Acid and Base Titrations - Equation Guide

Strong Acid + Strong Base:

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

Pre-Equivalence Region: $\qquad$ $\mathbf{pH = - log\left(\dfrac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)}$ $\qquad$ *or* $\qquad$ $\mathbf{pH = - log\left(\dfrac{n_{sa} - n_{sb}}{V_{total}}\right)}$

Equivalence: $\qquad$ **pH = 7**

Post-Equivalence Region: $\qquad$ $\mathbf{pH = 14 + log\left(\dfrac{n_{sb} - n_{sa}}{V_{sb} + V_{sa}}\right)}$ $\qquad$ *or* $\qquad$ $\mathbf{pH = 14 + log\left(\dfrac{n_{sb} - n_{sa}}{V_{total}}\right)}$

Strong Base + Strong Acid:

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

Pre-Equivalence Region: $\qquad$ $\mathbf{pH = 14 + log\left(\dfrac{n_{sb} - n_{sa}}{V_{sa} + V_{sb}}\right)}$ $\qquad$ *or* $\qquad$ $\mathbf{pH = 14 + log\left(\dfrac{n_{sb} - n_{sa}}{V_{total}}\right)}$

Equivalence: $\qquad$ **pH = 7**

Post-Equivalence Region: $\qquad$ $\mathbf{pH = - log\left(\dfrac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)}$ $\qquad$ *or* $\qquad$ $\mathbf{pH = - log\left(\dfrac{n_{sa} - n_{sb}}{V_{total}}\right)}$

Weak Acid + Strong Base:

Initial Region: $\qquad$ $\mathbf{pH = - log\sqrt{K_a * \dfrac{n_{wa}}{V_{wa}}}}$ $\qquad$ *or* $\qquad$ $\mathbf{pH = - log\sqrt{K_a * C_{wa}}}$

Pre-Equivalence Region: $\qquad$ $\mathbf{pH = pK_a + log\left(\dfrac{n_{sb}}{n_{wa} - n_{sb}}\right)}$

Half-Equivalence Region: $\qquad$ $\mathbf{pH = pK_a}$

Equivalence: $\qquad$ $\mathbf{pH = 14 + log\sqrt{\dfrac{K_w}{K_a} * \dfrac{n_{wa}}{\left(V_{wa} + V_{sb}\right)}}}$ $\qquad$ *or* $\qquad$ $\mathbf{pH = 14 + log\sqrt{K_b * C_{cb}}}$

Post-Equivalence Region: $\qquad$ $\mathbf{pH = 14 + log\left(\dfrac{n_{sb} - n_{wa}}{V_{sb} + V_{wa}}\right)}$ $\qquad$ *or* $\qquad$ $\mathbf{pH = 14 + log\left(\dfrac{n_{sb} - n_{wa}}{V_{total}}\right)}$

Weak Base + Strong Acid:

Initial Region: $\qquad$ $\mathbf{pH = 14 + log\sqrt{K_b * \dfrac{n_{wb}}{V_{wb}}}}$ $\qquad$ *or* $\qquad$ $\mathbf{pH = 14 + log\sqrt{K_b * C_{wb}}}$

Pre-Equivalence Region: $\qquad$ $\mathbf{pH = 14 - pK_b + log\left(\dfrac{n_{wb} - n_{sa}}{n_{sa}}\right)}$

Half-Equivalence Region: $\qquad$ $\mathbf{pH = 14 - pK_b}$

Equivalence: $\qquad$ $\mathbf{pH = - log\sqrt{\dfrac{K_w}{K_b} * \dfrac{n_{wb}}{\left(V_{wb} + V_{sa}\right)}}}$ $\qquad$ *or* $\qquad$ $\mathbf{pH = - log\sqrt{K_a * C_{ca}}}$

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

Acid and Base Titrations - Guide to Symbols

n_{sa} = moles of strong acid
n_{sb} = moles of strong base
n_{wa} = moles of weak acid
n_{wb} = moles of weak base
n_{ca} = moles of conjugate acid
n_{cb} = moles of conjugate base

V_{sa} = volume of strong acid
V_{sb} = volume of strong base
V_{wa} = volume of weak acid
V_{wb} = volume of weak base
V_{ca} = volume of conjugate acid
V_{cb} = volume of conjugate base

C_{sa} = concentration of strong acid
C_{sb} = concentration of strong base
C_{wa} = concentration of weak acid
C_{wb} = concentration of weak base
C_{ca} = concentration of conjugate acid
C_{cb} = concentration of conjugate base

K_a = acid dissociation constant for a weak acid
$pK_a = - \log K_a$
$K_a = 10^{-pKa}$

K_b = base dissociation constant for a weak base
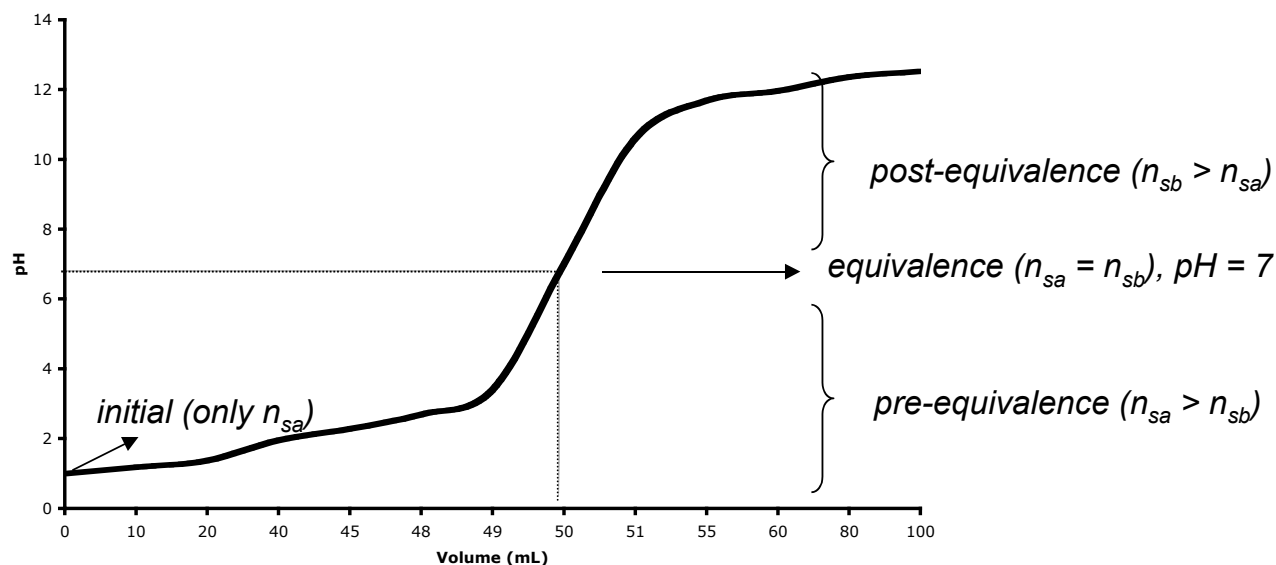$pK_b = - \log K_b$
$K_b = 10^{-pKb}$

$K_w = 10^{-14}$ = autoionization constant for water at 25 ˚C
Also, $K_w = [H_3O^+]*[OH^-] = K_a*K_b = 10^{-14}$

$pH = - \log [H_3O^+]$

$pOH = - \log [OH^-]$

$14 = pH + pOH = pK_a + pK_b$
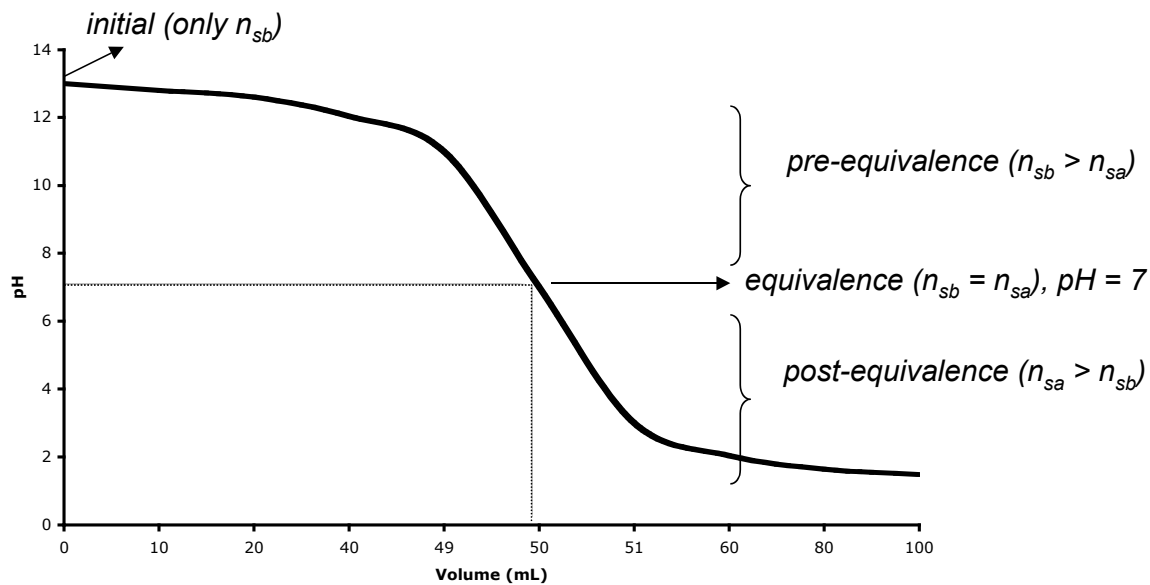
Strong Acid + Strong Base Titration - *Overview*

Initial: $\quad\quad$ pH = - log [H$_3$O$^+$]

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

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

Post-equivalence: pH $= 14 + \log\left(\dfrac{n_{sb} - n_{sa}}{V_{sb} + V_{sa}}\right)$
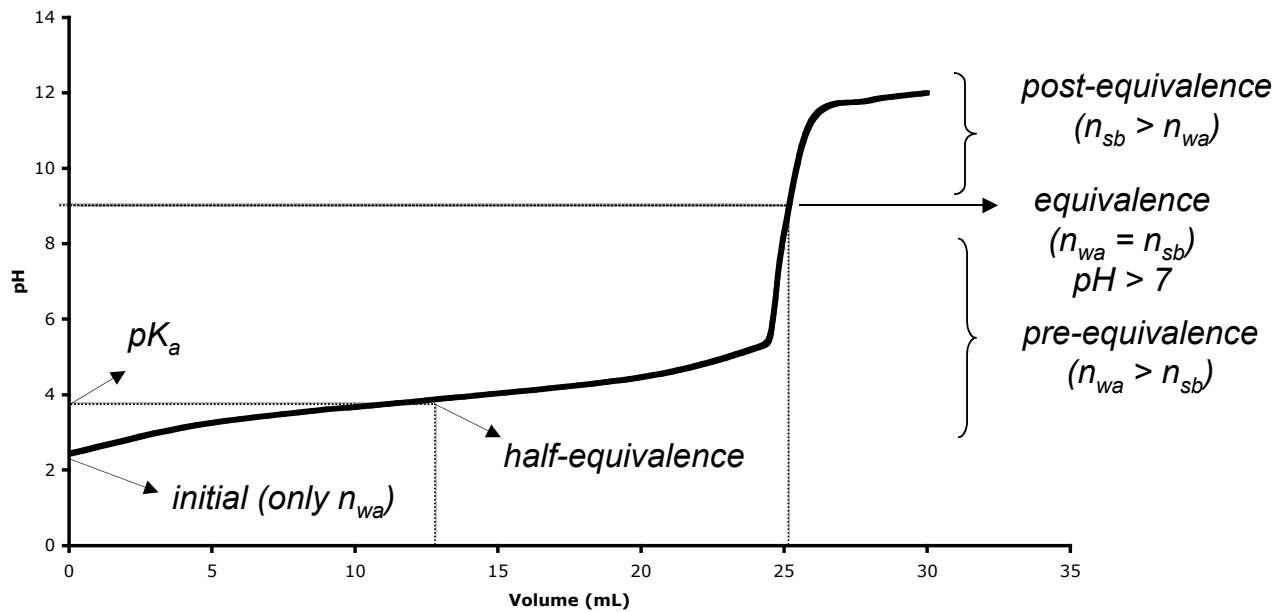
Strong Base + Strong Acid Titration - *Overview*

initial (only n_{sb})

pH axis values: 14, 12, 10, 8, 6, 4, 2, 0

Volume (mL) axis values: 0, 10, 20, 40, 49, 50, 51, 60, 80, 100

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

equivalence ($n_{sb} = n_{sa}$), pH = 7

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

Initial: $pH = 14 + \log[OH^-]$

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

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

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

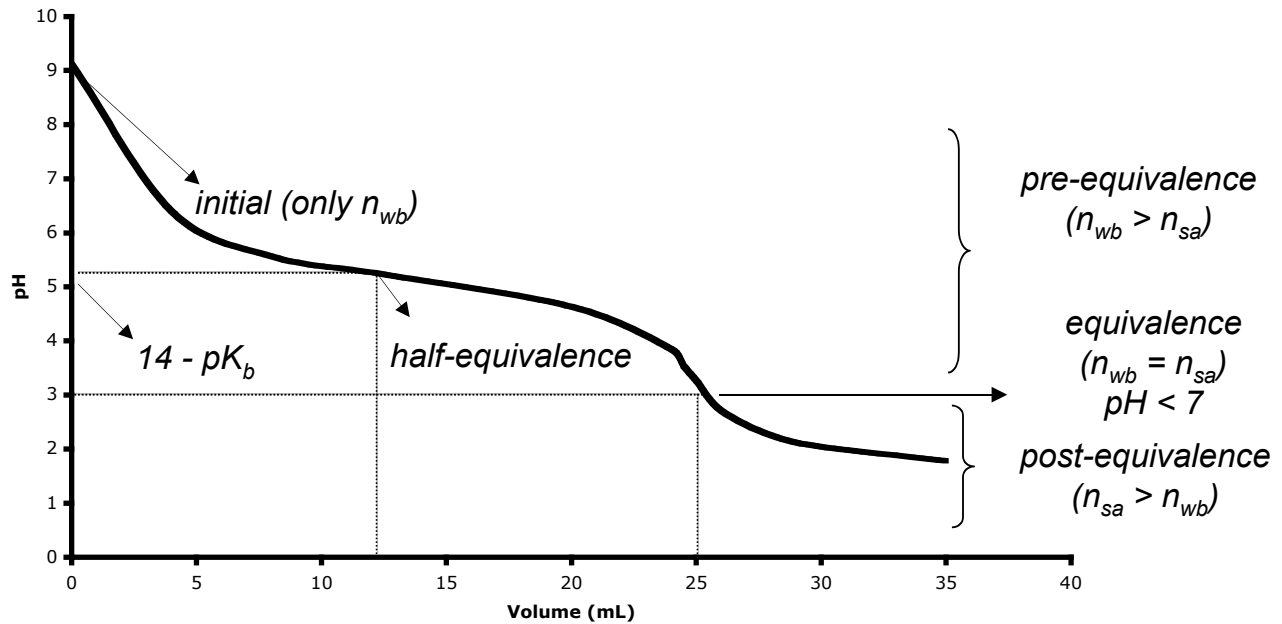# Weak Acid + Strong Base Titration - *Overview*

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

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

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

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

Weak Base + Strong Acid Titration - *Overview*

$$\text{Initial:} \quad pH = 14 + \log\sqrt{K_b C_b}$$

$$\text{Pre-equivalence:} \quad pH = 14 - pK_b + \log\left(\frac{n_{wb} - n_{sa}}{n_{sa}}\right)$$

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

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

CH 223 Guide to Acid and Base Titrations

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 [H$_3$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 [H$_3$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 H$_3$O$^+$ 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**

Note: **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:* $pH = - \log \left(\dfrac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}} \right)$

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

  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 mL = **0.0500 L**
  n_{sa} = 0.200 M * 0.0500 L = **0.0100 mol**
  C_{sb} = **0.100 M**
  V_{sb} = 0.0100 mol / 0.100 M = 0.100 L = **100. mL NaOH to the equivalence point**

At 0.00 mL: Initial point: $pH = - \log (n_{sa} / V_{sa}) = - \log (0.0100 \ mol / 0.0500 \ 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: $pH = -\log\left(\dfrac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)$

At 10.0 mL, $V_{sb} =$ **0.0100 L**, and $n_{sb} = 0.0100\ L * 0.100\ M =$ **0.00100 mol**
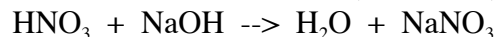
$$pH = -\log\left(\frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right) = -\log\left(\frac{0.0100 - 0.00100}{0.0500 + 0.0100}\right) = \mathbf{0.82}$$

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, $n_{sb} = 0.100\ L * 0.100\ M = 0.0100\ mol = n_{sa}$
Equal molar quantities of acid and base have been added; therefore,
$$HNO_3 + NaOH \longrightarrow H_2O + NaNO_3$$
$NaNO_3$ is a neutral salt, and the pH of water is 7; therefore, the equivalence pH is **7**.

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

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

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

The **titration graph** for a strong acid + strong base would look like this:
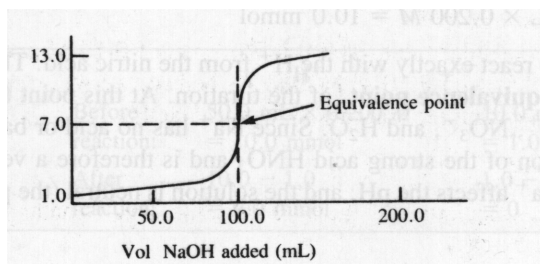
Notice the sharp slope around the equivalence point region - this is indicative of strong acid + strong base titrations. Note that the equivalence point pH is 7.0 - this is also what we would expect for this type of titration. Knowing how to predict the type of titration from a graph can be of considerable 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:* $\mathbf{pH = 14 + log \left(\dfrac{n_{sb} - n_{sa}}{V_{sb} + V_{sa}} \right)}$

  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:* $\mathbf{pH = - log \left(\dfrac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}} \right)}$

  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. mL = **0.100 L**

n_{sb} = 0.500 M * 0.100 L = **0.0500 mol**

C_{sa} = **1.00 M**

V_{sa} = 0.0500 mol / 1.00 M = 0.0500 L = **50.0 mL HCl to the equivalence point**

At 0.00 mL: Initial point: pH = 14 + log (n_{sb} / V_{sb}) = 14 + log (0.0500 mol / 0.100 L) = **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: pH = 14 + log $\left(\dfrac{n_{sb} - n_{sa}}{V_{sb} + V_{sa}} \right)$

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

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

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 L * 1.00 M = 0.0500 mol = n_{sb}

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

$$NaOH + HCl \longrightarrow H_2O + NaCl$$
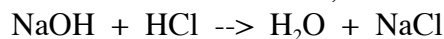
NaCl is a neutral salt, and the pH of water is 7; therefore, the equivalence pH is **7**.

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

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

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

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:
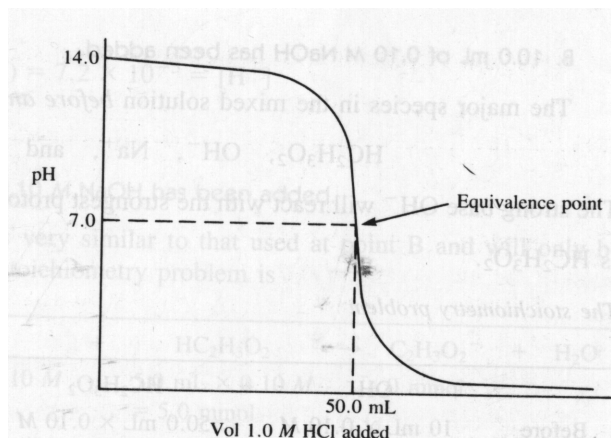

As in section 1, notice the sharp slope around the equivalence point region - this is indicative of strong base + strong acid titrations. Note that the equivalence point pH is 7.0 - this is also what we would expect for this type of titration. At first, the NaOH dominated the titration, and the graph 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 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,

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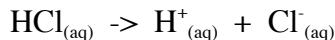
we would have 100% of the $HCl_{(aq)}$ converted to $H^+_{(aq)}$ and $Cl^-_{(aq)}$; no HCl would remain in solution.

If we had a solution of 1.00 M $HC_2H_3O_2$ in water,

$$HC_2H_3O_{2(aq)} \ <=> \ H^+_{(aq)} \ + \ C_2H_3O_2^-{}_{(aq)}$$

we would have roughly 99% of the $HC_2H_3O_2$ still present in solution; less than 1% of the $HC_2H_3O_{2(aq)}$ would ionize into $H^+_{(aq)}$ and $C_2H_3O_2^-{}_{(aq)}$. Weak acids and weak bases do not ionize completely in solution. Recall that if $HC_2H_3O_2$ is our weak acid, $C_2H_3O_2^-{}_{(aq)}$ 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:

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

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. $\frac{1}{2}\, n_{wa} = n_{sb}$), 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_{wa} = volume of weak acid initially present
        n_{wa} = moles of weak acid (= $C_{wa} * V_{wa}$)
        K_a = acid dissociation constant for the weak acid
        pK_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_{wa} / C_{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:* $\mathbf{pH = -\log \sqrt{K_a * \dfrac{n_{wa}}{V_{wa}}}}$

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

    $$[H_3O^+] = \sqrt{K_a * C_{wa}}$$

    and $C_{wa} = n_{wa} / V_{wa}$, just as $pH = -\log [H_3O^+]$.

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

    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,

    $$HA + NaOH \rightarrow HOH + Na^+ + A^-$$
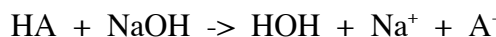
    The species A^- is the *conjugate base* of the weak acid HA, and it will react with water to re-form the weak acid:

    $$A^- + H_2O \Longleftrightarrow HA + OH^-$$
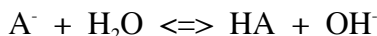
    The generation of OH^- from the conjugate base will affect pH.
    Fortunately, the weak acid / conjugate base system can be treated like a **buffer**; hence, the usefulness of the Henderson-Hasselbalch equation. Recall that the Henderson-Hasselbalch equation is

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

    [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:* $\mathbf{pH = pK_a}$

    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!*

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

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 [OH⁻] for a weak base, use:

$$[OH^-] = \sqrt{K_b * C_{cb}} = \sqrt{K_b * \dfrac{n_{cb}}{V_{cb}}}$$

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 [OH⁻] to pH provides the necessary equation

$$pH = 14 + \log \sqrt{\dfrac{K_w}{K_a} * \dfrac{n_{wa}}{(V_{wa} + V_{sb})}}$$

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:* $\mathbf{pH = 14 + \log \left(\dfrac{n_{sb} - n_{wa}}{V_{sb} + V_{wa}} \right)}$

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 $HC_2H_3O_2$ (K_a = 1.80*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.

$HC_2H_3O_2$ is a *weak acid*, NaOH is a *strong base*; the equivalence point should be *basic*
V_{wa} = 50.0 mL = **0.0500 L**
n_{wa} = 0.100 M * 0.0500 L = **0.00500 mol**
C_{sb} = **0.100 M**
V_{sb} = 0.00500 mol / 0.100 M = 0.0500 L = **50.0 mL NaOH to the equivalence point**
The **half-equivalence point** will be reached at (50.0 mL / 2) or **25.0 mL NaOH**
pK_a = - log K_a = - log (1.80*10⁻⁵) = **4.74**

At 0.00 mL: Initial point:

$$pH = - \log \sqrt{K_a * \dfrac{n_{wa}}{V_{wa}}} = - \log \sqrt{1.8 * 10^{-5} * \dfrac{0.00500}{0.0500}} = \mathbf{2.87}$$

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: <u>Pre-equivalence point:</u>

$$pH = pK_a + \log \frac{n_{sb}}{n_{wa} - n_{sb}} = 4.74 + \log \frac{0.00100}{0.00500 - 0.00100} = \textbf{4.14}$$

At 10.0 mL, $V_{sb} = \textbf{0.0100 L}$, and $n_{sb} = 0.0100 \text{ L} * 0.100 \text{ M} = \textbf{0.00100 mol}$
Note: 10.0 mL < 50.0 mL (equivalence point), so this point is in the pre-equivalence region

At 25.0 mL: <u>Half-equivalence point:</u> $pH = pK_a = \textbf{4.74}$

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

At 40.0 mL: <u>Pre-equivalence point:</u>

$$pH = pK_a + \log \frac{n_{sb}}{n_{wa} - n_{sb}} = 4.74 + \log \frac{0.00400}{0.00500 - 0.00400} = \textbf{5.34}$$

At 40.0 mL, $V_{sb} = \textbf{0.0400 L}$, and $n_{sb} = 0.0400 \text{ L} * 0.100 \text{ M} = \textbf{0.00400 mol}$
Note: 40.0 mL < 50.0 mL (equivalence point), so this point is in the pre-equivalence region

At 50.0 mL: <u>Equivalence point:</u>

$$pH = 14 + \log \sqrt{\frac{K_w}{K_a} * \frac{n_{wa}}{\left(V_{wa} + V_{sb}\right)}} = 14 + \log \sqrt{\frac{10^{-14}}{1.80 * 10^{-5}} * \frac{0.00500}{\left(0.0500 + 0.0500\right)}} = \textbf{8.72}$$

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: <u>Post-equivalence point:</u>

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

At 60.0 mL, $n_{sb} = 0.0600 \text{ L} * 0.100 \text{ M} = \textbf{0.00600 mol}$, 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:
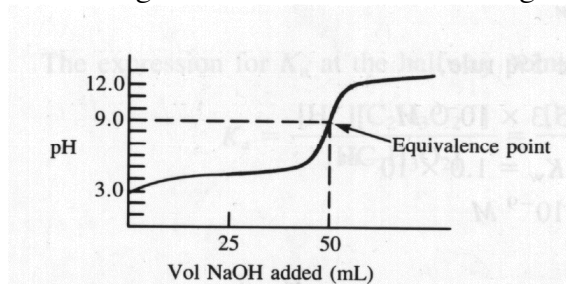
Note that the equivalence point is basic in a weak acid + strong base titration, a result of the conjugate base of the weak acid. Also note how the slope around the equivalence point is not as steep as it was when strong acids and bases were mixed together.

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

$$NH_{3(aq)} \; + \; H_2O_{(l)} \; <=> \; NH_{4}^{+}{}_{(aq)} \; + \; OH^{-}{}_{(aq)}$$
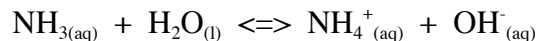
we would have roughly 99% of the ammonia still present in solution; less than 1% of the $NH_{3(aq)}$ would ionize with water into $NH_{4}^{+}{}_{(aq)}$ and $OH^{-}{}_{(aq)}$. Recall that $NH_{4}^{+}{}_{(aq)}$ will be the **conjugate acid** in this system. This lack of complete ionization forces a dependency 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 (= $C_{wb} * V_{wb}$)
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:* $\mathbf{pH = 14 + \log \sqrt{K_b * \dfrac{n_{wb}}{V_{wb}}}}$

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

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

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

    $$pH = 14 + \log \sqrt{K_b * \dfrac{n_{wb}}{V_{wb}}}$$

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

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

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,

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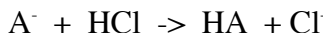
The species HA is the *conjugate acid* of the weak base A^-, and it will react with water to re-form the weak acid:

$$HA + H_2O \Longleftrightarrow A^- + H_3O^+$$
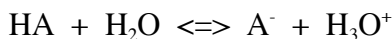
The generation of H_3O^+ from the conjugate acid will affect pH.

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

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

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

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

* *Why?* OK, here goes: for every mole of conjugate acid created, an equal number of moles of strong acid must be added, so [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 [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:* **pH = 14 - pK_b**

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 pK_b!* Converting to pH requires a simple but necessary calculation.

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

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:

$$[H_3O^+] = \sqrt{K_a * C_{ca}} = \sqrt{K_a * \frac{n_{ca}}{V_{ca}}}$$

For every mole of weak base, an equal number of moles of conjugate acid are created; hence, $n_{ca} = n_{wb}$.
The term V_{ca} must take into account the total volume present in solution, hence, $V_{ca} = V_{wb} + V_{sa}$.
K_a can be rewritten as K_w / K_b.
Converting $[H_3O^+]$ to pH provides the necessary equation

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

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

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 ($K_b = 1.80*10^{-5}$) 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*
$V_{wb} = 100.$ mL = **0.100 L**
$n_{wb} = 0.0500$ M * 0.100 L = **0.00500 mol**
$C_{sa} = $ **0.100 M**
$V_{sa} = 0.00500$ mol / 0.100 M = 0.0500 L = **50.0 mL HCl to the equivalence point**
The **half-equivalence point** will be reached at (50.0 mL / 2) or **25.0 mL HCl**
$pK_b = -\log K_b = -\log (1.80*10^{-5}) = $ **4.74**

At 0.00 mL: Initial point:

$$pH = 14 + \log \sqrt{K_b * \frac{n_{wb}}{V_{wb}}} = 14 + \log \sqrt{1.8*10^{-5} * \frac{0.00500}{0.100}} = \textbf{10.98}$$

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:

$$pH = 14 - pK_b + \log\left(\frac{n_{wb} - n_{sa}}{n_{sa}}\right) = 14 - 4.74 + \log\frac{0.00500 - 0.00100}{0.00100} = \textbf{9.86}$$

At 10.0 mL, $V_{sa} = \textbf{0.0100 L}$, and $n_{sa} = 0.0100\ L * 0.100\ M = \textbf{0.00100 mol}$
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: $pH = 14 - pK_b = 14 - 4.74 = \textbf{9.26}$

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

At 50.0 mL: Equivalence point:

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

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.
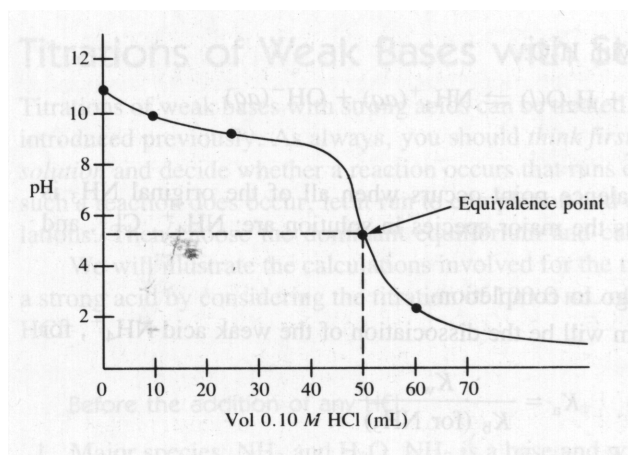*Notice* how the equivalence point pH is acidic as predicted.

At 60.0 mL: Post-equivalence point:

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

At 60.0 mL, $n_{sa} = 0.0600\ L * 0.100\ M = \textbf{0.00600 mol}$, 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.