

Weak Acid/Strong Base Titrations And Weak Base/Strong Acid Titrations

As with all titrations, those that involve the titration of a weak acid with a strong base or a weak base with strong acid have 4 distinct regions. Since the pH of an acid or base solution indicates the concentration of hydronium ion and the acidity of the solution, it is usually calculated or experimentally determined as we add titrant. The ubiquitous use of pH meters these days also makes it important that we learn methods to calculate the pH for the titration of an acid or a base. The volume range for each region is determined by the position of the equivalence point volume, and this quantity should be the first that is determined. You should review these concepts in your textbook: 1) Bronsted-Lowry acids and bases, 2) Lewis Acids and Bases, 3) autoprotolysis of water, and 4) the pH/pOH scale.

The typical titration curve plots the p function of a species (in this case pH) versus volume of titrant added. It is usually sigmoidal in shape. A large change in concentration of the analyte species at the equivalence point causes the p function to abruptly change. It is this change that we detect either by recording the pH versus titrant (derivative to detect the change) or by using a visual indicator. The change in the p function at the equivalence point should be almost instantaneous have an infinite slope. Gradual changes in the p function nearing the equivalence point can still be used, but the uncertainty in the position of the equivalence point volume is increased. This is why we study and calculate titrations curves. In the curve of Figure 1, we can see the effect of the starting concentration of the weak acid on the shape of the curve and the sharpness of the inflection point. The first inflection point is not as clear as the second. Note that the starting pH is different, but that the titration pH values are the same between 25% and 75% titrated due to buffering.

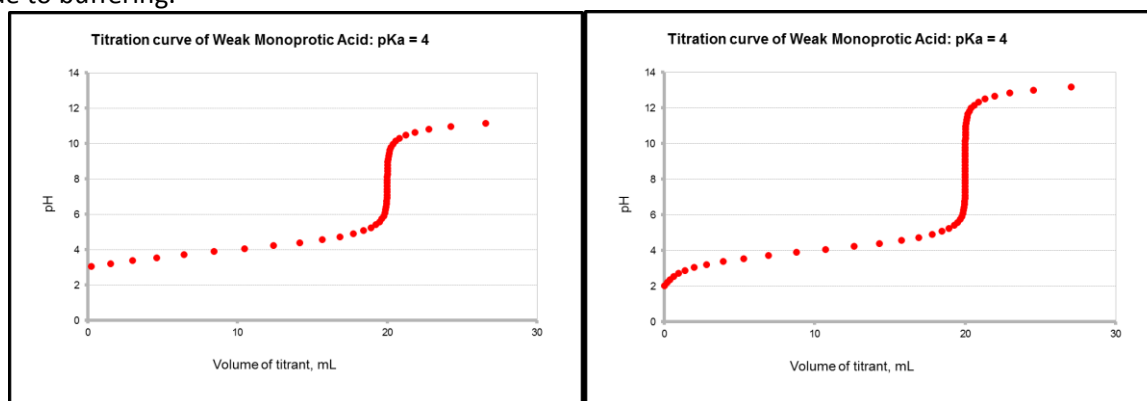
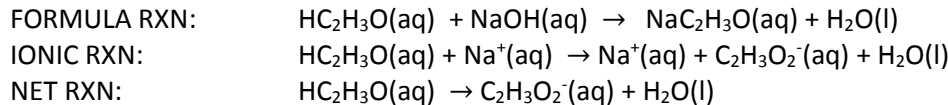


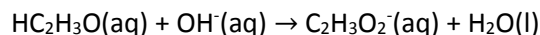
Figure 1: 20.00 mL of an a weak acid solution with a $K_a=1\times 10^{-4}$ is titrated with base in both plots. In the left plot $c_{HA} = 0.0100\text{ F}$ and $c_{NaOH} = 0.0100\text{ F}$ and in the right plot $c_{HA} = 1.00\text{ F}$ and $c_{NaOH} = 1.00\text{ F}$.

To keep it simple, let's consider the titration of 10.00 mL of a 0.100 M acetic acid solution with 0.200 M sodium hydroxide. The formal reaction is:



Let's examine the chemistry in the four regions so we can calculate the pH in each region.

The equivalence point volume can be found from the data given:

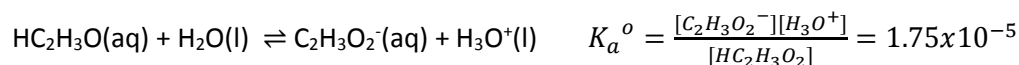


Q1: What is the equivalence point?

Region #1: Initial (0 mL titrant added)

Finding the pH (analyte)

Since titrant has not been added, the initial analyte solution has a known composition with an acetic acid concentration equal to 0.100 M. This is just a solution of the weak acid in water!



The acetic acid is in equilibrium with acetate, and is based on the dissociation of acetic acid.

Q2: Fill in the ICE chart for the 0.100 F acetic acid solution.

	$\text{HC}_2\text{H}_3\text{O}_2 (\text{aq})$	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$	$\text{H}_3\text{O}^+ (\text{aq})$
Initial					
Change					
Equilibrium					

$$K_a^o = \frac{[\text{C}_2\text{H}_3\text{O}_2^-][\text{H}_3\text{O}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.75 \times 10^{-5}$$

Making appropriate substitutions:

Q3: Make appropriate substitutions and solve for the roots.

Solving this specific problem:

$$K_a = 1.75 \times 10^{-5} =$$

$$x^2 + \underline{\hspace{1cm}} x + \underline{\hspace{1cm}} = 0$$

$$\text{Roots: } x = \underline{\hspace{1cm}} \quad x = \underline{\hspace{1cm}}$$

Variable forms of Equations:

$$K_a^o = \frac{x \cdot x}{c_{HA} - x} = 1.75 \times 10^{-5}$$

$$x^2 + K_a^o x - K_a^o \cdot c_{HA} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad a = 1 \quad b = K_a^o \quad c = -K_a^o \cdot c_{HA}$$

Q4: Which root can you eliminate and why?

NOTE: You could assume that $x \ll 0.1000 \text{ M}$. Your answer would be basically correct. This assumption will fail as the acid's formal concentration approaches the K_a^o of the acid. Its best if the ratio of the $\frac{c_{HA}}{K_a^o} \geq 100$. If this is not the case, then do NOT use the assumption. (A good exercise is to prove this to yourself!)

Q5: Prove whether or not the assumption is good here.

Q6: Determine the acetic acid, hydronium and acetate concentrations.

Therefore,

$$[\text{H}_3\text{O}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = \underline{\hspace{2cm}}$$

$$\text{Since } c_{\text{HAc}} = [\text{C}_2\text{H}_3\text{O}_2^-] + [\text{HC}_2\text{H}_3\text{O}]$$

$$[\text{HC}_2\text{H}_3\text{O}] = \underline{\hspace{2cm}}$$

***** You can now plug these back into the K_a^o expression to make sure they are right. *****

Q7: Verify these results by using the K_a expression.

Q8: Calculate the pH and pOH of the solution.

The pH is (ignoring activity)

$$\text{pH} = \underline{\hspace{2cm}}$$

$$\text{pOH} = \underline{\hspace{2cm}}$$

Let's find the percent dissociation and the percentage association in this solution (since the acid is weak):

Percent Dissociation is based on how much of the acid was lost as the ions in the solution. The solution started with a formal concentration of the weak acid. The concentration of hydronium or the conjugate base tells us how much of the acid was lost. When we ratio this to the formal concentration of the acid, we get the percent dissociation.

$$\alpha_{A^-} = \frac{[H_3O^+]}{c_{HA}} \text{ or } \frac{[A^-]}{c_{HA}}$$

The percent association is defined as the amount of undissociated acid left relative to the starting concentration.

$$\alpha_{HA} = \frac{[HA]}{c_{HA}}$$

Note that $\alpha_{A^-} + \alpha_{HA} = 1$ by definition.

Q9: Calculate the percent association and dissociation at this initial point:

$$\alpha_{A^-} = \qquad \qquad \qquad \alpha_{HA} =$$

Q10: What is the percentage dissociation of the acid? _____%

Extension:

If you know the pH of a solution in which a weak monoprotic acid is present, we can derive a relationship **between the pH and the alpha value** presented above. This is a very powerful method because the only assumption that is that the ionic strength is zero. We will show the results of the derivation for simplicity and leave the development to the student.

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

The pH at the initial point is 2.883 and the hydronium ion concentration is 0.00131 M, so $\alpha_{HA} = 0.987$ and $\alpha_{A^-} = 1 - \alpha_{HA} = 0.0130$. These are close to our values!

Q11: Verify these results.

Region #2: Pre-Equivalence (0 < Volume Titrant Added < Equivalent Point Volume)

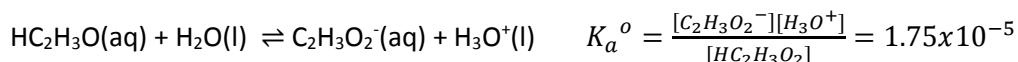
In this region, we have added a volume of titrant which is greater than 0, but less than the equivalence point volume. The titrant will ALWAYS be the limiting reagent in this case, and the analyte concentration will be determined as the difference between what we started out with and what was lost. We use an ICF chart to find the composition of the solution.

Q12: Fill in the ICF chart after the addition of 1.25 mL of hydroxide (titrant) solution:

	$HC_2H_3O_2(aq)$	$OH^-(aq)$	\rightleftharpoons	$C_2H_3O_2^-(aq)$	$H_2O(l)$
Initial					
Change					
Final					

We see that the solution now contains significant concentrations of both the weak acid and its conjugate base. These two will be in equilibrium with each other with the conjugate base acting as 'common ion.' (This is another type of common ion effect problem.) The presence of similar concentrations of both conjugates means the solution is an acid/base buffer. It will resist changes in pH upon the addition of a small amount of acid or base. The number of moles of acid or base you have to add to a buffer to get it to change pH by ± 1 is called the buffer capacity. You will see that buffer capacity is greatest when the pH of the buffer is near the pK_a of the acid that forms the buffer AND when the concentration of the conjugates increases. Class discussion will center on these ideas.

After the addition of the hydroxide ion titrant, the two conjugates come to equilibrium. It is through this equilibrium that we can determine the pH of the solution. The problem's solution begins by examining either the dissociation of the weak acid in water or the weak conjugate base in water. You will arrive at the same pH regardless. Here, we start with the acid dissociation because it involves hydronium ion directly.



Q13: Calculate the starting concentration of acetic acid and acetate in the solution from the ICF chart data.

$$c_{HC_2H_3O_2} = \frac{\text{mmol } HC_2H_3O_2 \text{ left}}{V_{total}} =$$

$$c_{C_2H_3O_2^-} = \frac{\text{mmol } C_2H_3O_2^- \text{ formed}}{V_{total}} =$$

Now that we have done the basic limiting reagent calculation, you also find the concentration of concentration of acid left over by using the following equation:

$$[HA] = \left(\frac{V_e - V_t}{V_e} \right) c_a \left(\frac{V_a}{V_a + V_t} \right)$$

Where V_e is the equivalence point volume, V_t is the volume of titrant you have added *before* the equivalence point, c_a is the original analytical concentration of the acid and V_a is the volume of the acid used. The term $\left(\frac{V_e - V_t}{V_e} \right)$ calculates the percentage of the analyte left and the term $\left(\frac{V_a}{V_a + V_t} \right)$ is the dilution factor. You can also find the amount of conjugate base by changing the first term to reflect the percent that the acid has been titrated:

$$[A^-] = \left(\frac{V_t}{V_e} \right) c_a \left(\frac{V_a}{V_a + V_t} \right)$$

Q14: Use these equations and verify the results you calculated in Q13.

Q15: Now fill in the ICE chart:

	$HC_2H_3O_2(aq)$	$H_2O(l)$	\rightleftharpoons	$C_2H_3O_2^-(aq)$	$H_3O^+(aq)$
Initial					
Change					
Equilibrium					

$$K_a^o = \frac{[C_2H_3O_2^-][H_3O^+]}{[HC_2H_3O_2]} = 1.75 \times 10^{-5}$$

Q16: Substitute and find the roots.

Solving this specific problem:

$$K_a^o = 1.75 \times 10^{-5} =$$

Variable forms of Equations:

$$K_a^o = \frac{(c_{A^-} - x) \cdot x}{c_{HA} - x} = 1.75 \times 10^{-5}$$

$$x^2 - (K_a^o + c_{A^-})x + K_a^o \cdot c_{HA} = 0$$

$$\text{Roots: } x = \underline{\hspace{2cm}} \quad x = \underline{\hspace{2cm}}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad a = 1 \quad b = -(K_a^o + c_{A^-}) \quad c = K_a^o \cdot c_{HA}$$

We would select the first one because the second would give a conjugate base concentration of ~ 0 .

NOTE: You could assume that $x \ll 0.0222 \text{ M}$. Your answer would be basically correct. This assumption will fail as the acid's formal concentration approaches the K_a^o of the acid. Its best if the ratio of the $\frac{c_{HA}}{K_a^o} \geq 100$. If this is not the case, then do NOT use the assumption. (A good exercise is to prove this to yourself!)

This assumption would result in the Henderson-Hassel Bach equation:

$$pH = pK_a + \log \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} =$$

Q17: Verify any assumptions.

Q18: Find the concentration of acetic acid. Acetate ion and hydronium ion.

Therefore,

$$[H_3O^+] = \underline{\hspace{2cm}}$$

$$[C_2H_3O_2^-] = \sim \underline{\hspace{2cm}}$$

$$[HC_2H_3O_2] = \sim \underline{\hspace{2cm}}$$

***** You can now plug these back into the K_a^o expression to make sure they are right. *****

Q19: Find the pH and pOH.

The pH is (ignoring activity)

$$pH = \underline{\hspace{2cm}}$$

$$pOH = \underline{\hspace{2cm}}$$

Let's find the percent dissociation and the percentage association in this solution (since the acid is weak):

We defined these quantities earlier after the initial point in the titration:

Q20: The formal concentration of the acid can be found from the mass balance for acetic acid:

$$c_{HC_2H_3O_2} = [HC_2H_3O_2] + [C_2H_3O_2^-] =$$

Q21: What is the percent dissociation and percent association after the addition of 1.25 mL,

$$\alpha_{A^-} = \frac{[C_2H_3O_2^-]}{c_{HA}} = \quad \quad \quad \alpha_{HA} = \frac{[HC_2H_3O_2]}{c_{HA}} =$$

This tells us that we are 25% titrated (1.25 mL/5.00 mL = 0.25).

Note that the pH here is less than the pK_a of the weak acid being titrated AND that the concentration of the weak acid is greater than the conjugate base. When the pH of a solution containing a weak acid is < its pK_a the acid form, HA, will be the dominate species. The following table summarizes what you will find at volumes that represent 50% titrated to 75% titrated. (You need to do these calculations on your own!)

Volume of Titrant	Percent Titrated	α_{HA}	α_{A^-}	pH	$[HC_2H_3O_2]$	$[C_2H_3O_2^-]$	
1.25	25%	0.75	0.25	4.279	0.0666 M	0.0222 M	pH < pK_a
2.50	50%	0.50	0.50	4.757	0.0400 M	0.0400 M	pH = pK_a
3.75	75%	0.25	0.75	5.234	0.0167 M	0.0500 M	pH > pK_a

What can you conclude about the dominate species as the titration passes through the pre-equivalence or 'buffer' region?

Extension:

Use the pH to find the alpha values at 50% and 75% titrated.

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

You will get similar values as above if you use the calculated hydronium ion concentration and the acid dissociation constant. You can do this on your own.

Q22: Verify these results using the hydronium ion concentration at this point.

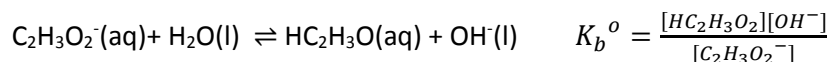
Region #3: Equivalence (Volume Titrant Added = Equivalent Point Volume)

Here we have added a volume of titrant that has reacted with ALL of the analyte in the solution. Both analyte and titrant are limiting in this case. We use an ICF chart to confirm these facts:

Q23: Complete the ICF chart after the addition of 5.00 mL of hydroxide ion solution:

	$HC_2H_3O_2(aq)$	$OH^-(aq)$	\rightleftharpoons	$C_2H_3O_2^-(aq)$	$H_2O(l)$
Initial					
Change					
Final					

After the reaction, all of the acetic acid has been converted into its conjugate base. The dissociation of this base with water is what will drive the pH of the solution. It is therefore incumbent that we look at the dissociation of the weak base in water. Note that the pH should now be BASIC.



The value of the base dissociation constant can be found by realizing that $K_a^o \times K_b^o = K_w^o$. You should prove this to yourself using the equilibrium constant expression for each one. Thus, at 25°C,

$$K_b^o = \frac{K_w^o}{K_a^o} = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.71 \times 10^{-10}$$

This is quite a weak base, and will not dissociate very much. We now proceed to the ICE chart

We first need the concentration of the acetate ion. We know that we started with 1.000 mmole of acetic acid. The addition of the hydroxide has now converted all of the acetic acid into acetate ion.

Q24: Find the concentration of acetate ion in the solution at the equivalence point:

$$c_{C_2H_3O_2^-} = \frac{\text{mmol } C_2H_3O_2^- \text{ formed}}{V_{total}} =$$

Q25: The acetate ion is in equilibrium with acetic acid, and is based on the dissociation of the acetate ion with water acid. Fill in the ICE chart for this solution.

	$C_2H_3O_2^-(aq)$	$H_2O(l)$	\rightleftharpoons	$HC_2H_3O_2(aq)$	$OH^-(aq)$
Initial					
Change					
Equilibrium					

$$K_b^o = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = 5.71 \times 10^{-10}$$

Q26: Make appropriate substitutions and find the roots.

Solving this specific problem:

$$K_b^o = \frac{x \cdot x}{0.0666 - x} = 5.71 \times 10^{-10}$$

Roots: $x = \underline{\hspace{2cm}}$ $x = \underline{\hspace{2cm}}$

Variable forms of Equations:

$$K_b^o = \frac{x \cdot x}{c_{A^-} - x} = 5.71 \times 10^{-10}$$

$$x^2 + K_b^o x - K_b^o \cdot c_{A^-} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad a = 1 \quad b = K_b^o \quad c = -K_b^o \cdot c_{A^-}$$

Q27: Which root is best and why?

NOTE: You could assume that $x \ll 0.0666$ M. Your answer would be correct. This assumption will fail as the bases's formal concentration approaches the K_b^o of the base. It's best if the ratio of the $\frac{c_{A^-}}{K_b^o} \geq 100$. If this is not the case, then do NOT use the assumption. (A good exercise is to prove this to yourself!)

Q28: Verify that any assumptions could be made.

Q29: Find the concentration of all species.

Therefore,

$$[OH^-] = [HC_2H_3O] = \underline{\hspace{2cm}}$$

$$[C_2H_3O_2^-] = \sim \underline{\hspace{2cm}}$$

***** You can now plug these back into the K_b^o expression to make sure they are right. *****

Q30: Find the pH and pOH at this point in the titration.

The pH is (ignoring activity)

$$pOH = \underline{\hspace{2cm}}$$

$$pOH = \underline{\hspace{2cm}}$$

Let's find the percent dissociation and the percentage association in this solution (since the base is weak):

Percent Dissociation is based on how much of the base was lost as hydroxide ion and acetic acid. In the ICE chart we started with all weak base, the concentration of hydroxide ion or the conjugate acid tells us how much was lost. When we ratio this to the formal concentration of the base, we get

$$\alpha_{HA} = \frac{[HA]}{c_{A^-}} \text{ or } \frac{[OH^-]}{c_{A^-}} \quad (\text{note that for the acid we used } \alpha_{A^-} \text{ for percent dissociation})$$

The percent association is defined as the amount of undissociated base left relative to the starting concentration.

$$\alpha_{A^-} = \frac{[A^-]}{c_{A^-}}$$

Note that $\alpha_{A^-} + \alpha_{HA} = 1$ by definition.

Q31: At the equivalence point we can find these values:

$$\alpha_{HA} = \frac{[OH^-]}{c_{A^-}} = \alpha_{A^-} \sim 0.999$$

Q32: So greater than _____% of the acetic acid in the solution is in the form of acetate ion.

Extension:

We can now confirm the alpha values based on pH. You should do that now.

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

Note that the alpha value for the base is basically 1 at this pH, and that the pH is much larger than the pK_a. This reinforced dominate species ideas we have discussed as well as Le Chatlier's principle.

Q33: Confirm these values.

Region #4: Post-Equivalence (Volume Titrant Added > Equivalent Point Volume)

In this region, we have added a volume which is greater than the equivalence point volume (5.00 mL). By definition, the titrant is in excess and the analyte is now the limiting reagent. In this particular titration we have excess hydroxide added to the acetate ion that was present at the equivalence point. Because we have two bases present, the strongest one will control the pH. Why?

The concentration of the excess hydroxide ion will let us find the pH.

Q34: For instance after the addition of 6.00 mL of hydroxide ion solution we have this ICF chart. Fill it in.

	$HC_2H_3O_2$ (aq)	OH^- (aq)	\rightleftharpoons	$C_2H_3O_2^-$ (aq)	H_2O (l)
Initial					
Change					
Final					

After the reaction, we can find the concentration excess hydroxide ion

Q35: We need the concentration of hydroxide ion from the F row of the ICF chart:

$$\frac{\text{mmol } OH^- \text{ left}}{V_{total}} =$$

We can also use this equation to find the concentration of excess titrant: $[OH^-] = \frac{(V_t - V_e)c_t}{V_a + V_t}$ where V_t is the volume of titrant added past the equivalence point, V_e is the equivalence point volume, V_t is the titrant volume and c_t is the concentration of the titrant.

Q36: Find the concentration of hydroxide ion and the pH and pOH.

$[OH^-] =$ _____

The pH is (ignoring activity)

pOH = _____

pH = _____

Add-ons:

Add more points to the pre-equivalence and post-equivalence regions.

Compare the shape of the titration curve when the value of the acid's K_a is changed.

Compare the curves when the starting concentration of the acid is increased.

Q25: Build an EXCEL worksheet where you make a place for the user to enter the volume of acid titrated, the molarity of the acid and the molarity of the base titrant. Keep the stoichiometry 1:1 between the analyte and titrant.

Q37: Use the starting titration data to calculate and label two cells one that calculate the millimoles of acid initially present and another that contains the equivalence point (in mL).

Q38: Create a column called 'Percent Titrated,' and fill it with values from 0 to 120 incremented in steps of 1. You can use the Fill function to do this quickly.

Q39: In the column to the right of the one you just created, use the percent titrated value to calculate the volume of titrant added at that point in mL.

Q30: You have 4 regions, add columns to calculate the concentration of each conjugate present using the equations provided for each region (not the ICF charts).

Q31: You can now calculate the hydronium ion concentration for the initial and pre-equivalence points as well as the equivalence and post equivalence points.

Q32: Plot the data (pH versus volume of titrant).

You can now change the starting variables and see what happens to the curve. You should do this as part of your studies.

Reverse the Titrant and the analyte and recalculate the titration curve.