Chapter 58 ACID-BASE TITRATIONS

We now head into old territory: titrations. We first discussed titrations way back in Chapter 15 and we only covered the stoichiometry aspects at that time. Here are a few points from then.

> ❝ ...Titration is a very old and very common laboratory method of analysis. Many students in their first exposure to chemistry lab end up doing one or more titrations. I won't go into the details of the operation, since it is a laboratory procedure and it is better handled when you can see the actual glassware and the manipulations involved. I'm going to give a general outline, primarily to show some of the terminology and to show how this fits into where we're at right now.
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> A titration is conducted to measure the amount of something in a sample. Let's say you have some compound (let's just call it compound X) in some sample, and you want to know how much of that compound is in there. To do a titration, you add a reactant to the sample which will react with compound X; the added reactant is called a "titrant". This titrant is added as a solution and at a known concentration. You add the titrant solution slowly to your sample until stoichiometric amounts are present. The point at which stoichiometric amounts are present is called the "equivalence point". When you reach this point, you note how much volume of the titrant solution was used. ❞
>
> ❝ The verb is "titrate". It basically means to add something in portions and in a controlled way to react with something else. In a titration, you titrate your sample with your titrant. You continue to add titrant until you reach the equivalence point; a visual clue (called an "indicator") usually tells you when you reach that point. A related term is "end point", which is the same as equivalence point if done ideally. (There's a technical difference, but I'm not doing all those details here.) When you reach equivalence point (or end point), then you're done. This is the point of stoichiometric amounts and this is the point upon which you base your stoichiometry calculations. ❞

In Example 5 in Chapter 15, we did a calculation for the amount of CH_3CO_2H in vinegar using NaOH but the stoichiometry part was all we could do at the time. We are now able to examine titrations in more detail. We will bring pH into the picture and we will also bring in equilibrium aspects which can apply.

By the way, we also did a problem with redox titration in Example 6 back then. Although there are other types of titration reactions which can be done, our sole focus here is the acid-base type.

58.1 More background

As noted in Chapter 15, the full experimental procedure will not be described but we will further the discussion a bit at this time. Here is a repeat and some expansion on the general operation of a titration. The process begins with some sample solution which contains an acid or a base and which can be weak or strong. You titrate the sample by adding a titrant solution; that solution contains a strong base or a strong acid at a known concentration. The reaction itself is a neutralization reaction. There are four common variations to titrations.

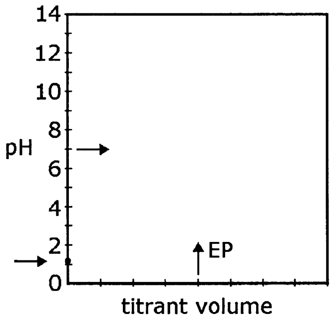
Strong acid-strong base (SA-SB)
Strong base-strong acid (SB-SA)
Weak acid-strong base (WA-SB)
Weak base-strong acid (WB-SA)

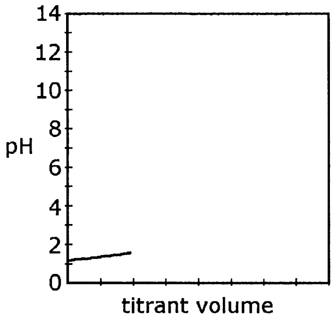
In each of these, the wording is sample-titrant. For example, WA-SB means the titration of a weak acid sample using a strong base as the titrant. During the process of any titration, you add the titrant slowly and in portions. At first, the titrant is the limiting reagent while the sample is in excess. As you continue adding titrant, you will reach a point where the sample and the titrant are in stoichiometric amounts, and that is the equivalence point. You can continue beyond this by adding more titrant, in which case the titrant is now the excess reagent. For purposes of the calculations which we will be doing, it will be important to know, at a given point along the way, which of the sample and titrant are in limiting, in excess or in stoichiometric amounts.

During the titration, there must be something which is monitoring the progress. A pH meter can be used, which is an electronic device which measures the pH directly. The equivalence point can then be determined from the variation in pH with the addition of titrant, as illustrated below. More commonly, an acid-base indicator is used. An acid-base indicator is a dye but not just any dye. The indicator itself is also a weak acid or base and each of its conjugate forms have different colors. The indicator has its own K_a and pK_a. When the pH of the solution is less than the indicator's pK_a, then there is more conjugate acid than conjugate base of the indicator; if the pH is sufficiently less than pK_a, then the color of the conjugate acid dominates. When the pH of the solution is greater than the indicator's pK_a, then there is more conjugate base than conjugate acid; if sufficiently more, then the color of the conjugate base dominates. When the pH of the solution is very close to the indicator's pK_a, then there can be a mix of colors. The color which is observed will also depend on the relative intensities of the separate colors involved. Overall, the general idea is that the color can change with pH. There are many indicators available and there are many different color combinations among those. An indicator is selected which will react with the titrant after the sample does (or at least close to it). Thus, when the indicator turns color, the sample has been neutralized. The end point is the point at which the color change occurs. Now we will technically distinguish equivalence point and end point: the equivalence point is the point at which the titrant has been added in stoichiometric amount with the sample, while the end point is the point at which the titrant has reacted with both the sample and the indicator. Indicators are intensely colored dyes, so they are usually present in only tiny mole amounts relative to the sample. Thus, their amount is considered insignificant, and it is common to assume that the equivalence point and end point are the same. We will follow this assumption, and the abbreviation EP will apply to either equivalence point or end point. Since the concentration of the titrant is known in advance, then its volume at EP gives you the moles of titrant used to react with the sample. This gives you the stoichiometry aspects from Chapter 15, which then leads to the determination of the moles of the acid or base in the sample. In this way, titrations have been used for many years to measure an unknown amount of acid or base in some solution. Besides stoichiometry, there is an added benefit when doing this with a pH meter since this provides a means to measure the value of the K_a of a weak acid or the K_b of a weak base.

Let's take a closer look at the variation in pH which occurs during a titration. You can plot these variations, and those plots are called titration curves. We will consider a general SA-SB titration for illustration. We'll do actual numbers in the next Section; for now, we will just look at the qualitative features of the curves.

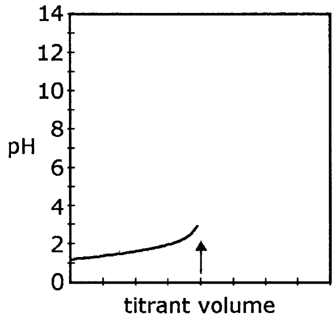
The starting point is the initial sample before adding any of the titrant. For present purposes, our sample begins at pH 1.20 as shown by the outside arrow, low on the vertical axis, in the diagram at right. The EP volume and pH = 7.00 are shown by the inside arrows. ☞

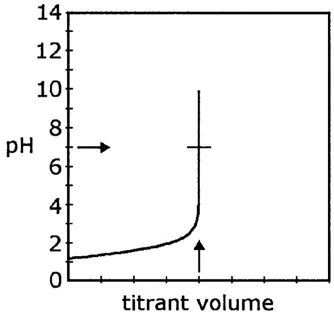




☜ The strong base titrant is now added incrementally. This raises the pH but the increase is only slight at first.

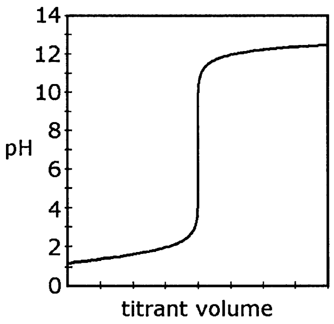
As you approach EP, the pH starts to increase more rapidly. ☞





☜ In the very immediate vicinity before, at and after the EP, the pH skyrockets, flying upward through pH 7.00 and beyond. This is a key feature of a titration: at EP, the pH soars through several pH units, all within an extremely small volume of titrant being added. This added volume could even be as small as a fraction of a drop of the titrant solution. In this time, the indicator does its job: with such a large jump in pH, the conjugate acid color changes abruptly to the conjugate base color. This is the signal which tells the experimentalist that s/he has reached EP. Historically, it is this immensely abrupt jump in pH which gives the abrupt color change and which made titration possible, convenient, and so important.

If you were only measuring the amount of unknown in the sample, then you would stop after the color change. For current purposes, we continue the titration curve past neutralization. In this range, the excess strong base of the titrant continues to raise the pH but the rise levels off considerably. ☞



This is the general pattern for the titration of any acid with a base. The pH rises throughout, and abruptly so at EP. The abruptness will depend on the concentrations and on whether a strong or weak acid is being titrated. It is useful to keep in mind that pH is the negative log of $[H^+]$. If the pH changes abruptly from pH 4 to pH 10, then $[H^+]$ is changing from 10^{-4} M to 10^{-10} M. That change of six pH units is a million-fold decrease in $[H^+]$, and that further emphasizes the enormity of change involved.

So that's the general picture. We will now get into the calculations of pH during a titration. For any titration, there are different approaches to the calculations depending on what part of the titration you are at. A titration can be broken into four Regions.

Region 1. Initial
This is the single, initial condition of the sample before any titrant has been added.

Region 2. PreEP
This is the region in the titration during which some titrant has been added but before EP.

Region 3. EP
This is the single condition of the solution at EP.

Region 4. PostEP
This is the region in the titration after EP.

The calculations to be done here for pH are not new; we've done these same calculations already in the prior four Chapters. We are now simply covering them as different parts of a titration procedure. You can use these calculations to generate the titration curves which are shown above. To generate an entire plot, you need lots of these calculations, so these are best done by computer. Nevertheless, you should be able to do representative samples of the calculations which are involved. Of the four common variations of titrations, we will only cover two: SA-SB and WA-SB. These two will be enough to illustrate the process, although your instructor may add SB-SA and/or WB-SA. Furthermore for our purposes, we limit to monoprotic acid samples and monobasic titrants. There are more parts involved for polyprotic samples and there are more complications in the calculations which require more and more approximations, so I'm just leaving those out. In actuality, there are a few complications for monoprotic WA-SB titrations and those will get brief mention at the very end of the Chapter.

As we go, there will be one thing which you must keep in mind: as you do a titration, the sample volume is increasing because you are adding titrant solution to it. These volume changes are usually considerable. Keep this in mind, since you typically need to know the current volume at each point along the way. Throughout, we assume that the volumes of sample + titrant are directly additive.

58.2 SA-SB

We start with the titration of 25.00 mL of 0.1000 M HNO_3 using 0.1000 M KOH. We will now calculate the pH of the sample solution after the addition of various volumes of titrant. Before we get underway, let's spell out some preliminaries.

Start with a balanced equation.

$$HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$$

The acid and base react in a 1:1 ratio. The products of the neutralization are water and a salt. The salt is a neutral salt and it will have no effect on pH. This is important and it will always be true for any SA-SB titration. Remember this.

You'll need to work with moles. Find your moles of nitric acid in the sample from the given volume and molarity.

$$0.02500 \text{ L} \times 0.1000 \text{ mol } HNO_3/\text{L} = 0.002500 \text{ mol } HNO_3$$

Since nitric acid is strong, that 0.002500 mol HNO_3 is the same as 0.002500 mol H^+ + 0.002500 mol NO_3^-, but only the former has a pH effect.

For the present illustration, we will calculate the EP in advance. This means we calculate the volume of KOH solution which is needed to reach EP and that's a stoichiometry problem.

$$0.02500 \text{ L acid soln} \times \frac{0.1000 \text{ mol HNO}_3}{\text{L acid soln}} \times \frac{\text{mol KOH}}{\text{mol HNO}_3} \times \frac{\text{L base soln}}{0.1000 \text{ mol KOH}} = 0.02500 \text{ L base soln}$$

We need 25.00 mL of the base titrant to hit EP.

OK, that's enough preliminaries. Let's start into the pH calculations from the very beginning and proceed through the four Regions in order.

- Region 1: Initial

This is easy. We are given $[HNO_3]$ = 0.1000 M; since it's a strong acid, then $[H^+]$ = 0.1000 M which gives pH = 1.00. Region 1 is done.

Keep in mind that we only do pH's to a maximum of two decimal places. We have more sigfigs in some of the numbers for these titration examples, but we still limit pH to two decimals.

- Region 2: PreEP

We already calculated EP to be at 25.00 mL. We will illustrate the PreEP Region at three prior volumes: 10.00 mL, 20.00 mL and 24.50 mL.

▸ pH after addition of 10.00 mL titrant

Before EP, the titrant base is the limiting reagent and the sample acid is in excess. All of the added titrant has reacted to neutralize some of the acid, and some acid is left over. We need to know that excess amount.

We started with	0.002500 mol HNO_3 initial
We added 10.00 mL of 0.1000 M KOH	0.001000 mol KOH added
The difference is the moles of excess acid	0.001500 mol HNO_3 excess

The limiting amount of KOH has formed salt; that amounts to 0.001000 mol KNO_3 but that has no pH effect. 0.001500 mol HNO_3 remains in excess, and that will determine the pH. For the pH, you need $[H^+]$. You have the moles H^+; the current volume is 35.00 mL (25.00 mL sample + 10.00 mL titrant).

$$[H^+] = \frac{0.001500 \text{ mol H}^+}{0.03500 \text{ L}} = 0.04286 \text{ M}$$

This gives a pH of 1.37. Thus, after adding 10.00 mL titrant, the pH has increased from 1.00 initially to 1.37.

All calculations before EP follow this setup. The titrant is limiting, the sample is in excess. The $[H^+]$ is determined by the amount of the excess strong acid, and you calculate the pH from that.

▸ pH after addition of 20.00 mL titrant

Same procedure:

We started with	0.002500 mol HNO_3 initial
We added 20.00 mL of 0.1000 M KOH	0.002000 mol KOH added
The difference is the moles of excess acid	0.000500 mol HNO_3 excess

The pH is determined by the amount of H^+ from the excess HNO_3. The total volume at this stage of the game is 45.00 mL. Plug everything in.

$$[H^+] = \frac{0.000500 \text{ mol H}^+}{0.04500 \text{ L}} = 0.0111 \text{ M}$$

This gives a pH of 1.95.

Your turn.

……

Example 1. Determine the pH after addition of 24.50 mL of titrant.

……

We started with ________________ mol HNO_3 initial

We added 24.50 mL of 0.1000 M KOH ________________ mol KOH added

The difference is the moles of excess acid ________________ mol HNO_3 excess

That and the total volume lead to $[H^+]$ from the excess HNO_3.

$$[H^+] = \underline{\hspace{3cm}} = \underline{\hspace{3cm}}$$

This gives a pH of __________.

As you can see by the series of calculations so far, the pH is creeping up, even moreso on this last one. We are just shy of EP right now, and the creep is about to soar.

- Region 3: EP

We know the EP is 25.00 mL of titrant. What's the pH? How would you calculate that? Well, you don't have to. Since acid and base are in stoichiometric amounts, neither is in excess. You have 50.00 mL of salt solution; the salt is KNO_3 which has no pH effect. So what determines the pH now? The only thing giving H^+ right now is autoionization, so the pH is 7.00. That's all there is to this. Note that 7.00 is a large jump in pH relative to the prior values.

- Region 4: PostEP

We will illustrate the calculations in this Region for three different volumes: 25.50 mL, 30.00 mL, and 40.00 mL.

- pH after addition of 25.50 mL titrant

After EP, the titrant base is now the excess reagent and the original acid is limiting. All of the acid in the sample has reacted to form neutral salt, but some base is left over. Now we need to know the excess amount of the base. We'll set this up similar to the way before, but now the base is on top since it's the greater amount.

We added 25.50 mL of 0.1000 M KOH	0.002550 mol KOH added
We started with	0.002500 mol HNO_3 initial
The difference is the moles of excess base	0.000050 mol KOH excess

That amount of strong base will determine the pH. We have an extra step to get to pH this time since we are dealing with OH^- as the excess. First find $[OH^-]$. The current volume is 50.50 mL.

$$[OH^-] = \frac{0.000050 \text{ mol } OH^-}{0.05050 \text{ L}} = 0.00099 \text{ M}$$

That gives pOH = 3.00 and subtracting that from 14.00 gives pH = 11.00. Note the large jump in pH relative to the pH at EP.

- pH after addition of 30.00 mL titrant

Same procedure:

We added 30.00 mL of 0.1000 M KOH	0.003000 mol KOH added
We started with	0.002500 mol HNO_3 initial
The difference is the moles of excess base	0.000500 mol KOH excess

Current volume is 55.00 mL. Those numbers go into finding $[OH^-]$.

$$[OH^-] = \frac{0.000500 \text{ mol } OH^-}{0.05500 \text{ L}} = 0.00909 \text{ M}$$

Now, pOH = 2.04 and pH = 11.96. The pH continues to rise but the rise is leveling off.

Your turn.

Example 2. Calculate the pH after addition of 40.00 mL of titrant.

We added 40.00 mL of 0.1000 M KOH ________________ mol KOH added

We started with ________________ mol HNO_3 initial

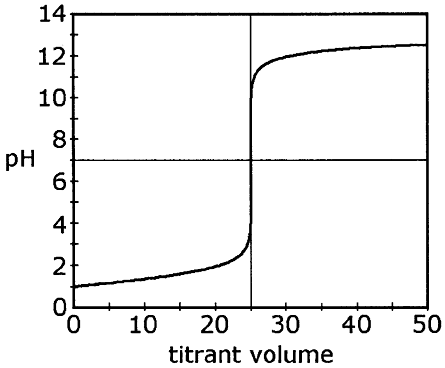
The difference is the moles of excess base ________________ mol KOH excess

Find [OH^-].

$$[OH^-] = \frac{\qquad\qquad}{} = \underline{\qquad\qquad}$$

Then calculate pOH = ___________ and finally pH = ___________. This step gives another increase, albeit small, in the pH.

This completes our series of calculations. The titration curve for the entire titration is shown at right. The crosshairs show the EP. Note again the huge jump, nearly vertical, through the EP. If you were titrating an unknown amount of acid using only a pH meter and no indicator, then that jump in the plot tells you where the equivalence point is.



We now summarize the four Regions and types of calculations for SA-SB cases.

Region 1. Initial
The calculation for pH follows the usual method (Chapter 54) for a strong acid.

Region 2. PreEP
Before EP, the titrant base is the limiting reagent and the sample acid is in excess. The calculation of pH is based entirely on the amount of the excess acid which remains.

Region 3. EP
The acid and base are in stoichiometric amounts. The salt product is neutral and the pH is determined by autoionization, for which pH = 7.00.

Region 4: PostEP
After EP, the titrant base is now the excess reagent and the original acid is limiting. The calculation of pH begins by finding the amount of the excess base which remains. This is then converted to pH.

In the series of calculations just illustrated, we progressed from zero to higher and higher amounts of added titrant, going through the four Regions sequentially. In a preliminary step, we calculated the EP, so we knew what Region we were in at the various times. The sequential approach is a nice approach for setting up multiple calculations for a given titration, but there are variations to the types of problems which can be presented to you. For example, for some general titration problem, you may only be asked for the volume of titrant at EP and the pH at EP. In that case, you must calculate the volume by the usual stoichiometry but the pH will be 7.00. In another problem, you may be asked for one arbitrary point along the way. In that case, you can do this without ever knowing EP. There is a bottom line approach for problems of this general type:

> For any point along the way in an SA-SB titration, find the moles of acid and the moles of base; whoever is in excess will determine the pH. If they are equal, then you are at EP and the pH is 7.00.

Let's do an example following this bottom line approach. We'll change the setup.

A 30.00 mL sample of 0.08621 M perchloric acid is titrated using 0.06381 M sodium hydroxide. Calculate the pH after the addition of 37.64 mL of titrant.

A balanced equation can be useful.

$$HClO_4(aq) + NaOH(aq) \rightarrow NaClO_4(aq) + H_2O(l)$$

The salt is $NaClO_4$ which is a neutral salt. Again, the salt from every SA-SB titration will be neutral.

So what Region are we in for this titration? The numbers are not so obvious as to whether we are before, at or after EP but that won't matter in the end. We first find the moles of acid and the moles of base.

mol $HClO_4$: 0.03000 L × 0.08621 mol $HClO_4$/L = 0.002586 mol $HClO_4$

mol NaOH: 0.03764 L × 0.06381 mol NaOH/L = 0.002402 mol NaOH

Notice that there's more acid than base, so acid is in excess. How much excess?

$$\begin{array}{l} 0.002586 \text{ mol acid} \\ \underline{0.002402 \text{ mol base}\qquad} \\ 0.000184 \text{ mol excess acid} \end{array}$$

The mol of excess acid corresponds to the mol H^+ remaining. That and the current volume give $[H^+]$.

$$[H^+] = \frac{0.000184 \text{ mol } H^+}{0.06764 \text{ L}} = 0.00272 \text{ M}$$

From that, we get pH = 2.57. You're done. By the way, since acid was in excess and titrant was limiting, this is before EP.

Your turn. Same titration of $HClO_4$ with NaOH but using different volumes of titrant.

……

Example 3. Calculate the pH after the addition of 47.81 mL titrant.

……

Get the moles of each.

mol $HClO_4$: ____________ L × ____________ mol $HClO_4$/L = ____________ mol $HClO_4$

mol NaOH: ____________ L × ____________ mol NaOH/L = ____________ mol NaOH

Are they the same or different amounts? If different, which one is the larger amount? How much is the excess amount? What's the total volume? Put it all together and get the pH.

Was this before, at or after EP?

Go again.

……

Example 4. Calculate the pH after the addition of 40.53 mL titrant.

……

Get the moles of each.

mol $HClO_4$: ____________ L × ____________ mol $HClO_4$/L = ____________ mol $HClO_4$

mol NaOH: ____________ L × ____________ mol NaOH/L = ____________ mol NaOH

Now what? What's the pH?

Was this before, at or after EP?

I won't give you the answers separately for these last two Examples, but I'll give you a clue: the two pH's added together come to 18.78.

This ends the SA-SB titrations. We now turn to WA-SB. These are more involved.

58.3 WA-SB

A WA-SB titration has the same four Regions as for SA-SB, but the type of calculation is different within three of them. We'll first set this up sequentially again, illustrating the calculations involved in those Regions. We'll use the same concentrations as for the HNO_3/KOH titration. This new titration will involve a sample of 25.00 mL of 0.1000 M $C_3H_7CO_2H$ titrated with 0.1000 M KOH. $C_3H_7CO_2H$ is called butyric acid or butanoic acid. Despite the use of this compound in our illustration here, I certainly hope you never actually do a titration of butyric acid. It has a very remarkable quality, namely its odor. Have you ever smelled butyric acid? Most people would say no but many people have indeed smelled it. It's one of the principal smell components in vomit. It's one of many products formed during the digestive breakdown of foods. The pure compound has an incredibly bad smell.

We will again start with some preliminaries. First, a balanced equation.

$$C_3H_7CO_2H(aq) + KOH(aq) \rightleftharpoons KC_3H_7CO_2(aq) + H_2O(l)$$

The products of the neutralization are water and a salt. The salt is potassium butyrate, where butyrate is the anion name for $C_3H_7CO_2^-$. Notice that we already have a key difference between WA-SB and SA-SB titrations: the salt product is no longer neutral. In all cases of WA-SB in our coverage, the salt contains a weak base anion. This is important and you need to remember it. It will change the approach in several Regions, as will be seen.

Now, let's get the initial moles of acid in the sample.

$$0.02500\ \text{L} \times 0.1000\ \text{mol}\ C_3H_7CO_2H/\text{L} = 0.002500\ \text{mol}\ C_3H_7CO_2H$$

Finally, we will again find EP before getting underway.

$$0.02500\ \text{L acid soln} \times \frac{0.1000\ \text{mol}\ C_3H_7CO_2H}{\text{L acid soln}} \times \frac{\text{mol KOH}}{\text{mol}\ C_3H_7CO_2H} \times \frac{\text{L base soln}}{0.1000\ \text{mol KOH}}$$

The EP is again at 25.00 mL of titrant.

We now proceed with various pH calculations, using the same titrant volumes as for the HNO_3 examples earlier.

- Region 1: Initial

Before adding any KOH, the sample only contains $C_3H_7CO_2H(aq)$. This is a weak acid dissociation problem of the type covered in Chapter 55. It's yours.

Example 5. Calculate the pH of the starting 0.1000 M $C_3H_7CO_2H$.

Balanced equation:

K_a expression:

Initial [$C_3H_7CO_2H$] is given as 0.1000 M.

Fill in a table:

	[$C_3H_7CO_2H$]	[H^+]	[$C_3H_7CO_2^-$]
Initial:			
Changes:			
Equilibrium:			

Plug into K_a and do what you have to do.

The pH comes to 2.92. Be sure you can get that.

- Region 2: PreEP

We will illustrate the PreEP Region at the same three volumes as before: 10.00 mL, 20.00 mL and 24.50 mL.

▸ pH after addition of 10.00 mL titrant

Before EP, the titrant base is the limiting reagent and the sample acid is in excess. All of the added KOH has reacted to neutralize some of the acid, and some acid is left over. We need to know these amounts.

We started with	0.002500 mol $C_3H_7CO_2H$ initial
We added 10.00 mL of 0.1000 M KOH	0.001000 mol KOH added
The difference is the moles of excess acid	0.001500 mol $C_3H_7CO_2H$ excess

This titration is now different from an SA-SB titration because the salt product contains a basic anion. The amount of the basic anion derives directly from the amount of KOH that was added; thus, the 0.001000 mol of added OH^- has reacted with 0.001000 mol of the initial acid to form 0.001000 mol of $C_3H_7CO_2^-$. Currently the solution contains 0.001000 mol of the weak base $C_3H_7CO_2^-$ and 0.001500 mol of excess weak acid $C_3H_7CO_2H$. Since these are a weak conjugate pair, and since both are present in appreciable amounts, we invoke the No-Change Guideline. As such, this is a job for HH.

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{\text{base}}{\text{acid}}$$

The base and acid amounts can be plugged in directly as moles. You also need $\mathrm{p}K_a = 4.82$.

$$\mathrm{pH} = 4.82 + \log\frac{0.001000}{0.001500} = 4.82 + \log(0.6667) = 4.82 - 0.1761 = 4.64$$

This is all you do. Since you can use moles directly in HH, you don't need to worry about the current volume in these cases.

All WA-SB calculations before EP follow this setup. The titrant is limiting, the sample is in excess. A conjugate pair is present in appreciable amounts, and HH is the way to go.

▸ pH after addition of 20.00 mL titrant

Same procedure.

We started with	0.002500 mol $C_3H_7CO_2H$ initial
We added 20.00 mL of 0.1000 M KOH	0.002000 mol KOH added
The difference is the moles of excess acid	0.000500 mol $C_3H_7CO_2H$ excess

You have 0.002000 mol $C_3H_7CO_2^-$ and 0.000500 mol $C_3H_7CO_2H$. Plug everything into HH.

$$\mathrm{pH} = 4.82 + \log\frac{0.002000}{0.000500} = 4.82 + \log(4.00) = 4.82 + 0.602 = 5.42$$

The pH continues to increase.

Your turn.

……

Example 6. Calculate the pH after addition of 24.50 mL of titrant.

……

We started with	____________ mol $C_3H_7CO_2H$ initial
We added 24.50 mL of 0.1000 M KOH	____________ mol KOH added
The difference is the moles of excess acid	____________ mol $C_3H_7CO_2H$ excess

Plug into HH.

$$\mathrm{pH} = 4.82 + \log\frac{\qquad\qquad}{\qquad\qquad} = \underline{\qquad\qquad}$$

The pH is steadily increasing as to be expected. We are again just shy of EP, and things are about to take off.

- Region 3: EP

EP is 25.00 mL of titrant. What's the pH? How would you calculate that? Well, it's not just autoionization as in the HNO_3 titration. You now have a salt solution of potassium butyrate and the $C_3H_7CO_2^-$ anion is a weak base. You now have to do a base dissociation problem of Chapter 56 type. (See Example 11 in that Chapter.) This one's yours. Notice that you will now need your current volume.

……

Example 7. Calculate the pH at the equivalence point.

……

Balanced equation:

K_b expression:

Find the value of K_b:

Initial moles of $C_3H_7CO_2^-$ (before dissociation):

Current volume:

Initial $[C_3H_7CO_2^-]$:

Table, bottom line:

	$[C_3H_7CO_2^-]$	$[C_3H_7CO_2H]$	$[OH^-]$
Equilibrium:			

Plug into K_b and do what you have to do.

The pH comes to 8.76. Be sure you can get that. Note the large increase in pH relative to the prior calculation.

- Region 4: PostEP

We will illustrate the calculations in this Region for three different volumes as before: 25.50 mL, 30.00 mL, and 40.00 mL.

▸ pH after addition of 25.50 mL titrant

After EP, the titrant base is now the excess reagent and the original acid is limiting. All of the acid in the sample has reacted to form salt, but some KOH is left over. Let's calculate the amount of each. KOH is on top since it's the greater amount.

We added 25.50 mL of 0.1000 M KOH	0.002550 mol KOH added
We started with	0.002500 mol $C_3H_7CO_2H$ initial
The difference is the moles of excess base	0.000050 mol KOH excess

We have a solution of 0.002500 mol of the salt $KC_3H_7CO_2$, which is a weak base, and 0.000050 mol of strong base KOH. Now what do we do? Well, who is dominating the system with respect to OH^-? Is it the strong base or is it some wussy weak base with a piddly K_b of 10^{-10}? Even though there's 50 times more weak base than strong base, the strong base is fully dissociated and the weak base is hardly dissociated at all. The OH^- from KOH pushes the weak base dissociation equilibrium even further to the left. At this point in the titration, you only need to consider the amount of strong base which is in excess. This will be general in our coverage for any WA-SB titration. The calculation is the same type as done for the HNO_3 titration after EP. The current volume is 50.50 mL.

$$[OH^-] = \frac{0.000050 \text{ mol } OH^-}{0.05050 \text{ L}} = 0.00099 \text{ M}$$

You also get the same answer as for the HNO_3 case: pOH = 3.00 and pH = 11.00. Note again the large jump in pH relative to EP.

- pH after addition of 30.00 mL titrant

Same procedure. You only need the excess strong base.

We added 30.00 mL of 0.1000 M KOH	0.003000 mol KOH added
We started with	0.002500 mol $C_3H_7CO_2H$ initial
The difference is the moles of excess base	0.000500 mol KOH excess

Current volume is 55.00 mL. Those numbers go to $[OH^-]$.

$$[OH^-] = \frac{0.000500 \text{ mol } OH^-}{0.05500 \text{ L}} = 0.00909 \text{ M}$$

Now, pOH = 2.04 and pH = 11.96. The pH continues to rise but the rise is leveling off.

Your turn again.

……

Example 8. Calculate the pH after addition of 40.00 mL of titrant.

……

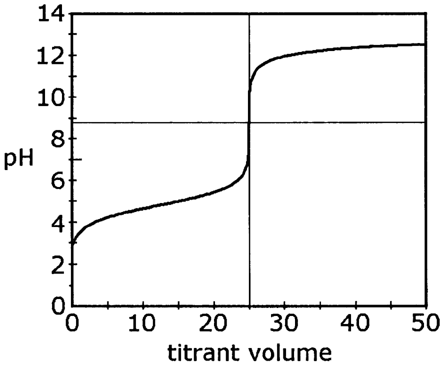
We added 40.00 mL of 0.1000 M KOH	________________ mol KOH added
We started with	________________ mol $C_3H_7CO_2H$ initial
The difference is the moles of excess base	________________ mol KOH excess

Find $[OH^-]$.

$$[OH^-] = \frac{\qquad\qquad}{\qquad\qquad} = \underline{\qquad\qquad}$$

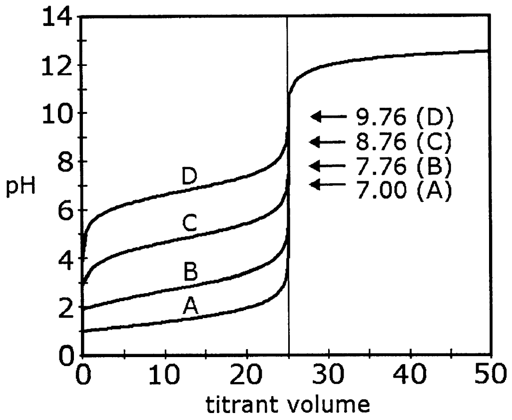
Then find pOH = __________ and finally pH = __________. The result is another increase, albeit small, in the pH.

The titration curve for this entire titration is shown at right. The crosshairs again show the EP. Compared to the prior titration curve for HNO_3, there are three features to note. First, the jump through the EP is less pronounced, although it is still obvious. Second, the pH at EP is now above 7.00 since the salt product is basic. Third, there is an initial kick early in the titration. These are characteristic features of a WA-SB titration, although it depends on how weak is weak. Let's pause on this butyric example for a moment and look more generally at the variations in the titration curves for acids of different strengths.



Consider the overlay plot below of four different titrations, all involving 25.00 mL of 0.1000 M acid sample, titrated with 0.1000 M KOH. Curve A is the prior SA-SB example using nitric acid. Curve C is the butyric acid WA-SB example with $K_a = 1.5 \times 10^{-5}$. Curves B and D are for weak acids with K_a of 1.5×10^{-3} and 1.5×10^{-7}, respectively.

A: Strong B: $K_a = 1.5 \times 10^{-3}$ C: $K_a = 1.5 \times 10^{-5}$ D: $K_a = 1.5 \times 10^{-7}$



The pH at EP is listed for each curve. Here are the notable results of this comparison. In all cases, the results past EP (25.00 mL) are the same because those pH's are determined solely by excess titrant. For EP and before that, however, there are considerable differences in the curves. As the acid gets weaker, the vertical stretch of pH through the EP is less pronounced, the actual pH at EP is higher, and the initial kick at the start of the titration is greater. Since the rise through EP diminishes as the acid is weaker, this becomes more difficult to distinguish for very weak acids, and titration can be problematic in those cases.

By the way, there is an important feature to note for the titration of weak acids in general. When you are at one-half of the volume of EP, then you are at one-half of neutralization. At this point, the amounts of the conjugate pair are equal, so their ratio is one. Plugging this into HH,

$$\text{pH} = \text{p}K_a + \log(1.00) = \text{p}K_a + 0.000 = \text{p}K_a$$

we find that the observed pH is equal to the pK_a. This is one way of measuring values of K_a for weak acids. At 12.50 mL titrant volume in the graph, the pH is equal to the pK_a for curves B, C and D.

Let me make a point about the term "neutralization" here. There is a twist to the meaning with respect to weak acids. While the adjective "neutral" refers to a condition with pH = 7.00, the point of "neutralization" is defined by stoichiometry and not by pH. At neutralization, an acid and base are in stoichiometric amounts, but the pH may not be 7.00. For the neutralization of a strong acid and strong base, the pH is 7.00 but, for the neutralization of a weak acid with a strong base, then the pH will be above 7.00. Be aware of this. Again, the pH at neutralization in the four curves in the graph are 7.00, 7.76, 8.76 and 9.76.

We now end the comparisons and return to our example using butyric acid. Here is a summary for the four Regions and types of calculations for WA-SB cases.

Region 1. Initial
The calculation for pH follows the usual method (Chapter 55) for a weak acid.

Region 2. PreEP
Before EP, the titrant base is the limiting reagent and the sample acid is in excess. Both members of the conjugate pair are present, so the pH is determined using HH. For HH, the amount of conjugate base derives from the amount of added titrant; the amount of conjugate acid is the excess amount.

Region 3. EP
The acid and base are in stoichiometric amounts. The salt product is a weak base, and the pH is determined in the usual manner for base dissociation (Chapter 56).

Region 4. PostEP
After EP, the titrant base is now the excess reagent and the original acid is limiting. The calculation of pH begins by finding the amount of the excess strong base which remains. This is then converted to pH.

The butyric series of calculations again illustrates a sequential progression through a titration, but there will again be variations to the types of problems encountered. For example, if you are asked for the volume of titrant at EP and the pH at EP, then you have a stoichiometry problem and a weak base dissociation problem. If you are asked for some arbitrary point in the titration, then you can follow a bottom line approach:

For any point along the way in a WA-SB titration, find the moles of acid and the moles of base.
If the sample acid is in excess, then do HH.
If the titrant base is in excess, use the excess amount of base only.
If the moles are equal, you're at EP and you need to set up a base dissociation.

Let's do an example following the bottom line approach, using a different set of conditions.

A 20.00 mL sample of 0.05825 M hypochlorous acid is titrated using 0.07228 M sodium hydroxide. Calculate the pH after the addition of 17.67 mL of titrant.

A balanced equation can be useful.

$$\mathrm{HClO}(aq) + \mathrm{NaOH}(aq) \rightleftharpoons \mathrm{NaClO}(aq) + \mathrm{H_2O}(l)$$

The salt is NaClO which is basic. Again, the salt from every WA-SB titration will be basic.

We'll start with calculating the initial moles of acid and the added moles of base.

mol HClO: 0.02000 L × 0.05825 mol HClO/L = 0.001165 mol HClO

mol NaOH: 0.01767 L × 0.07228 mol NaOH/L = 0.001277 mol NaOH

There's more base than acid, so base is in excess and this is after EP. How much excess base is there?

$$\begin{array}{l} 0.001277 \text{ mol base} \\ \underline{0.001165 \text{ mol acid}} \\ \hline 0.000112 \text{ mol excess base} \end{array}$$

Only the amount of excess strong base matters. Find [OH⁻].

$$[\mathrm{OH^-}] = \frac{0.000112 \text{ mol OH}^-}{0.03767 \text{ L}} = 0.00297 \text{ M}$$

From that, we get pOH = 2.53 and then pH = 11.47. You're done.

Your turn. Same titration of HClO with NaOH but different volumes of titrant.

Example 9. Calculate the pH after the addition of 16.12 mL titrant.

Get moles of each.

mol HClO:

mol NaOH:

Now what?

What's the pH?

Was this before, at or after EP?

Go again.

Example 10. Calculate the pH after the addition of 12.06 mL titrant.

Get moles of each.

mol HClO:

mol NaOH:

Now what?

What's the pH?

Was this before, at or after EP?

Again, I won't give you the answers separately for these two Examples, but I'll give the pH's together: the two pH's add to 17.99.

58.4 Summary

I'm going to rewrite the summaries of the four Regions in a different fashion now in order to make this a bit more compact for either SA-SB or WA-SB titrations. This General Summary will follow the bottom line approaches as illustrated previously.

General Summary

- Before adding titrant, the pH of the sample is determined by the usual method for a strong or weak acid.
- Upon adding some titrant, compare the number of moles of initial acid to the number of moles of added base. There are three possibilities.

  If the initial moles of acid exceeds the added moles of base, then this is before EP. Do one of the following.

  SA-SB: Calculate pH directly from the amount of excess acid only.
  WA-SB: Calculate the pH via HH using the moles of added base and the moles of excess acid.

  If the initial moles of acid equals the added moles of base, then this is at EP.

  SA-SB: pH = 7.00.
  WA-SB: Set up a base dissociation problem and calculate pH via OH^-.

  If the amount of base is more than the amount of acid, then this is after EP. You simply calculate pH via OH^- from the excess amount of titrant.

Just keep in mind that, at any point along the way in a titration, you are comparing how much acid and base are present relative to each other.

Let me wrap up titrations at this time with a technical point.

For WA-SB in Region 2, we use HH. As in the case of buffers, our use of HH in titrations follows the No-Change Guideline. Recall the caveats from Section 57.1 regarding that Guideline.

> ❝ Exceptions to this will occur as K_a or K_b gets bigger (> 10^{-3} or so), and/or concentrations get very dilute (< 0.01 M or so), and/or the conjugate ratio itself becomes very large or very small. So, yes, complications can happen. There are more complex equations which are more general but we will not do those. For our purposes, we will follow the "often" outcome. I shall summarize this outcome as the No-Change Guideline.
>
> **No-Change Guideline**
> For a solution which begins with appreciable amounts of both members of a conjugate pair, then the shift to equilibrium will often be small. Assume there are no significant changes to the amounts of the conjugate acid and base which are present.
>
> Subject to the caveats as duly noted, we will use this No-Change Guideline for buffers in the present Chapter and later for titrations in the next Chapter. ❞

Later is now. Complications to HH can arise in WA-SB titrations due to the extremes in the conjugate ratio which can be encountered. The conjugate ratio (base/acid) will be very small in the first mL's of the titration and the ratio will be very large in the final mL's before EP. Those areas can be prone to errors in the calculations, but the extent of those errors will depend on the concentration and on the size of K_a. Although more complex equations do exist, we are not going to worry about this. For typical calculations using weak acids in the 10^{-4} to 10^{-8} K_a range and at 0.05 to 0.1 M or so, the calculations as done here are satisfactory. I did show an example of a weak acid with $K_a = 1.5 \times 10^{-3}$ in the overlay comparison graph; for that graph, I did use the exact equations to plot that curve but that was for illustration purposes. For your purposes, stick to the manner of calculation as done here, and you'll be good to go.

In fact, we are good to go on acids and bases in general. We continue the aqueous emphasis into the next two Chapters but with equilibria of a different sort.

Problems

1. True or false.
   a. During the titration of a strong, monoprotic acid sample with a strong base titrant, the solution is neutral at the equivalence point.
   b. In the titration of HBrO with KOH, the solution is basic at the equivalence point.
   c. Before the equivalence point in a titration, the titrant is in excess.
   d. In an acid-base titration, stoichiometric amounts of the acid and base are present at the equivalence point.
   e. During the titration of an acid sample with a base titrant, the pH jump through the equivalence point will be larger for weaker acids.

2. Consider the titration of 20.00 mL of 0.07319 M HBr with 0.09051 M KOH.
   a. What volume of titrant (in mL) is needed to reach equivalence point?
   b. What is the pH of the original sample?
   c. What is the pH after the addition of 8.61 mL of titrant?
   d. What is the pH at the equivalence point?

3. Consider the titration of 24.00 mL of 0.1062 M HI with 0.07841 M NaOH.
   a. What is the pH after the addition of 16.19 mL of titrant?
   b. What is the pH after the addition of 23.18 mL of titrant?
   c. What is the pH after the addition of 36.32 mL of titrant?

4. Consider the titration of 25.00 mL of 0.08404 M formic acid (HCO_2H) using 0.05070 M KOH.
   a. What volume of titrant (in mL) is needed to reach equivalence point?
   b. What is the pH of the original sample?
   c. What is the pH after the addition of 19.52 mL of titrant?
   d. What is the pH at the equivalence point?

5. Consider the titration of 20.00 mL of 0.07561 M benzoic acid ($C_6H_5CO_2H$) with 0.08204 M NaOH.
   a. What is the pH after the addition of 11.17 mL of titrant?
   b. What is the pH after the addition of 18.43 mL of titrant?
   c. What is the pH after the addition of 22.00 mL of titrant?