# Chapter 16
# AQUEOUS IONIC EQUILIBRIA

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## Buffers

A **buffer solution** resists drastic changes in pH when a <u>small amount</u> of acid or base is added, or when diluted.

**Composition**: It consists of a **weak acid (HA)** and its **conjugate base (A⁻)** usually in the form of its salt, **NaA**
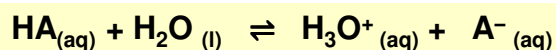
**Examples** of buffers:

- Acetic acid-sodium acetate = $HC_2H_3O_2$ and $NaC_2H_3O_2$

- Carbonic acid-sodium bicarbonate = $H_2CO_3$ and $NaHCO_3$

- $H_3PO_3$ and _____ (ID conj. base)
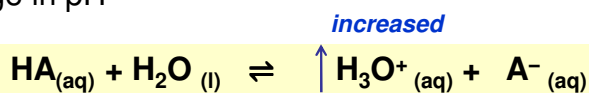
- $Na_2HPO_4$ and _____ (ID conj. base)

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**Buffers** – Cont.

*Q. How does a buffer resist changes in pH?*

➤ Through equilibrium between the weak acid (HA) and its conjugate base (A⁻):

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + A^-{}_{(aq)}$$

➤ *Add an acid*: Added **H₃O⁺** *increases [H₃O⁺];* Shifts equilibrium to the left to use up added $H_3O^+$; Virtually no change in pH
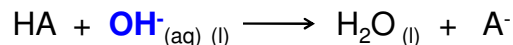
*increased*

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons \uparrow H_3O^+{}_{(aq)} + A^-{}_{(aq)}$$

⬅ **Equilibrium shifts**

➤ [HA] increases slightly while [A⁻] drops a little

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**Buffers** – Cont.

➤ *Add a base*: Added **OH⁻** *reacts with HA to produce A⁻*

$$HA + OH^-{}_{(aq)\,(l)} \longrightarrow H_2O_{(l)} + A^-$$

➤ [HA] decreases slightly while [A⁻] increases a little

Exercise: (a) What happens when NaOH is added to a buffer composed of $HC_2H_3O_2$ and $NaC_2H_3O_2$? (b) What happens when HCl is added to this buffer?

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**Buffers** – Cont.


**Some common buffers**

| Buffer Name | Composition | Useful pH (Approx.) |
|---|---|---|
| Acetate | $HC_2H_3O_2/C_2H_3O_2^-$ | 5 |
| Carbonate | $H_2CO_3/HCO_3^-$ | 7 |
| Phosphate | $H_2PO_4^-/HPO_4^{2-}$ | 7 |
| Ammonia | $NH_4^+/NH_3$ | 10 |

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**The Carbonic-Acid-Bicarbonate Buffer in the Blood**

By far the most important buffer for maintaining acid-base balance in the blood is the carbonic-acid-bicarbonate buffer. The simultaneous equilibrium reactions of interest are:

$$H^+_{(aq)} + HCO_3^-_{(aq)} \rightleftharpoons H_2CO_{3\,(aq)} \rightleftharpoons H_2O_{(l)} + CO_{2\,(g)}$$
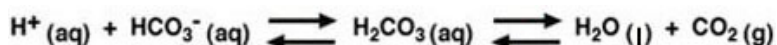
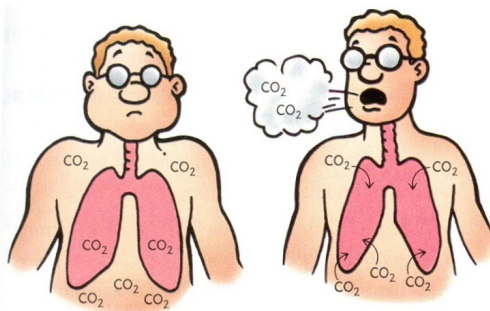During **acidosis**, the pH of blood drops below its normal level of ~ 7.4. What can be done to bring the pH back to 7.4?

➤ Induce <u>hyperventilation</u> (Expel $CO_2$ at a faster rate; Equil. shifts to the right to use up $H^+$)

During **alkalosis**, the pH of blood rises. What can be done to bring the pH back to 7.4?

➤ <u>Hypoventilate</u> (Keep $CO_2$ in your lungs by holding your breath; Equil. shifts to the left to replenish $H^+$)

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## Action of Buffers



❖ During alkalosis (blood pH rises) the <u>acid component</u> (carbonic acid) of our *biological buffer* neutralizes the excess base and restores the pH to around 7.4, the normal pH of blood.

❖ During **acidosis** (blood pH drops), the <u>base component</u> (carbonate) neutralizes the excess acid and restores the pH to around 7.4.
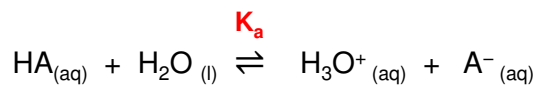
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## Calculating the pH of buffers

### *Henderson-Hasselbalch equation*

➢ Relates the <u>pH of a buffer</u> solution to the <u>concentration</u> of buffer components

➢ Simply a rearranged version of the $K_a$ expression for HA.
  *Derivation:*

$$HA_{(aq)} + H_2O_{(l)} \overset{K_a}{\rightleftharpoons} H_3O^+_{(aq)} + A^-_{(aq)}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Rearranging gives:

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

Take the (-) logarithm of both sides of the equation

*Recall*: **log (MN) = log M + log N**

$$- \log[H_3O^+] = - \log K_a - \log\frac{[HA]}{[A^-]}$$

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or $\quad -\log [H_3O^+] = -\log K_a + \log \dfrac{[A^-]}{[HA]}$

*Recall*: Switch numerator and denominator in log function = change sign of log

Convert to p-function:

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

**Conj. base**

**Weak acid**

**Applies to HA**

**Henderson-Hasselbalch (H-H) equation**

***Properties of the H-H equation:***

1. When **HA is half-neutralized** (i.e. $[A^-] = [HA]$), **pH = pK$_a$**

   ❖ The term $\log \dfrac{[A^-]}{[HA]} = 0$

2. For *every power-of-10 change in the ratio $[A^-]/[HA]$,* the **pH changes** by **1 unit**

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## Calculating the pH of a buffer

Exercise: What is the pH of a buffer that is 0.12 M in lactic acid ($HC_3H_5O_3$) and 0.10 M in sodium lactate? $K_{a \text{ (lactic acid)}} = 1.4 \times 10^{-4}$

Solution: When $K_a$ and [ ]s are given, we can use the H-H equation directly to calculate pH of buffers

**H-H equation:** $\quad pH = pK_a + \log \dfrac{[C_3H_5O_3^-]}{[HC_3H_5O_3]}$

**Conj. Base**
(fr. salt)

**Weak acid**

*Answer:* **pH = 3.77**

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# ACID-BASE TITRATIONS
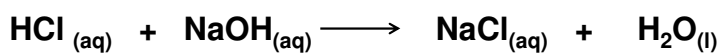
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## (1) Strong Acid-Strong Base Titrations

*Abbreviations*

$V_{H+}$ = volume of strong acid

$V_{OH-}$ = volume of strong base

$V_{ep}$ = volume of <u>titrant</u> acid or base needed to reach the equivalence point

*Example:* A 50.00 mL solution of 0.0100 M NaOH is titrated with 0.100 M HCl. Calculate the the volume of HCl needed to reach the equivalence point.
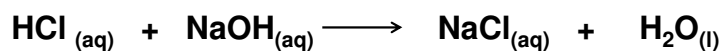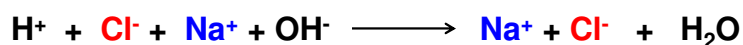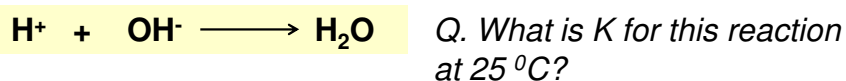
*Molecular equation:*

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

**pH-neutral salt**

$Na^+$ and $Cl^-$ = both **S.I.**

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**(1) SA-SB Titrations** – *Cont.*

*Molecular equation:*

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

*Ionic equation:* (Ionize all aqueous species)

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O$$

*Net ionic equation:* (Cancel identical species left and right of arrow)

$$H^+ + OH^- \longrightarrow H_2O$$
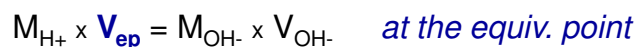
*Q. What is K for this reaction at 25 $^0$C?*

$$K = 1/K_w$$

➢ Very large K; **SA-SB titration reaction goes to completion**

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**S.A. – S.B. Titrations** (Cont.)

*WORK:* To determine $V_{ep}$

Since the reaction stoichiometry is 1:1

mol $H^+$ = mol $OH^-$   ***at the equiv. point***

Thus,   $M_{H+} \times V_{H+} = M_{OH-} \times V_{OH-}$

Since HCl is the titrant we substitute $V_{ep}$ for $V_{H+}$:

$$M_{H+} \times \mathbf{V_{ep}} = M_{OH-} \times V_{OH-} \quad \textit{at the equiv. point}$$

or

$$V_{ep} = \frac{M_{OH-} \times V_{OH-}}{M_{H+}} \qquad V_{ep} = \frac{(50.00 \text{ mL})(0.0100 \text{ M})}{0.100 \text{ M}}$$
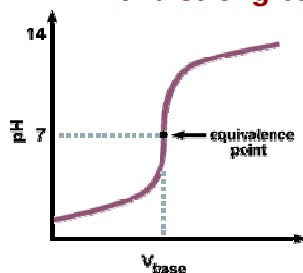
Substituting the given quantities we get:
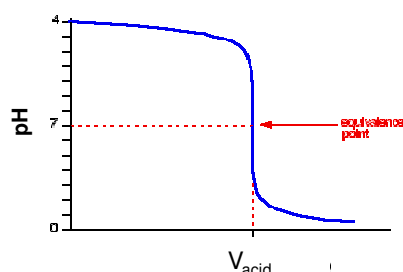
$$V_{ep} = 5.00 \text{ mL}$$

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## Titration Curves: *Strong acid-strong base titration*

**Strong acid titrated with a strong base**

**Strong base titrated with a strong acid**



> **pH is acidic before the equiv. pt. (Only $H^+$ in sol'n)**

> **pH = 7 at the equiv. pt.**

> **pH is basic beyond the equiv. pt. (due to $x$'s $OH^-$)**

> **pH is basic before the equiv. pt. (Only $OH^-$ in sol'n)**

> **pH = 7 at the equiv. pt.**

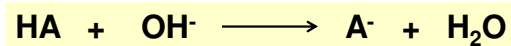> **pH is acidic beyond the equiv. pt. (due to $x$'s $H^+$)**

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## (2) Weak Acid-Strong Base Titrations

**HA**          **Titrant** (always the strong species)

*Titration reaction:*

$$HA \; + \; OH^- \longrightarrow A^- \; + \; H_2O$$

**Weak acid    Titrant          Conj. base**

> $K = 1/K_{b \, (A-)}$ = very large; Reaction goes to completion

GOAL: Calculate the solution pH at different $V_{OH^-}$

*Example:* Consider the titration of 25.00 mL of 0.0500 M formic acid with 0.0500 M NaOH. Calculate the pH of solution at the following volumes of NaOH added: 10.00 mL and $V_{ep}$.

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**W.A. – S.B. Titrations** (Cont.)

**Before the equivalence point**

**pH when $V_{OH^-} < V_{ep}$**

> ➢ Some HA have reacted to form $A^-$

> ➢ Mixture of unreacted HA and $A^-$ = **a buffer!**

We have to know $V_{ep}$ and # mol HA and $OH^-$ initially present :

$$V_{ep} = \frac{M_{HA} \times V_{HA}}{M_{OH^-}} \quad = [(0.0500\ M)(25.00\ mL)]/(0.0500\ M) \quad V_{ep} = 25.00\ mL$$

Initial mol HA = initial [HA] $\times V_{HA}$ = (0.0500 mol/L)(0.025 L)
= $1.25 \times 10^{-3}$ mol

Initial mol $OH^-$ = [$OH^-$] $\times V_{OH^-}$ = (0.0500 mol/L)(0.010 L)
= $5.00 \times 10^{-4}$ mol

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**W.A. – S.B. Titrations** (Cont.)

**Before the equivalence point** (Cont.)

**pH when $V_{OH^-} < V_{ep}$**
> ➢ Remember that we have a buffer at this point
> ➢ Set up ICA table – can use **moles!** (Since mole ratio = M ratio in H-H equation)

| Titration reaction: | HA | + | OH$^-$ $\longrightarrow$ | A$^-$ | + H$_2$O |
|---|---|---|---|---|---|
| **Initial (mol)** | $1.25 \times 10^{-3}$ | | $5.00 \times 10^{-4}$ | 0 | --- |
| **Change:** | $- 5.00 \times 10^{-4}$ | | $- 5.00 \times 10^{-4}$ | $+ 5.00 \times 10^{-4}$ | --- |
| **After (mol)** | $7.5 \times 10^{-4}$ | | 0 | $5.00 \times 10^{-4}$ | --- |

> ➢ Use H-H equation and $pK_{a\ (HA)}$ to calculate pH
>    $K_a = 1.80 \times 10^{-4}$ for formic acid ; $pK_a = 3.74$

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**W.A. – S.B. Titrations** (Cont.)

**Before the equivalence point** (Cont.)

**pH when $V_b < V_{ep}$**

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

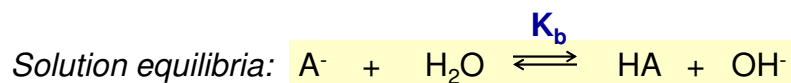$$pH = 3.74 + log\left(\frac{5.0 \times 10^{-4}}{7.5 \times 10^{-4}}\right)$$

pH = 3.56     when $V_{OH^-}$ = 10.00 mL

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**W.A. – S.B. Titrations** (Cont.)

**At the equivalence point:**

**pH when $V_{OH^-} = V_{ep}$ = 25.00 mL**

*What species is in solution?*
  ➤ All of HA has been converted to ***A⁻, a weak base***
  ➤ Hydrolysis of $A^-$ will determine solution pH

$$\overset{K_b}{Solution\ equilibria:\ A^- + H_2O \rightleftharpoons HA + OH^-}$$

  ➤ First, calc. $[A^-]$, then use $K_b$ and $[A^-]$ to calc. pH of solution

$$[A^-] = \frac{mol\ A^-}{V_{tot}} = \frac{initial\ mol\ HA}{V_{tot}} = \frac{(0.0500\ M)(25.00\ mL)}{(25.00 + 25.00)\ mL}$$

$$[A^-] = 0.0250\ M$$

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**W.A. – S.B. Titrations** (Cont.)

**Region 2:  At the equivalence point**

**pH when $V_{OH^-}$ =  $V_{ep}$** = 25.00 mL    (Cont.)

$[A^-] = 0.0250$ M        $K_b = K_w/(1.80 \times 10^{-4}) = 5.56 \times 10^{-11}$

$$K_b = \frac{y^2}{[A^-] - y}$$

Substituting and solving for y gives:

y = $[OH^-]$ = $1.18 \times 10^{-6}$ M

pOH = 5.93

pH = 8.07    **At the equiv. pt.**

➢ **pH** at the equiv. pt. **> 7** because **$A^-$ is a weak base**

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**Summary: W.A. – S.B. Titrations**

(1) Before the equiv. pt. ($V_{OH^-}$ <  $V_{ep}$)
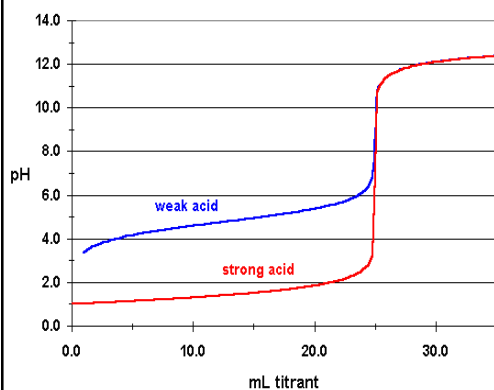
➢ Mixture of unreacted HA and $A^-$ = buffer

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

pH = $pK_a$ when $V_b$ = ½ $V_e$

(2) At the equiv. pt. ($V_{OH^-}$ = $V_{ep}$)

➢ Only $A^-$ in solution; Use $K_b$ equil. to calculate pH

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## Titration Curve: *Weak acid-strong base titration* (versus *strong acid-strong base titration*)



Three **major differences** between this curve and that of a SA-SB titration (in red):

1. The WA solution has a higher initial pH. (Less $H^+$ per mol HA for a weak acid)

2. pH rises more rapidly at the start, but less rapidly near the equivalence point => *formation of buffer!*

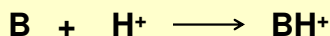3. **pH at equiv. pt. > 7.00** *=> formation of A⁻, a weak base!*

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http://www.chemicool.com/img1/graphics/titration-strong-weak.gif

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# Weak Base-Strong Acid Titrations

B      **Titrant** (always)

*Net ionic equation:*    **B + H⁺ ⟶ BH⁺**

*What is K for this reaction at 25 $^0C$?*

➤ Very large K; reaction goes to completion    *K = 1/K$_a$*
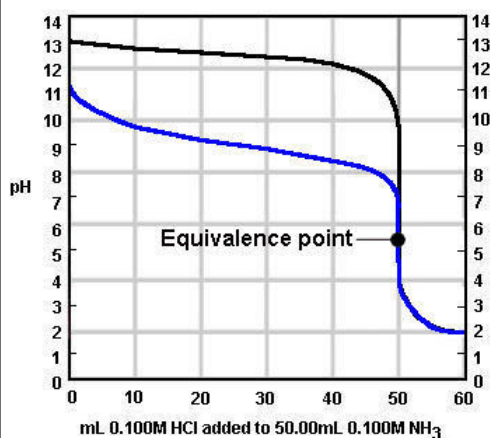
**Before the equivalence point: when $V_{H+} < V_e$**

➤ Mixture of unreacted B and BH⁺ = *a buffer!*

➤ Use the H-H equation to calc. pH; Use $pK_{a\,(BH+)}$

**At the equivalence point**

➤ All of B has reacted; Only BH⁺, a weak acid, in solution

➤ Use $K_{a\,(BH+)}$ equil. to calculate pH

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## Titration Curve: *Weak base-strong acid titration*



mL 0.100M HCl added to 50.00mL 0.100M $NH_3$

**NOTES:**

1. The WA solution has lower initial pH.

2. pH drops quickly at the start, but less near the equiv. pt.
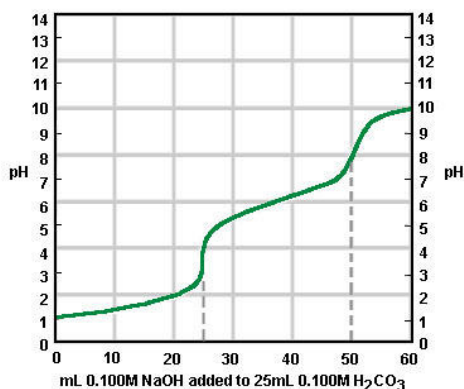
3. pH at the equiv. pt. $\neq$ 7

**POINT OF EMPHASIS :** The **equiv. pt.** for a **WB-SA titration** has a **pH < 7.00**.

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http://www.chem.ubc.ca/courseware/pH/section14/content.html

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# Titrations of Polyprotic Systems

**Titration Curve: *Weak diprotic acid–strong base titration***



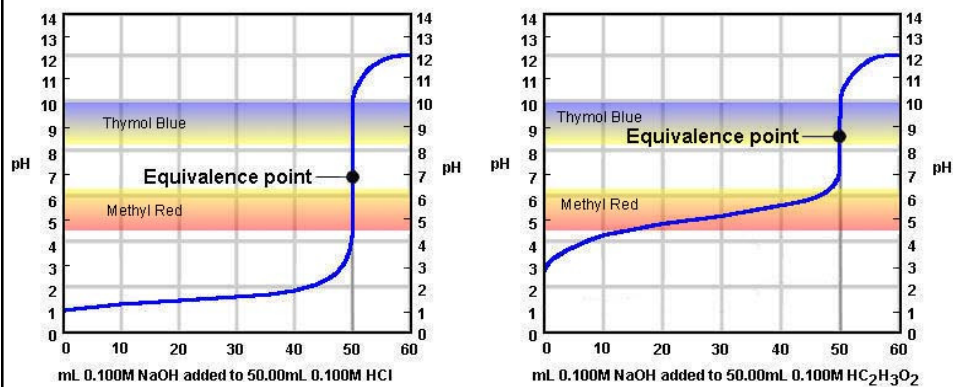mL 0.100M NaOH added to 25mL 0.100M $H_2CO_3$

**NOTES:**

1. There are 2 breaks in the titration curve corresponding to successive deprotonation of the 2 acidic H's.

2. The volume of titrant at the 2nd equivalence point $V_{e2}$, is 2 x $V_{e1}$. (Discussed in class in details)

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http://www.chem.ubc.ca/courseware/pH/section14/content.html

# Acid-Base Indicators

Titrations of both a SA and a WA with a strong base, using **methyl red** and **thymol blue** as possible indicators.



mL 0.100M NaOH added to 50.00mL 0.100M HCl

mL 0.100M NaOH added to 50.00mL 0.100M $HC_2H_3O_2$

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http://www.chem.ubc.ca/courseware/pH/section15/index.html

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# Acid-Base Indicators – *Cont.*

**SA titration (left):** both indicators begin to change color at the equiv. pt. (50 mL of base) so both work equally well.

**WA titration:** thymol blue changes color at the equivalence point, but *methyl red begins to change color after only 15mL of base* are added, which is far from the equivalence point, illustrating the importance of choosing an appropriate indicator.

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