

CH 223 Spring 2025:

“Titration Calculations (online)” Lab - Instructions

Note: This is the lab for section W1 of CH 223 only.

- *If you are taking section 01 or section H1 of CH 223, please use this link:*
<http://mhchem.org/q/4a.htm>
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Step One:

Watch the lab video for the “Titration Calculations” lab, found here:

<http://mhchem.org/v/g.htm>

There is no data to record in this video.

Step Two:

Complete the four problems in this lab using page Ib-4-25. You will need to create and submit four computer generated graphs with this report, plus you need to submit additional page(s) showing detailed calculations of your work for this lab. Include your name on page Ib-4-25!

Step Three:

Submit your lab (page Ib-4-25 *plus* the graphs *and* work pages *only* to avoid a point penalty) **as a *single* PDF file to the instructor via email (mike.russell@mhcc.edu) on Wednesday, April 23 by 11:59 PM.** I recommend a free program (ex: CamScanner, <https://camscanner.com>) or a website (ex: CombinePDF, <https://combinepdf.com>) to convert your work to a PDF file.

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

Acid and Base Titrations - Equation Guide

Strong Acid + Strong Base: (SA + SB)

Initial Region: $\text{pH} = -\log (n_{\text{sa}} / V_{\text{sa}})$

or $\text{pH} = -\log (C_{\text{sa}})$

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

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

Equivalence: $\text{pH} = 7$

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

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

Strong Base + Strong Acid: (SB + SA)

Initial Region: $\text{pH} = 14 + \log (n_{\text{sb}} / V_{\text{sb}})$

or $\text{pH} = 14 + \log (C_{\text{sb}})$

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

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

Equivalence: $\text{pH} = 7$

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

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

Weak Acid + Strong Base: (WA + SB)

Initial Region: $\text{pH} = -\log \sqrt{K_a \cdot \frac{n_{\text{wa}}}{V_{\text{wa}}}}$

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

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

Half-Equivalence Region: $\text{pH} = \text{p}K_a$

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

or $\text{pH} = 14 + \log \sqrt{K_b \cdot C_{\text{wb}}}$

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

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

Continued on next page

Weak Base + Strong Acid: (*WB* + *SA*)

Initial Region: $\text{pH} = 14 + \log \sqrt{K_b \cdot \frac{n_{wb}}{V_{wb}}}$ *or* $\text{pH} = 14 + \log \sqrt{K_b \cdot C_{wb}}$

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

Half-Equivalence Region: $\text{pH} = \text{p}K_a$

Equivalence: $\text{pH} = -\log \sqrt{\frac{K_w}{K_b} \cdot \frac{n_{wb}}{(V_{wb} + V_{sa})}}$ *or* $\text{pH} = -\log \sqrt{K_a \cdot C_{wa}}$

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

Guide to Symbols

n = moles

V = volume (L)

C = concentration (M or mol/L)

sa = strong acid

sb = strong base

wa = weak acid

wb = weak base

K_a = acid dissociation constant for a weak acid

pK_a = $-\log K_a$

K_a = $10^{-\text{p}K_a}$

K_b = base dissociation constant for a weak base

pK_b = $-\log K_b$

K_b = $10^{-\text{p}K_b}$

K_w = 10^{-14} = autoionization constant for water at 25 °C

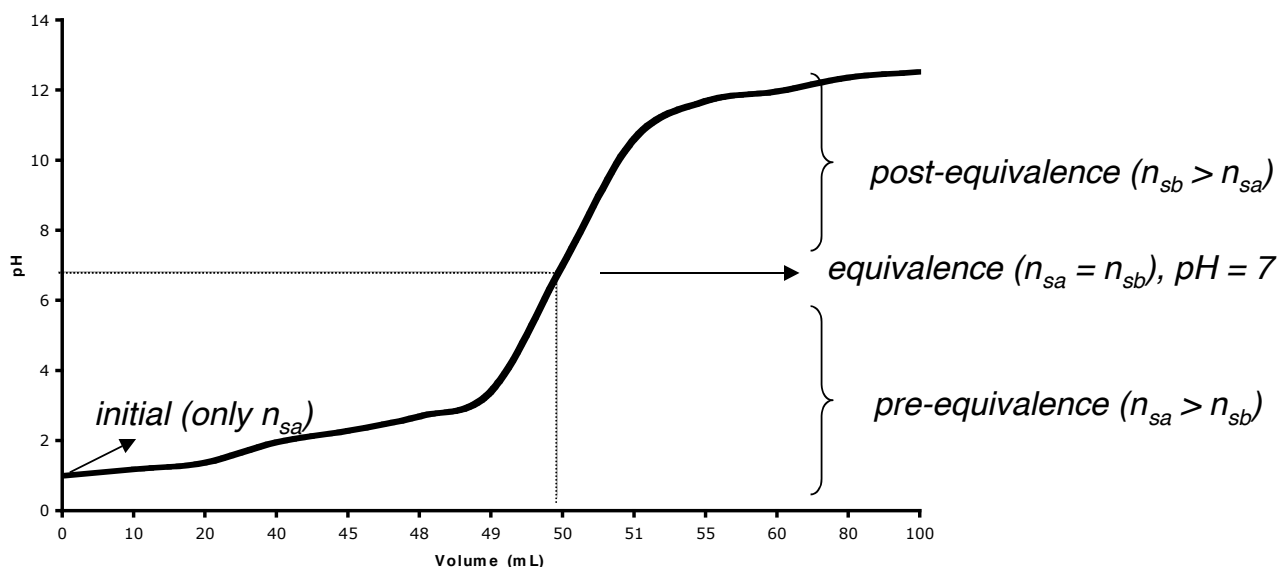
Also, **K_w** = $[\text{H}_3\text{O}^+][\text{OH}^-] = K_a \cdot K_b = 10^{-14}$

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

pOH = $-\log [\text{OH}^-]$

14 = $\text{pH} + \text{pOH} = \text{p}K_a + \text{p}K_b$

Strong Acid + Strong Base Titration - *Overview*



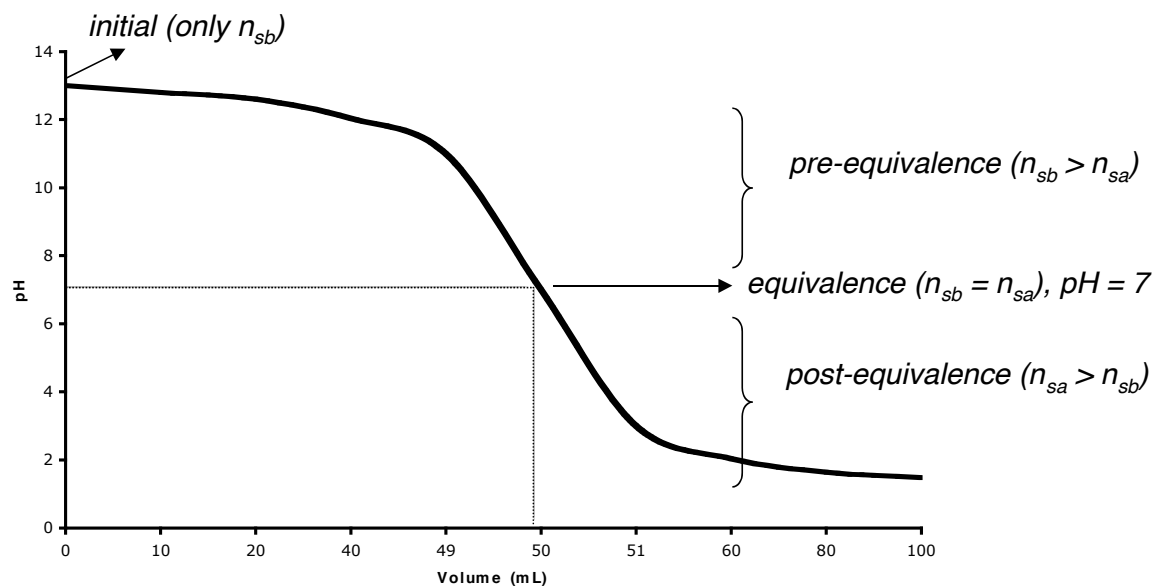
Initial: $pH = -\log [n_{sa} / V_{sa}]$

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

Equivalence: $pH = 7$ (neutral salt + water)

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

Strong Base + Strong Acid Titration - *Overview*



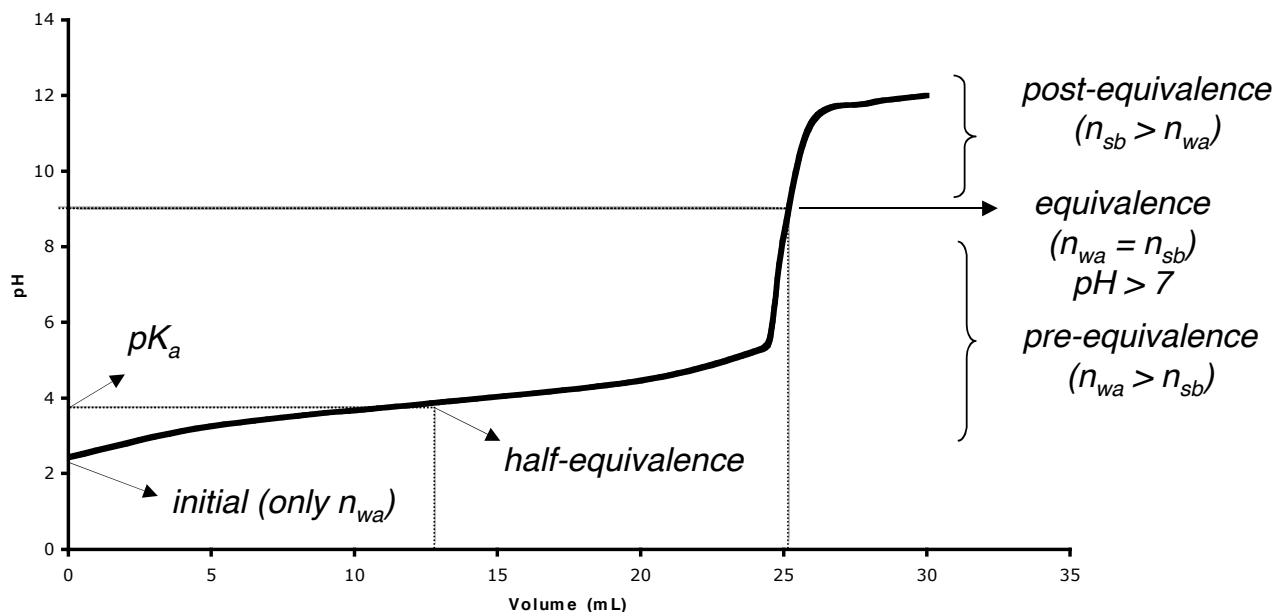
Initial: $pH = 14 + \log \left[\frac{n_{sb}}{V_{sb}} \right]$

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

Equivalence: $pH = 7$ (neutral salt + water)

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

Weak Acid + Strong Base Titration - *Overview*



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Initial:

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

Pre-equivalence:

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

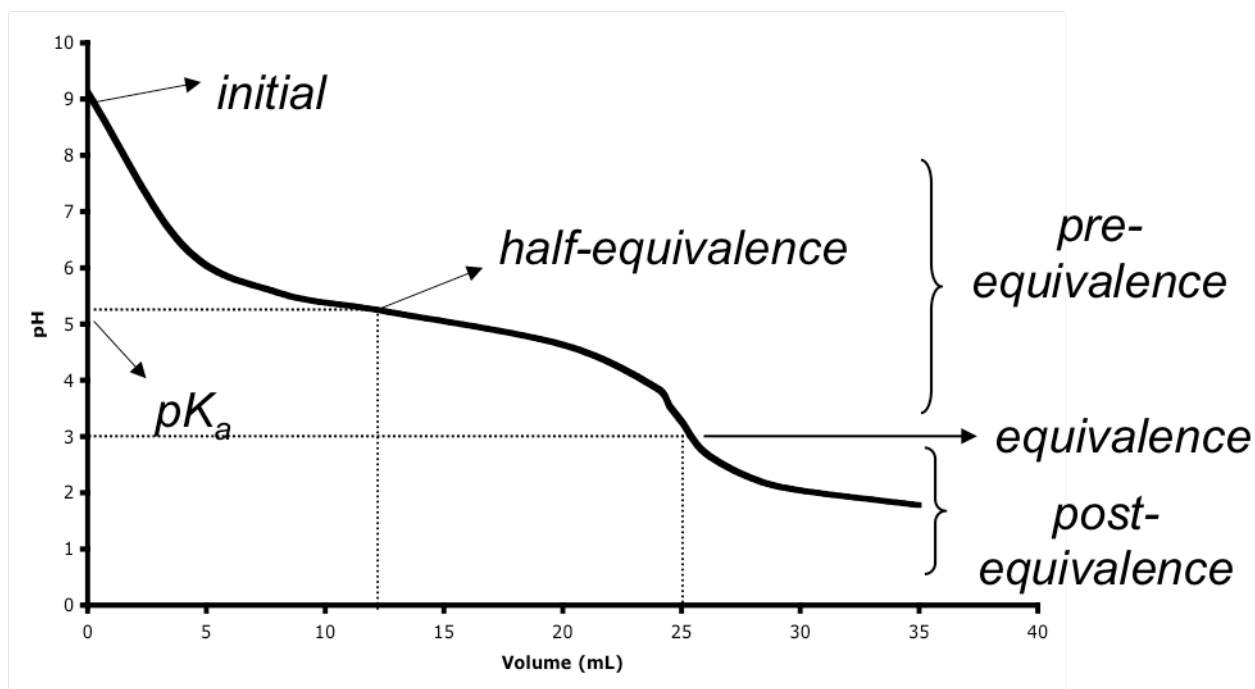
Equivalence:

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

Post-equivalence:

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

Weak Base + Strong Acid Titration - *Overview*



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:

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

CH 223 Guide to Acid and Base Titration Calculations

Acid and base titrations can be a challenging concept for students to conquer in CH 223. This handout will help prepare you for the types of problems associated with titrations.

A **titration** is an experimental procedure whereby a solution (usually either acidic or basic) is added dropwise to a second solution (usually either acidic or basic.) One solution will be acidic while the other will be basic. The solution that is added dropwise is called the **titrant**. Titrations are often graphed using **pH** as the y-axis and **Volume of Titrant (mL)** as the x-axis. Sometimes a second y-axis is used to plot the first derivative; we shall explore this concept in the labs during CH 223.

pH is defined as the negative log of the hydronium concentration, i.e. **pH = - log [H₃O⁺]**. All of the calculations given below reflect this basic idea. Values of pH less than seven indicate acidic conditions, while pH values greater than seven indicate basic conditions; a pH reading of 7 is neutral (neither acidic nor basic). Weak acids, weak bases, strong acids and strong bases require different formulas to find the concentration of [H₃O⁺]; hence, there are different mathematical approaches to titrations depending on the substituents being titrated. We shall concern ourselves only with **monoprotic** acids and bases - those that have only one equivalent of H₃O⁺ or OH⁻ to offer.

We will study four monoprotic titration combinations:

- **Strong acid titrated with strong base:** the pH is initially acidic but becomes more basic as the strong base titrant is added
- **Strong base titrated with strong acid:** the pH is initially basic but becomes more acidic as the strong acid titrant is added
- **Weak acid titrated with strong base:** the pH is initially somewhat acidic but becomes more basic as the strong base titrant is added
- **Weak base titrated with strong acid:** the pH is initially somewhat basic but becomes more acidic as the strong acid titrant is added

Weak acid + weak base titration combinations require an intensive analysis of K_a and K_b constants and are of limited versatility; hence, we will cover only the first four types of titrations.

Before you begin calculations for *any* titration in CH 223, do the following:

- 1) Determine if solution to be titrated contains an acid or a base, and determine if it is strong or weak.
- 2) Determine if the titrant is an acid or base and if it is weak or strong
- 3) If the solution contains a weak acid, find the **K_a**; if a weak base, find **K_b**.
- 4) Refer to the appropriate section:
 - **Strong Acid** (solution) titrated with a **Strong Base**: **Section One**
 - **Strong Base** (solution) titrated with a **Strong Acid**: **Section Two**
 - **Weak Acid** (solution) titrated with a **Strong Base**: **Section Three**
 - **Weak Base** (solution) titrated with a **Strong Acid**: **Section Four**

Notes: **Weak acids with weak bases** and **weak bases with weak acids** will not be covered in CH 223.

Polyprotic acid and base titrations will not be mathematically covered in CH 223. **Redox titrations** will be covered in the subsequent electrochemistry chapter. Additional information on pH calculations can be found in the Web-only handout "**A Closer Look at Titrations**" available on the CH 223 website

Section One: Strong Acid + Strong Base (SA + SB) Titration

Equivalence Point pH = 7 neutral

Before you begin:

Strong acids titrated with strong bases will neutralize each other at the equivalence point. Therefore, you should expect to see a neutral pH when the quantity of acid equals the quantity of base added.

Determine the following quantities:

V_{sa} = volume of strong acid initially present

n_{sa} = moles of strong acid ($= C_{sa} * V_{sa}$)

C_{sb} = concentration of strong base

V_{sb} = volume of strong base to reach equivalence point ($= n_{sa} / C_{sb}$)

Analysis Section:

There are **four regions** in SA + SB titrations that require specific approaches to calculate the pH:

- **Initial Region: $pH = -\log(n_{sa} / V_{sa})$**

The pH will reflect the strong acid only - no strong base has been added.

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

The pH will reflect the remaining acid in solution after some neutralization with strong base.

$n_{sa} > n_{sb}$ in this region.

- **Equivalence: $pH = 7$**

$n_{sa} = n_{sb}$, so water and a neutral salt will be produced at this point.

- **Post-Equivalence Region: $pH = 14 + \log\left(\frac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}}\right)$**

The pH will reflect the excess base remaining after neutralizing the strong acid.

$n_{sb} > n_{sa}$ in this region.

Example: Titrate 50.0 mL of 0.200 M HNO_3 with 0.100 M NaOH. Determine the pH after 0.00, 10.0, 100. and 150. mL of NaOH has been added.

HNO_3 is a *strong acid*, NaOH is a *strong base*; the equivalence point $pH = 7$

$V_{sa} = 50.0 \text{ mL} = \mathbf{0.0500 \text{ L}}$

$n_{sa} = 0.200 \text{ M} * 0.0500 \text{ L} = \mathbf{0.0100 \text{ mol}}$

$C_{sb} = \mathbf{0.100 \text{ M}}$

$V_{sb} = 0.0100 \text{ mol} / 0.100 \text{ M} = 0.100 \text{ L} = \mathbf{100. \text{ mL NaOH to the equivalence point}}$

At 0.00 mL: Initial point: $pH = -\log(n_{sa} / V_{sa}) = -\log(0.0100 \text{ mol} / 0.0500 \text{ L}) = \mathbf{0.70}$

The pH reflects only the strong acid; no strong base has been added at this point.

At 10.0 mL: Pre-equivalence point: $\text{pH} = -\log \left(\frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}} \right)$

At 10.0 mL, $V_{sb} = 0.0100 \text{ L}$, and $n_{sb} = 0.0100 \text{ L} * 0.100 \text{ M} = 0.00100 \text{ mol}$

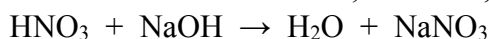
$$\text{pH} = -\log \left(\frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}} \right) = -\log \left(\frac{0.0100 - 0.00100}{0.0500 + 0.0100} \right) = 0.82$$

Note: 10.0 mL < 100. mL (equivalence point), so this point is in the pre-equivalence region

At 100. mL: **Equivalence point, pH = 7**

At 100.0 mL, $n_{sb} = 0.100 \text{ L} * 0.100 \text{ M} = 0.0100 \text{ mol} = n_{sa}$

Equal molar quantities of acid and base have been added; therefore,



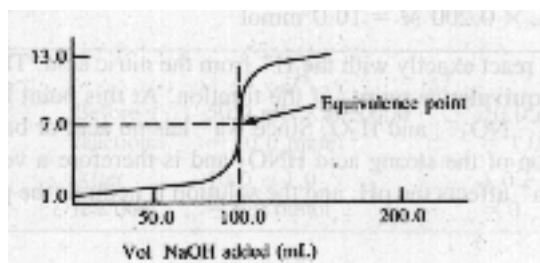
NaNO_3 is a neutral salt, and the pH of water is 7; therefore, the equivalence pH is 7.

At 150. mL: Post-equivalence point: $\text{pH} = 14 + \log \left(\frac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}} \right)$

At 150.0 mL, $n_{sb} = 0.150 \text{ L} * 0.100 \text{ M} = 0.0150 \text{ mol}$, which is larger than n_{sa} . This point lies in the post-equivalence region, so:

$$\text{pH} = 14 + \log \left(\frac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}} \right) = 14 + \log \left(\frac{0.0150 - 0.0100}{0.150 + 0.0500} \right) = 12.40$$

The **titration graph** for a strong acid + strong base would look like this:



Notice the sharp slope around the equivalence point region - this is indicative of strong acid + strong base titrations. Note that the equivalence point pH is 7.0 - this is also what we would expect for this type of titration. Knowing how to predict the type of titration from a graph can be of considerable assistance to you in CH 223.

Section Two: Strong Base + Strong Acid (SB + SA) Titration

Equivalence Point pH = 7 *neutral*

Analysis of this type of titration is very similar to the analysis for a Strong Acid + Strong Base (Section 1, above) *except* that the strong base will be dominant initially, followed by a slow erosion with a strong acid. Notice the subtle changes to the equations in this section when compared to section 1; you should see a pattern developing which can help you in your calculations.

Before you begin:

As in section 1, strong bases titrated with strong acids will neutralize each other at the equivalence point. Therefore, you should expect to see a neutral pH when the quantity of base equals the quantity of acid added.

Determine the following quantities:

V_{sb} = volume of strong base initially present

n_{sb} = moles of strong base ($= C_{sb} * V_{sb}$)

C_{sa} = concentration of strong acid

V_{sa} = volume of strong acid to reach equivalence point ($= n_{sb} / C_{sa}$)

Analysis Section:

There are **four regions** in SB + SA titrations that require specific approaches to calculate the pH:

- **Initial Region: $pH = 14 + \log (n_{sb} / V_{sb})$**

The pH will reflect the strong base only - no strong acid has been added.

Note the presence of "14" in the equation; this is due to the fact that:

$$pOH = -\log (n_{sb} / V_{sb})$$

and

$$14 = pH + pOH$$

Combining these equations and solving for pH gives $pH = 14 + \log (n_{sb} / V_{sb})$.

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

The pH will reflect the remaining base in solution after some neutralization with strong acid.

$n_{sb} > n_{sa}$ in this region.

- **Equivalence: $pH = 7$**

$n_{sb} = n_{sa}$, so water and a neutral salt will be produced at this point.

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

The pH will reflect the excess acid remaining after neutralizing the strong base.

$n_{sa} > n_{sb}$ in this region.

Example: Titrate 100. mL of 0.500 M NaOH with 1.00 M HCl. Determine the pH after 0.00, 25.0, 50.0 and 80.0 mL of NaOH has been added.

NaOH is a *strong base*, HCl is a *strong acid*; the equivalence point pH = 7

$$V_{sb} = 100. \text{ mL} = \mathbf{0.100 \text{ L}}$$

$$n_{sb} = 0.500 \text{ M} * 0.100 \text{ L} = \mathbf{0.0500 \text{ mol}}$$

$$C_{sa} = \mathbf{1.00 \text{ M}}$$

$$V_{sa} = 0.0500 \text{ mol} / 1.00 \text{ M} = 0.0500 \text{ L} = \mathbf{50.0 \text{ mL HCl to the equivalence point}}$$

At 0.00 mL: Initial point: $\text{pH} = 14 + \log (n_{sb} / V_{sb}) = 14 + \log (0.0500 \text{ mol} / 0.100 \text{ L}) = \mathbf{13.70}$

The pH reflects only the strong base; no strong acid has been added at this point.

At 25.0 mL: Pre-equivalence point: $\text{pH} = 14 + \log \left(\frac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}} \right)$

At 25.0 mL, $V_{sa} = \mathbf{0.0250 \text{ L}}$, and $n_{sa} = 0.0250 \text{ L} * 1.00 \text{ M} = \mathbf{0.0250 \text{ mol}}$

$$\text{pH} = 14 + \log \left(\frac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}} \right) = \mathbf{14 + \log \left(\frac{0.0500 - 0.0250}{0.100 + 0.0250} \right) = 13.30}$$

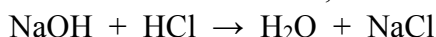
Note: 25.0 mL < 50.0 mL (equivalence point), so this point is in the pre-equivalence region

Notice how there is little pH change upon adding this much acid. Strong base + strong acid pH curves change slowly until the equivalence point is reached, then the change becomes quite noticeable.

At 50.0 mL: **Equivalence point, pH = 7**

At 50.0 mL, $n_{sa} = 0.0500 \text{ L} * 1.00 \text{ M} = 0.0500 \text{ mol} = n_{sb}$

Equal molar quantities of base and acid have been added; therefore,



NaCl is a neutral salt, and the pH of water is 7; therefore, the equivalence pH is 7.

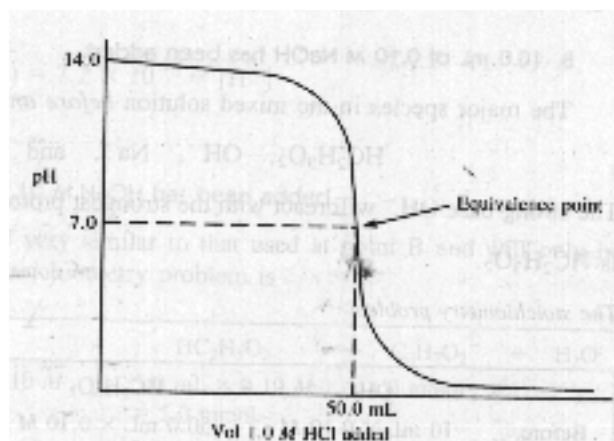
At 80.0 mL: Post-equivalence point: $\text{pH} = -\log \left(\frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}} \right)$

At 80.0 mL, $n_{sa} = 0.0800 \text{ L} * 1.00 \text{ M} = \mathbf{0.0800 \text{ mol}}$, which is larger than n_{sb} . This point lies in the post-equivalence region, so:

$$\text{pH} = -\log \left(\frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}} \right) = \mathbf{-\log \left(\frac{0.0800 - 0.0500}{0.0800 + 0.100} \right) = 0.78}$$

Notice how the pH changed rapidly between 25.0 mL of acid added (still quite basic) and 80.0 mL of acid added (where the pH is quite acidic). As the concentration of strong acids and bases increases, the titration curves will show a steeper equivalence point.

The **titration graph** for a strong base + strong acid would look like this:

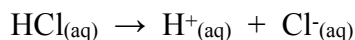


As in section 1, notice the sharp slope around the equivalence point region - this is indicative of strong base + strong acid titrations. Note that the equivalence point pH is 7.0 - this is also what we would expect for this type of titration. At first, the NaOH dominated the titration, and the graph pH was quite basic. At the conclusion of the titration, HCl dominated and overcame the NaOH present in solution, and the pH became quite acidic. Remembering simple facts can aid your analysis of titrations in CH 223.

Section Three: Weak Acid + Strong Base (WA + SB) Titration

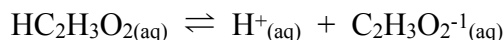
Equivalence Point $\text{pH} > 7$ basic

Weak acids and weak bases have incomplete ionization in solution, which is in marked contrast to their strong acid and strong base counterparts. For example, if we have a solution of 1.00 M HCl in water,



we would have 100% of the $\text{HCl}_{(\text{aq})}$ converted to $\text{H}^{+}_{(\text{aq})}$ and $\text{Cl}^{-}_{(\text{aq})}$; no HCl would remain in solution.

If we had a solution of 1.00 M $\text{HC}_2\text{H}_3\text{O}_2$ in water,



we would have roughly 99% of the $\text{HC}_2\text{H}_3\text{O}_2$ still present in solution; less than 1% of the $\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}$ would ionize into $\text{H}^{+}_{(\text{aq})}$ and $\text{C}_2\text{H}_3\text{O}_2^{-}_{(\text{aq})}$. Weak acids and weak bases do not ionize completely in solution. Recall that if $\text{HC}_2\text{H}_3\text{O}_2$ is our weak acid, $\text{C}_2\text{H}_3\text{O}_2^{-}_{(\text{aq})}$ will be the **conjugate base** in this system. Strong acids and bases do not have effective conjugate acids or bases.

To account for the discrepancy in ionization behavior, we will use the **acid equilibrium constant, K_a** , and the **base equilibrium constant, K_b** , in our calculations. Recall that K_a and K_b are related to K_w , the autoionization of water constant, by the following expression:

$$K_w = K_a * K_b$$

To speed our calculations when the weak acid or weak base is present in excess, we can use the **Henderson-Hasselbalch equation**. We will use a slightly modified form in this section, but the generic equation is:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Conj. base}]}{[\text{acid}]}$$

where $\text{pH} = \text{pH}$ of system
 $\text{p}K_a = -\log K_a = -\log$ (acid dissociation constant for weak acid in buffer)
 $[\text{Conj. base}] =$ concentration *or* moles of base in solution
 $[\text{acid}] =$ concentration *or* moles of weak acid in solution

The Henderson-Hasselbalch equation tells us that when the moles of the strong base added equal one-half the moles of weak acid initially present (i.e. $\frac{1}{2} n_{\text{wa}} = n_{\text{sb}}$), a special condition occurs; this point is called the **half-equivalence point**, and $\text{pH} = \text{p}K_a$ here. Therefore, we need to add an additional region to our calculations, the **half-equivalence region**.

Before you begin: Determine the following quantities:

V_{wa} = volume of weak acid initially present
 n_{wa} = moles of weak acid ($= C_{\text{wa}} * V_{\text{wa}}$)
 K_a = acid dissociation constant for the weak acid
 $\text{p}K_a = -\log K_a$ (this is a just a unitless number)
 C_{sb} = concentration of strong base
 V_{sb} = volume of strong base to reach equivalence point ($= n_{\text{wa}} / C_{\text{sb}}$)
Also remember that at room temperature, $K_w = 10^{-14}$

Analysis Section: There are **five regions** in WA + SB titrations in which to calculate the pH:

- Initial Region:* $\text{pH} = -\log \sqrt{K_a \cdot \frac{n_{wa}}{V_{wa}}}$

The pH will reflect the weak acid only - no strong base has been added. Recall that for weak acids,

$$[\text{H}_3\text{O}^+] = \sqrt{K_a \cdot C_{wa}}$$

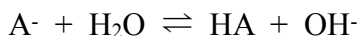
and $C_{wa} = n_{wa} / V_{wa}$, just as $\text{pH} = -\log [\text{H}_3\text{O}^+]$.

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

Because $n_{wa} > n_{sb}$ in this region, the pH will be affected by two factors: 1) the remaining weak acid in the solution, and 2) the *conjugate base* present upon addition of strong base. For weak acids HA reacting with strong base NaOH,



The species A^- is the *conjugate base* of the weak acid HA, and it will react with water to re-form the weak acid:



The generation of OH^- from the conjugate base will affect pH.

Fortunately, the weak acid / conjugate base system can be treated like a **buffer**; hence, the usefulness of the Henderson-Hasselbalch equation. Recall that the Henderson-Hasselbalch equation is

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Conj. base}]}{[\text{acid}]}$$

$[\text{Conj. base}]$ and $[\text{acid}]$ can be re-written as n_{sb} and $(n_{wa} - n_{sb})$, respectively*, or

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

* *Why?* OK, here goes: for every mole of conjugate base created, an equal number of moles of strong base must be added, so $[\text{Conj. base}] = n_{sb}$. Also, the moles of weak acid present in solution will depend on how many moles of strong base have been added, so $[\text{acid}] = (n_{wa} - n_{sb})$.

Note that there is **no volume dependence in the pre-equivalence region**; you need not calculate total volume, etc. in this region *if* using the Henderson-Hasselbalch equation.

- Half-Equivalence Region:* $\text{pH} = \text{p}K_a$

At half-equivalence, $1/2 n_{wa} = n_{sb}$, and the log term in the pre-equivalence equation goes to zero ($\log 1 = 0$). Note that *you can predict the pH of any weak acid system at half-equivalence by calculating the $\text{p}K_a$!*

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

At the equivalence point, $n_{wa} = n_{sb}$, and the only factor affecting pH is the conjugate base (see discussion on pre-equivalence, above.) To find $[\text{OH}^-]$ for a weak base, use:

$$[\text{OH}^-] = \sqrt{K_b \cdot C_{wb}} = \sqrt{K_b \cdot \frac{n_{wb}}{V_{wb}}}$$

For every mole of weak acid, an equal number of moles of conjugate base are created; hence, $n_{cb} = n_{wa}$.

The term V_{cb} must take into account the total volume present in solution, hence, $V_{cb} = V_{wa} + V_{sb}$.

K_b can be rewritten as K_w / K_a .

Converting $[\text{OH}^-]$ to pH provides the necessary equation

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

Note that in titrations of weak acids with strong bases, the equivalence point pH will be affected by the pH of the conjugate base only; no weak acid remains in solution. Therefore, expect basic pH values at the equivalence point in weak acid + strong base titrations.

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

The pH will reflect the excess strong base remaining after neutralizing the weak acid. ($n_{sb} > n_{wa}$)

Note that the contribution of the *conjugate base* will have no appreciable effect on the pH assuming even a small portion of strong base is present in solution; therefore, it is omitted from the calculation.

Example: Titrate 50.0 mL of 0.100 M $\text{HC}_2\text{H}_3\text{O}_2$ ($K_a = 1.80 \times 10^{-5}$) with 0.100 M NaOH. Determine the pH after 0.00, 10.0, 25.0, 40.0, 50.0 and 60.0 mL of NaOH has been added.

$\text{HC}_2\text{H}_3\text{O}_2$ is a *weak acid*, NaOH is a *strong base*; the equivalence point should be *basic*

$V_{wa} = 50.0 \text{ mL} = \mathbf{0.0500 \text{ L}}$

$n_{wa} = 0.100 \text{ M} \times 0.0500 \text{ L} = \mathbf{0.00500 \text{ mol}}$

$C_{sb} = \mathbf{0.100 \text{ M}}$

$V_{sb} = 0.00500 \text{ mol} / 0.100 \text{ M} = 0.0500 \text{ L} = \mathbf{50.0 \text{ mL NaOH to the equivalence point}}$

The **half-equivalence point** will be reached at (50.0 mL / 2) or **25.0 mL NaOH**

$\text{p}K_a = -\log K_a = -\log (1.80 \times 10^{-5}) = \mathbf{4.74}$

At 0.00 mL: Initial point:

$$\text{pH} = -\log \sqrt{K_a \cdot \frac{n_{wa}}{V_{wa}}} = -\log \sqrt{1.80 \times 10^{-5} \cdot \frac{0.00500}{0.0500}} = \mathbf{2.87}$$

The pH reflects only the weak acid; no strong base has been added at this point.

Note how the initial pH of a weak acid is considerably more basic than the initial pH of a strong acid; this is due to the incomplete ionization of the weak acid (and the resulting dependency on K_a .)

At 10.0 mL: Pre-equivalence point:

$$\text{pH} = \text{p}K_a + \log \left(\frac{n_{sb}}{n_{wa} - n_{sb}} \right) = 4.74 + \log \left(\frac{0.00100}{0.00500 - 0.00100} \right) = 4.14$$

At 10.0 mL, $V_{sb} = 0.0100 \text{ L}$, and $n_{sb} = 0.0100 \text{ L} * 0.100 \text{ M} = 0.00100 \text{ mol}$

Note: 10.0 mL < 50.0 mL (equivalence point), so this point is in the pre-equivalence region

At 25.0 mL: Half-equivalence point: $\text{pH} = \text{p}K_a = 4.74$

This is a simple calculation but one which gives tremendous insight into the system being studied.

At 40.0 mL: Pre-equivalence point:

$$\text{pH} = \text{p}K_a + \log \left(\frac{n_{sb}}{n_{wa} - n_{sb}} \right) = 4.74 + \log \left(\frac{0.00400}{0.00500 - 0.00400} \right) = 5.34$$

At 40.0 mL, $V_{sb} = 0.0400 \text{ L}$, and $n_{sb} = 0.0400 \text{ L} * 0.100 \text{ M} = 0.00400 \text{ mol}$

Note: 40.0 mL < 50.0 mL (equivalence point), so this point is in the pre-equivalence region

At 50.0 mL: Equivalence point:

$$\text{pH} = 14 + \log \sqrt{\frac{K_w}{K_a} \cdot \frac{n_{wa}}{(V_{wa} + V_{sb})}} = 14 + \log \sqrt{\frac{10^{-14}}{1.8 \times 10^{-5}} \cdot \frac{0.00500}{(0.0500 + 0.0500)}} = 8.72$$

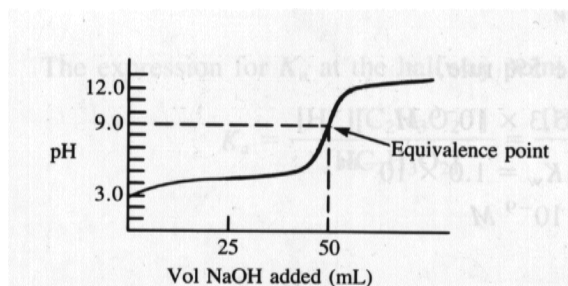
Note that this equation looks somewhat nasty, but really it's just a good old "plug and chug" equation. *Notice* how the equivalence pH is basic as predicted.

At 60.0 mL: Post-equivalence point:

$$\text{pH} = 14 + \log \left(\frac{n_{sb} - n_{wa}}{V_{sb} + V_{wa}} \right) = 14 + \log \left(\frac{0.00600 - 0.00500}{0.0600 + 0.0500} \right) = 11.96$$

At 60.0 mL, $n_{sb} = 0.0600 \text{ L} * 0.100 \text{ M} = 0.00600 \text{ mol}$, which is larger than n_{wa} . This point lies in the post-equivalence region.

The **titration graph** for a weak acid + strong base would look like the diagram below:

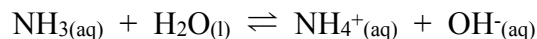


Note that the equivalence point is basic in a weak acid + strong base titration, a result of the conjugate base of the weak acid. Also note how the slope around the equivalence point is not as steep as it was when strong acids and bases were mixed together.

Section Four: Weak Base + Strong Acid (WB + SA) Titration

Equivalence Point $\text{pH} < 7$ acidic

As discussed in section three (WA + SB), weak acids and bases do not ionize completely in solution. For example, if we had a solution of 1.00 M NH_3 (ammonia, a weak base) in water,



we would have roughly 99% of the ammonia still present in solution; less than 1% of the $\text{NH}_3(\text{aq})$ would ionize with water into $\text{NH}_4^+(\text{aq})$ and $\text{OH}^-(\text{aq})$. Recall that $\text{NH}_4^+(\text{aq})$ will be the **conjugate acid** in this system. This lack of complete ionization forces a dependency upon the **base equilibrium constant, K_b** , in our calculations.

As before, to speed our calculations when the weak base is present in excess, we can use the **Henderson-Hasselbalch equation**. We will use a slightly modified form for this section. The **half-equivalence point** will also be of use to use just as it was in the WA + SB titration.

Before you begin:

Determine the following quantities:

V_{wb} = volume of weak base initially present

n_{wb} = moles of weak base ($= C_{wb} \cdot V_{wb}$)

K_b = base dissociation constant for the weak base

$\text{p}K_b = -\log K_b$ (this is just a unitless number)

C_{sa} = concentration of strong acid

V_{sa} = volume of strong acid to reach equivalence point ($= n_{wb} / C_{sa}$)

Also remember that at room temperature, $K_w = 10^{-14}$

Analysis Section:

There are **five regions** in WB + SA titrations that require specific approaches to calculate the pH:

• *Initial Region:* $\text{pH} = 14 + \log \sqrt{K_b \cdot \frac{n_{wb}}{V_{wb}}}$

The pH will reflect the weak base only - no strong acid has been added. Recall that for weak bases,

$$[\text{OH}^-] = \sqrt{K_b \cdot C_{wb}}$$

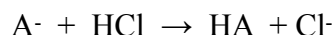
and $C_{wb} = n_{wb} / V_{wb}$. Recall that $\text{pOH} = -\log [\text{OH}^-]$ and that $\text{pH} + \text{pOH} = 14$; therefore,

$$\text{pH} = 14 + \log \sqrt{K_b \cdot \frac{n_{wb}}{V_{wb}}}$$

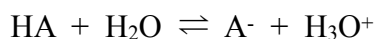
- *Pre-Equivalence Region:* This region uses a modified version of the Henderson-Hasselbalch equation to calculate pH:

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

Because $n_{wb} > n_{sa}$ in this region, the pH will be affected by two factors: 1) the remaining weak base in the solution, and 2) the *conjugate acid* present upon addition of strong acid. For a weak base A^- reacting with strong acid HCl ,



The species HA is the *conjugate acid* of the weak base A^- , and it will react with water to re-form the weak acid:



The generation of H_3O^+ from the conjugate acid will affect pH.

As in the weak acid / strong base scenario, the weak base / conjugate acid system can be treated like a *buffer*; hence, the usefulness of the Henderson-Hasselbalch equation. Recall that the Henderson-Hasselbalch equation is

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Conj. base}]}{[\text{acid}]}$$

We will modify the Henderson-Hasselbalch equation to our weakly basic system. $[\text{Conj. base}]$ and $[\text{acid}]$ can be re-written as $(n_{wb} - n_{sa})$ and n_{sa} , respectively*, and since $\text{p}K_a + \text{p}K_b = 14$, we can re-write our equation as

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

* *Why?* OK, here goes: for every mole of conjugate acid created, an equal number of moles of strong acid must be added, so $[\text{acid}] = n_{sa}$. Also, the moles of weak base present in solution will depend on how many moles of strong acid have been added, therefore $[\text{Conj. base}]$ is $(n_{wb} - n_{sa})$.

Note that there is **no volume dependence in the pre-equivalence region**; you need not calculate total volume, etc. in this region *if* using the Henderson-Hasselbalch equation.

- *Half-Equivalence Region:* $\text{pH} = \text{p}K_a$

At half-equivalence, $1/2 n_{wb} = n_{sa}$, and the log term in the pre-equivalence equation goes to zero ($\log 1 = 0$). Note that *you can predict the pOH of any weak base system at half-equivalence by calculating the $\text{p}K_b$ or the pH via $\text{p}K_a$!* Converting to pH requires a simple but necessary calculation.

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

At the equivalence point, $n_{wb} = n_{sa}$, and the only factor affecting pH is the conjugate acid (see discussion on pre-equivalence, above.) To find $[\text{H}_3\text{O}^+]$ for a weak acid:

$$[\text{H}_3\text{O}^+] = \sqrt{K_a \cdot C_{wa}} = \sqrt{K_a \cdot \frac{n_{wa}}{V_{wa}}}$$

For every mole of weak base, an equal number of moles of conjugate acid are created; hence, $n_{wa} = n_{wb}$.

The term V_{wa} must take into account the total volume present in solution, hence, $V_{wa} = V_{wb} + V_{sa}$.

K_a can be rewritten as K_w / K_b .

Converting $[\text{H}_3\text{O}^+]$ to pH provides the necessary equation

$$\text{pH} = -\log \sqrt{\frac{K_w}{K_b} \cdot \frac{n_{wb}}{(V_{wb} + V_{sa})}}$$

Note that in titrations of weak bases with strong acids, the equivalence point pH will be affected by the pH of the conjugate acid only; no weak base or strong acid remains in solution. Therefore, expect acidic pH values at the equivalence point in weak base + strong acid titrations.

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

The pH will reflect the excess strong acid remaining after neutralizing the weak base.

$n_{sa} > n_{wb}$ in this region.

Note that the contribution of the *conjugate acid* will have no appreciable effect on the pH assuming even a small portion of strong acid is present in solution; therefore, it is omitted from the calculation.

Example: Titrate 100. mL of 0.0500 M NH_3 ($K_b = 1.80 \times 10^{-5}$) with 0.100 M HCl. Determine the pH after 0.00, 10.0, 25.0, 50.0 and 60.0 mL of HCl has been added.

NH_3 is a *weak base*, HCl is a *strong acid*; the equivalence point should be *acidic*

$V_{wb} = 100. \text{ mL} = \mathbf{0.100 \text{ L}}$

$n_{wb} = 0.0500 \text{ M} \times 0.100 \text{ L} = \mathbf{0.00500 \text{ mol}}$

$C_{sa} = \mathbf{0.100 \text{ M}}$

$V_{sa} = 0.00500 \text{ mol} / 0.100 \text{ M} = 0.0500 \text{ L} = \mathbf{50.0 \text{ mL HCl to the equivalence point}}$

The **half-equivalence point** will be reached at (50.0 mL / 2) or **25.0 mL HCl**

$\text{p}K_a = -\log (K_w / K_b) = -\log (10^{-14} / 1.80 \times 10^{-5}) = \mathbf{9.26}$

At 0.00 mL: Initial point:

$$\text{pH} = 14 + \log \sqrt{K_b \cdot \frac{n_{wb}}{V_{wb}}} = \mathbf{14 + \log \sqrt{1.8 \times 10^{-5} \cdot \frac{0.00500}{0.100}} = 10.98}$$

The pH reflects only the weak base; no strong acid has been added at this point.

Note how the initial pH of a weak base is considerably more acidic than the initial pH of a strong base; this is due to the incomplete ionization of the weak base (and the resulting dependency on K_b .)

At 10.0 mL: Pre-equivalence point:

$$\text{pH} = \text{p}K_a + \log \left(\frac{n_{wb} - n_{sa}}{n_{sa}} \right) = 9.26 + \log \left(\frac{0.00500 - 0.00100}{0.00100} \right) = 9.86$$

At 10.0 mL, $V_{sa} = 0.0100 \text{ L}$, and $n_{sa} = 0.0100 \text{ L} * 0.100 \text{ M} = 0.00100 \text{ mol}$

Note: 10.0 mL < 50.0 mL (equivalence point), so this point is in the pre-equivalence region

At 25.0 mL: Half-equivalence point: $\text{pH} = \text{p}K_a = 14 - \text{p}K_b = 14 - 4.74 = 9.26$

Although simple, this calculation gives tremendous insight into the system being studied.

At 50.0 mL: Equivalence point:

$$\text{pH} = -\log \sqrt{\frac{K_w}{K_b} \cdot \frac{n_{wb}}{(V_{wb} + V_{sa})}} = -\log \sqrt{\frac{10^{-14}}{1.80 \times 10^{-5}} \cdot \frac{0.00500}{(0.0500 + 0.100)}} = 5.37$$

Note that this equation looks somewhat nasty, but really it's just a good old "plug and chug" equation. All of the values have been calculated, and the application will become easier with time.

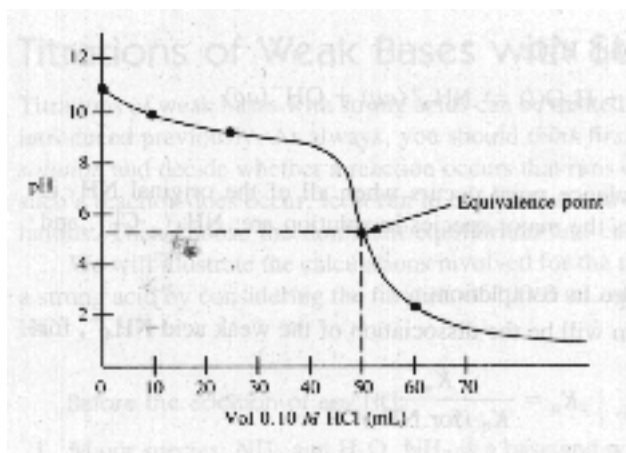
Notice how the equivalence point pH is acidic as predicted.

At 60.0 mL: Post-equivalence point:

$$\text{pH} = -\log \left(\frac{n_{sa} - n_{wb}}{V_{sa} + V_{wb}} \right) = -\log \left(\frac{0.00600 - 0.00500}{0.0600 + 0.100} \right) = 2.20$$

At 60.0 mL, $n_{sa} = 0.0600 \text{ L} * 0.100 \text{ M} = 0.00600 \text{ mol}$, which is larger than n_{wb} . This point lies in the post-equivalence region.

The **titration graph** for a weak base + strong acid would look like this:



Note that the equivalence point is acidic in a weak base + strong acid titration, a result of the conjugate acid of the weak base. Also note how the slope around the equivalence point is not as steep as it was when strong acids and bases were mixed together.

CH 223 Titration Calculations - *The Problems*

Exercises: *Complete these problems using the worksheet on the next page. Also, construct a graph of pH versus Volume of Titrant for each problem. Staple calculations to the back of the worksheet on separate paper. All pH calculations should be reported to the hundredths place.*

1. You wish to titrate 50.00 mL of a 0.100 M HCl solution with 0.100 M NaOH. Calculate the pH after the addition of 0.00 mL, 10.00 mL, 20.00 mL, 40.00 mL, 45.00 mL, 48.00 mL, 49.00 mL, 50.00 mL, 51.00 mL, 55.00 mL, 60.00 mL, 80.00 mL and 100.00 mL of NaOH. Plot the results of your calculations as pH versus mL of NaOH added.
2. You wish to titrate 38.00 mL of a 0.1680 M KOH solution with 0.1120 M HNO₃. Calculate the pH after the addition of 0.00 mL, 5.00 mL, 12.70 mL, 29.99 mL, 51.00 mL, 55.50 mL, 57.00 mL, 61.20 mL, 74.70 mL, 82.20 mL, 88.50 mL, 92.30 mL and 100.00 mL of HNO₃. Plot the results of your calculations as pH versus mL of HNO₃ added.
3. A 25.00 mL solution of 0.100 M lactic acid (HC₃H₅O₃, pK_a = 3.85) is titrated with 0.100 M LiOH. Calculate the pH after the addition of 0.00 mL, 4.00 mL, 8.00 mL, 12.50 mL, 20.00 mL, 24.00 mL, 24.50 mL, 25.00 mL, 26.00 mL, 28.00 mL, 30.00 mL, 35.00 mL and 40.00 mL of LiOH. Plot the results of your calculations as pH versus mL of LiOH added.
4. A student titrates 29.00 mL of 0.2250 M pyridine (K_b = 1.7*10⁻⁹) with 0.3750 M HBr. Calculate the pH after the addition of 0.00 mL, 2.00 mL, 3.60 mL, 5.00 mL, 6.50 mL, 8.70 mL, 9.90 mL, 10.00 mL, 10.80 mL, 15.00 mL, 17.40 mL, 18.70 mL and 36.00 mL of HBr. Plot the results of your calculations as pH versus mL of HBr added.

CH 223 Titration Calculations *Answer Sheet*

Name: _____

Provide answers to the questions (found on the previous page) using the sheet below.

- **Report *all* pH values to the hundredths place.**
- ***Circle* the equivalence point and the half-equivalence point (if appropriate) volume** on the handout
- Include computer generated **graphs** (using Excel, etc.) of the titrations **and all necessary calculations** on separate paper **stapled** to the **back** of this handout (put this page on **top** for full credit!)

<i>Question #1</i>		<i>Question #2</i>		<i>Question #3</i>		<i>Question #4</i>	
Volume NaOH	pH	Volume HNO ₃	pH	Volume LiOH	pH	Volume HBr	pH
0.00		0.00		0.00		0.00	
10.00		5.00		4.00		2.00	
20.00		12.70		8.00		3.60	
40.00		29.99		12.50		5.00	
45.00		51.00		20.00		6.50	
48.00		55.50		24.00		8.70	
49.00		57.00		24.50		9.90	
50.00		61.20		25.00		10.00	
51.00		74.70		26.00		10.80	
55.00		82.20		28.00		15.00	
60.00		88.50		30.00		17.40	
80.00		92.30		35.00		18.70	
100.00		100.00		40.00		36.00	

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