Note: This is the lab for section 01 and H1 of CH 223 only.

- If you are taking section W1 of CH 223, please use this link:
  http://mhchem.org/q/4b.htm

Step One:

Print this lab! You will need a printed (hard copy) version of pages I-4-2 through I-4-125 to complete this lab. If you do not turn in a printed copy of the lab, there will be a 2-point deduction.

Step Two:

Bring the printed copy of the lab with you on Wednesday, April 20. 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 I-4-25!

Step Three:

Complete the lab work and calculations on your own, then turn it in (your lab (page I-4-25 plus the graphs and work page only to avoid a point penalty) at the beginning of recitation to the instructor on Wednesday, April 27. The graded lab will be returned to you the following week during recitation.

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: \[ \text{pH} = - \log \left( \frac{n_{sa}}{V_{sa}} \right) \quad \text{or} \quad \text{pH} = - \log \left( C_{sa} \right) \]

Pre-Equivalence Region: \[ \text{pH} = - \log \left( \frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}} \right) \quad \text{or} \quad \text{pH} = - \log \left( \frac{n_{sa} - n_{sb}}{V_{total}} \right) \]

Equivalence: \[ \text{pH} = 7 \]

Post-Equivalence Region: \[ \text{pH} = 14 + \log \left( \frac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}} \right) \quad \text{or} \quad \text{pH} = 14 + \log \left( \frac{n_{sb} - n_{sa}}{V_{total}} \right) \]

**Strong Base + Strong Acid: (SB + SA)**

Initial Region: \[ \text{pH} = 14 + \log \left( \frac{n_{sb}}{V_{sb}} \right) \quad \text{or} \quad \text{pH} = 14 + \log \left( C_{sb} \right) \]

Pre-Equivalence Region: \[ \text{pH} = 14 + \log \left( \frac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}} \right) \quad \text{or} \quad \text{pH} = 14 + \log \left( \frac{n_{sb} - n_{sa}}{V_{total}} \right) \]

Equivalence: \[ \text{pH} = 7 \]

Post-Equivalence Region: \[ \text{pH} = - \log \left( \frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}} \right) \quad \text{or} \quad \text{pH} = - \log \left( \frac{n_{sa} - n_{sb}}{V_{total}} \right) \]

**Weak Acid + Strong Base: (WA + SB)**

Initial Region: \[ \text{pH} = - \log \sqrt{K_a \cdot \frac{n_{wa}}{V_{wa}}} \quad \text{or} \quad \text{pH} = - \log \sqrt{K_a \cdot C_{wa}} \]

Pre-Equivalence Region: \[ \text{pH} = pK_a + \log \left( \frac{n_{sb}}{n_{wa} - n_{sb}} \right) \]

Half-Equivalence Region: \[ \text{pH} = pK_a \]

Equivalence: \[ \text{pH} = 14 + \log \sqrt{\frac{K_w \cdot n_{wa}}{K_a (V_{wa} + V_{sb})}} \quad \text{or} \quad \text{pH} = 14 + \log \sqrt{K_b \cdot C_{wb}} \]

Post-Equivalence Region: \[ \text{pH} = 14 + \log \left( \frac{n_{sb} - n_{wa}}{V_{sb} + V_{wa}} \right) \quad \text{or} \quad \text{pH} = 14 + \log \left( \frac{n_{sb} - n_{wa}}{V_{total}} \right) \]

Continued on next page
**Weak Base + Strong Acid:** \((WB + SA)\)

**Initial Region:**
\[
\text{pH} = 14 + \log \left( \frac{K_b \cdot n_{wb}}{V_{wb}} \right) \quad \text{or} \quad \text{pH} = 14 + \log \sqrt{K_b \cdot C_{wb}}
\]

**Pre-Equivalence Region:**
\[
\text{pH} = pK_a + \log \left( \frac{n_{wb} - n_{sa}}{n_{sa}} \right)
\]

**Half-Equivalence Region:**
\[
\text{pH} = pK_a
\]

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

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

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**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
  \[pK_a = -\log K_a\]
  \[K_a = 10^{-pK_a}\]

- \(K_b\) = base dissociation constant for a weak base
  \[pK_b = -\log K_b\]
  \[K_b = 10^{-pK_b}\]

- \(K_w = 10^{-14}\) = autoionization constant for water at 25 °C
  Also, \(K_w = [H_3O^+] \cdot [OH^-] = K_a \cdot K_b = 10^{-14}\)

- \(\text{pH} = -\log [H_3O^+]\)
- \(\text{pOH} = -\log [OH^-]\)
- \(14 = \text{pH} + \text{pOH} = pK_a + pK_b\)
Strong Acid + Strong Base Titration - *Overview*

![Graph showing pH vs. volume with three regions: initial (only \( n_{sa} \)), equivalence (\( n_{sa} = n_{sb} \), pH = 7), and post-equivalence (\( n_{sb} > n_{sa} \)).]

\[ \text{Initial:} \quad \text{pH} = - \log \left[ \frac{n_{sa}}{V_{sa}} \right] \]
\[ \text{Pre-equivalence:} \quad \text{pH} = - \log \left( \frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}} \right) \]
\[ \text{Equivalence:} \quad \text{pH} = 7 \text{ (neutral salt + water)} \]
\[ \text{Post-equivalence:} \quad \text{pH} = 14 + \log \left( \frac{n_{sb} - n_{sa}}{V_{sb} + V_{sa}} \right) \]
Strong Base + Strong Acid Titration - Overview

![Graph showing pH vs. volume for titration](image)

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

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

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

**Post-equivalence:** \[ \text{pH} = -\log \left( \frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}} \right) \]
Weak Acid + Strong Base Titration - *Overview*

Initial:  
\[ \text{pH} = -\log\sqrt{K_a C_{wa}} \]

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

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

Post-equivalence:  
\[ \text{pH} = 14 + \log\left(\frac{n_{sb} - n_{wa}}{V_{sb} + V_{wa}}\right) \]
Weak Base + Strong Acid Titration - *Overview*

- **Initial:** $\text{pH} = 14 + \log \sqrt{\frac{K_b C_{wb}}{n_{wb} - n_{sa}}}$
- **Pre-equivalence:** $\text{pH} = \text{pK}_a + \log \left( \frac{n_{wb} - n_{sa}}{n_{sa}} \right)$
- **Equivalence:** $\text{pH} = -\log \left( \frac{K_w}{K_b} \left( \frac{n_{wb}}{V_{wb} + V_{sa}} \right) \right)$
- **Post-equivalence:** $\text{pH} = - \log \left( \frac{n_{sa} - n_{wb}}{V_{sa} + V_{wb}} \right)$
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. \( \text{pH} = - \log [\text{H}_3\text{O}^+] \). 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 \([\text{H}_3\text{O}^+]\); 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 \(\text{H}_3\text{O}^+\) or \(\text{OH}^-\) 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:**

\[
\begin{align*}
V_{sa} &= \text{volume of strong acid initially present} \\
n_{sa} &= \text{moles of strong acid} (= C_{sa} \times V_{sa}) \\
C_{sb} &= \text{concentration of strong base} \\
V_{sb} &= \text{volume of strong base to reach equivalence point} (= n_{sa} \div C_{sb})
\end{align*}
\]

**Analysis Section:**

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

- **Initial Region:** \[ \text{pH} = -\log \left( \frac{n_{sa}}{V_{sa}} \right) \]
  The pH will reflect the strong acid only - no strong base has been added.

- **Pre-Equivalence Region:** \[ \text{pH} = -\log \left( \frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}} \right) \]
  The pH will reflect the remaining acid in solution after some neutralization with strong base. \( n_{sa} > n_{sb} \) in this region.

- **Equivalence:** \[ \text{pH} = 7 \]
  \( n_{sa} = n_{sb} \), so water and a neutral salt will be produced at this point.

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

\[
\begin{align*}
V_{sa} &= 50.0 \text{ mL} = 0.0500 \text{ L} \\
n_{sa} &= 0.200 \text{ M} \times 0.0500 \text{ L} = 0.0100 \text{ mol} \\
C_{sb} &= 0.100 \text{ M} \\
V_{sb} &= 0.0100 \text{ mol} / 0.100 \text{ M} = 100. \text{ mL} \text{ NaOH to the equivalence point}
\end{align*}
\]

**At 0.00 mL:** **Initial point:** \[ \text{pH} = -\log \left( \frac{n_{sa}}{V_{sa}} \right) = -\log (0.0100 \text{ mol}/0.0500 \text{ L}) = 0.70 \]

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 \( n_{sb} = 0.0100 \text{ L} \times 0.100 \text{ M} = 0.00100 \text{ mol} \)

\[ \text{pH} = -\log \left( \frac{0.0100 - 0.00100}{0.0500 + 0.0100} \right) = 0.82 \]

**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, \( n_{sb} = 0.100 \text{ L} \times 0.100 \text{ M} = 0.0100 \text{ mol} = n_{sa} \)

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

\[ \text{HNO}_3 + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{NaNO}_3 \]

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, \( n_{sb} = 0.150 \text{ L} \times 0.100 \text{ M} = 0.0150 \text{ mol} \), which is larger than \( n_{sa} \). This point lies in the post-equivalence region, so:

\[ \text{pH} = 14 + \log \left( \frac{0.0150 - 0.0100}{0.150 + 0.0500} \right) = 12.40 \]

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 (= \( C_{sb} \times V_{sb} \))
- \( C_{sa} \) = 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: \( pH = 14 + \log \left( \frac{n_{sb}}{V_{sb}} \right) \)
  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:
  \[ pOH = - \log \left( \frac{n_{sb}}{V_{sb}} \right) \]
  \[ and \]
  \[ 14 = pH + pOH \]
  Combining these equations and solving for pH gives \( pH = 14 + \log \left( \frac{n_{sb}}{V_{sb}} \right) \).

• 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

\[
\begin{align*}
V_{sb} &= 100. \text{ mL} = 0.100 \text{ L} \\
n_{sb} &= 0.500 \text{ M} \times 0.100 \text{ L} = 0.0500 \text{ mol} \\
C_{sa} &= 1.00 \text{ M} \\
V_{sa} &= 0.0500 \text{ mol} / 1.00 \text{ M} = 0.0500 \text{ L} = 50.0 \text{ mL} \text{ HCl to the equivalence point}
\end{align*}
\]

**At 0.00 mL:** Initial point: \( \text{pH} = 14 + \log \left( \frac{n_{sb}}{V_{sb}} \right) = 14 + \log \left( \frac{0.0500 \text{ mol}}{0.100 \text{ L}} \right) = 13.70 \)

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, \( V_{sa} = 0.0250 \text{ L} \), and \( n_{sa} = 0.0250 \text{ L} \times 1.00 \text{ M} = 0.0250 \text{ mol} \)

\[
\begin{align*}
\text{pH} &= 14 + \log \left( \frac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}} \right) \\
&= 14 + \log \left( \frac{0.0500 - 0.0250}{0.100 + 0.0250} \right) = 13.30
\end{align*}
\]

**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, \( \text{pH} = 7 \)

At 50.0 mL, \( n_{sa} = 0.0500 \text{ L} \times 1.00 \text{ M} = 0.0500 \text{ mol} = n_{sb} \)

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

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

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, \( n_{sa} = 0.0800 \text{ L} \times 1.00 \text{ M} = 0.0800 \text{ mol} \), which is larger than \( n_{sb} \). This point lies in the post-equivalence region, so:

\[
\begin{align*}
\text{pH} &= -\log \left( \frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}} \right) \\
&= -\log \left( \frac{0.0800 - 0.0500}{0.0800 + 0.100} \right) = 0.78
\end{align*}
\]

**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 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,

\[ \text{HCl}(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \]

we would have 100% of the HCl\(_{\text{(aq)}}\) converted to H\(^+\)(aq) and Cl\(^-\)(aq); no HCl would remain in solution. If we had a solution of 1.00 M HC\(_2\)H\(_3\)O\(_2\) in water,

\[ \text{HC}_2\text{H}_3\text{O}_2(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-\text{(aq)} \]

we would have roughly 99% of the HC\(_2\)H\(_3\)O\(_2\) still present in solution; less than 1% of the HC\(_2\)H\(_3\)O\(_2\)(aq) would ionize into H\(^+\)(aq) and C\(_2\)H\(_3\)O\(_2^-\)(aq). Weak acids and weak bases do not ionize completely in solution. Recall that if HC\(_2\)H\(_3\)O\(_2\) is our weak acid, C\(_2\)H\(_3\)O\(_2^-\)(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:

\[ \text{pH} = \text{pK}_a + \log \left( \frac{[\text{Conj. base}]}{[\text{acid}]} \right) \]

where
- pH = pH of system
- pK\(_a\) = -log K\(_a\) = - log (acid dissociation constant for weak acid in buffer)
- [Conj. base] = concentration or moles of base in solution
- [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 pH = pK\(_a\) here. Therefore, we need to add an additional region to our calculations, the half-equivalence region.

Before you begin: Determine the following quantities:
- \( V_{\text{wa}} \) = volume of weak acid initially present
- \( n_{\text{wa}} \) = moles of weak acid (= C\(_{\text{wa}}\) * \( V_{\text{wa}} \))
- K\(_a\) = acid dissociation constant for the weak acid
- pK\(_a\) = - log K\(_a\) (this is a just a unitless number)
- C\(_{\text{sb}}\) = concentration of strong base
- \( V_{\text{sb}} \) = 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:** \( pH = -\log \sqrt{k_a \cdot \frac{n_{wa}}{V_{wa}}} \)

  The pH will reflect the weak acid only - no strong base has been added. Recall that for weak acids,
  \[
  [H_3O^+] = \sqrt{k_a \cdot c_{wa}}
  \]
  and \( c_{wa} = \frac{n_{wa}}{V_{wa}} \), just as \( pH = -\log [H_3O^+] \).

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

  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,
  \[
  HA + NaOH \rightarrow HOH + Na^+ + A^-
  \]
  The species A\(^-\) is the conjugate base of the weak acid HA, and it will react with water to re-form the weak acid:
  \[
  A^- + H_2O \rightleftharpoons HA + OH^-
  \]
  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
  \[
  pH = pK_a + \log \left( \frac{[\text{Conj. base}]}{[\text{acid}]} \right)
  \]
  [Conj. base] and [acid] can be re-written as \( n_{sb} \) and \( (n_{wa} - n_{sb}) \), respectively*, or
  \[
  pH = pK_a + \log \frac{n_{sb}}{n_{wa} - n_{sb}}
  \]

* Why?  OK, here goes: for every mole of conjugate base created, an equal number of moles of strong base must be added, so [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 [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:** \( pH = pK_a \)

  At half-equivalence, \( \frac{1}{2} n_{wa} = n_{sb} \), 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 \( pK_a \)!
\[ \text{Equivalence: } \text{pH} = 14 + \log \sqrt{\frac{K_w \cdot n_{wa}}{K_a \left( V_{wa} + V_{sb} \right)}} \]

At the equivalence point, \( n_{wa} = n_{sb} \), and the only factor affecting \( \text{pH} \) 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 \( \text{pH} \) provides the necessary equation

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

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

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

The \( \text{pH} \) 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 \( \text{pH} \) assuming even a small portion of strong base is present in solution; therefore, it is omitted from the calculation.

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

HC\(_2\)H\(_3\)O\(_2\) is a weak acid, NaOH is a strong base; the equivalence point should be basic

\( V_{wa} = 50.0 \text{ mL} = 0.0500 \text{ L} \)
\( n_{wa} = 0.100 \text{ M} \times 0.0500 \text{ L} = 0.00500 \text{ mol} \)
\( C_{sb} = 0.100 \text{ M} \)
\( V_{sb} = 0.00500 \text{ mol} / 0.100 \text{ M} = 0.0500 \text{ L} = 50.0 \text{ mL NaOH to the equivalence point} \)

The half-equivalence point will be reached at \((50.0 \text{ mL} / 2)\) or \(25.0 \text{ mL NaOH} \)

\( pK_a = - \log K_a = - \log (1.80 \times 10^{-5}) = 4.74 \)

At 0.00 mL: Initial point:

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

The \( \text{pH} \) 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:**

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

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

*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:**  pH = $pK_a = 4.74$

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

At 40.0 mL:  **Pre-equivalence point:**

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

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

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

At 50.0 mL:  **Equivalence point:**

$$\text{pH} = 14 + \log\left[\frac{K_w}{K_a} \cdot \frac{n_{wa}}{V_{wa} + V_{sb}}\right] = 14 + \log\left[\frac{10^{-14}}{1.8 \times 10^{-5}} \cdot \frac{0.00500}{0.0500 + 0.0500}\right] = 8.72$$

*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, $n_{sb} = 0.0600 \text{ L} \times 0.100 \text{ M} = 0.00600 \text{ mol}$, 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:

![Titration Graph](image)

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 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 NH₃ (ammonia, a weak base) in water,

\[ \text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \]

we would have roughly 99% of the ammonia still present in solution; less than 1% of the \( \text{NH}_3(aq) \) would ionize with water into \( \text{NH}_4^+(aq) \) and \( \text{OH}^-(aq) \). Recall that \( \text{NH}_4^+(aq) \) 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 (= \( C_{wb} \times V_{wb} \))
- \( K_b \) = base dissociation constant for the weak base
- \( pK_b = - \log K_b \) (this is a 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:

\[
\text{pH} = pK_a + \log \left( \frac{n_{wb} - n_{sa}}{n_{sa}} \right)
\]

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,

\[
A^- + \text{HCl} \rightarrow \text{HA} + \text{Cl}^-
\]

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

\[
\text{HA} + \text{H}_2\text{O} \rightleftharpoons A^- + \text{H}_3\text{O}^+
\]

The generation of \( \text{H}_3\text{O}^+ \) 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

\[
\text{pH} = pK_a + \log \left( \frac{[\text{Conj. base}]}{[\text{acid}]} \right)
\]

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

\[
\text{pH} = pK_a + \log \left( \frac{n_{wb} - n_{sa}}{n_{sa}} \right)
\]

*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 \([\text{Conj. base}] = (n_{wb} - n_{sa})\).

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:** \( \text{pH} = pK_a \)

At half-equivalence, \( \frac{1}{2} n_{wb} = n_{sa} \), and the log term in the pre-equivalence equation goes to zero (\( \log 1 = 0 \)). Note that you can predict the \( \text{pOH} \) of any weak base system at half-equivalence by calculating the \( pK_b \) or the \( \text{pH} \) via \( pK_a \)! 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 \([H_3O^+]\) for a weak acid:

\[ [H_3O^+] = \sqrt{K_a \cdot C_{wa}} = \sqrt{K_a \cdot \frac{n_{wa}}{V_{wa}}} \]

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 \([H_3O^+]\) to pH provides the necessary equation

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

\( \text{Note} \) 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.

\( \text{Note} \) 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 \( \text{NH}_3 \) (\( K_b = 1.80 \times 10^{-5} \)) with 0.100 M \( \text{HCl} \). Determine the pH after 0.00, 10.0, 25.0, 50.0 and 60.0 mL of \( \text{HCl} \) has been added.

\( \text{NH}_3 \) is a **weak base**, \( \text{HCl} \) is a **strong acid**; the equivalence point should be **acidic**

\( V_{wb} = 100. \text{ mL} = 0.100 \text{ L} \)

\( n_{wb} = 0.0500 \text{ M} \times 0.100 \text{ L} = 0.00500 \text{ mol} \)

\( C_{sa} = 0.100 \text{ M} \)

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

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

\( pK_a = - \log \left( K_w / K_b \right) = - \log \left( 10^{-14} / 1.80 \times 10^{-5} \right) = 9.26 \)

At 0.00 mL:  **Initial point:**

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

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:**

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

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

*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:**  
$$\text{pH} = pK_a = 14 - pK_b = 14 - 4.74 = 9.26$$

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, $n_{sa} = 0.0600 \text{ L} \times 0.100 \text{ M} = 0.00600 \text{ mol}$, 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.
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, pKₐ = 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 (Kₜ = 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.
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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** volume (if appropriate) 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.

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