H_5OH, 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: $\mathbf{C_6H_5OH(aq) + OH^{-1}(aq) \rightleftarrows C_6H_5O^{-1}(aq) + H_2O(l)}$ 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^{+1}, H_3O^{+1}, OH^{-1}, and $C_6H_5O^{-1}$? c) What is the pH of the solution at the equivalence point?

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End of Chapter Problems: *Answers*

1. a) pH decreases; b) pH increases; c) no change to pH
2. a. pH > 7 b. pH < 7 c. pH = 7
3. pH = 9.25
4. 4.7 g
5. a) pH = 5.62 b) $[Na^{+1}] = 3.23 \times 10^{-2}$ mol/L, $[H_3O^{+1}] = 6.5 \times 10^{-12}$ mol/L, $[OH^{-1}] = 1.5 \times 10^{-3}$ mol/L, and $[C_6H_5O^{-1}] = 3.07 \times 10^{-2}$ mol/L c) pH = 11.19

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

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