

Lecture 12: Modeling the titration experiment—the monoprotic case.

The classic acid-base titration, with its nostalgic use of out-dated oversized glassware, stills finds itself the center of attention in lectures on water chemistry. This lecture will attempt to explain the fondness for the experiment.

First, the word titration. As a general definition, it is the idea that one would compare some unknown amount of material to a standard set of known amounts. That more general idea will never disappear. There will always be unknown amounts of stuff, and there will always be utility in finding out how much unknown you have by comparing it to known amounts of stuff.

In the classic experiment which you watch me do in class, an amount of unknown is dissolved in a known volume, V_1 ,



to produce an unknown concentration, M_1 . To this unknown, a known volume, V_2 , of a known concentration of titrant, M_2 , traditionally from a piece of glassware called a buret which allows for easy measurement of volume.

If there is a relationship between the known and unknown material that can be expressed, for example, a stoichiometric relationship, then it must be true that at some point the amount of the known material will be equal to the amount of the unknown material.

$$\text{moles}_1 = \text{moles}_2$$

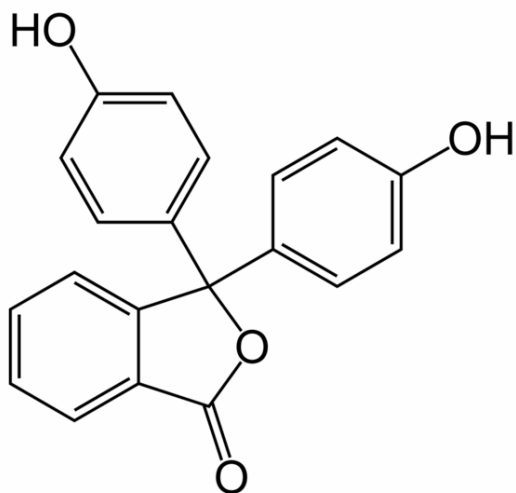
Or expressed as concentrations and volumes,

$$M_1V_1 = M_2V_2$$

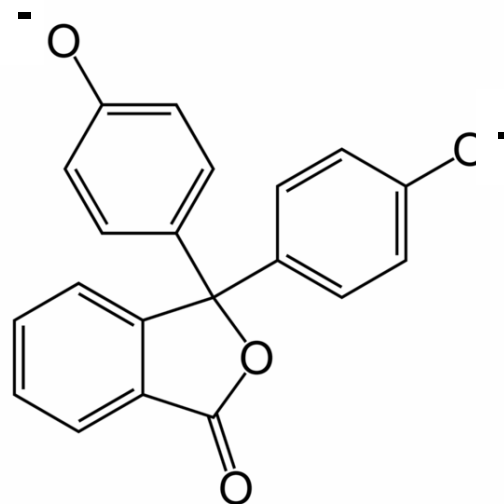
and since we know three of the four values, we can solve for the unknown.

Indicators. Of course the trick is having some indication of when the equality is true. There are many approaches to this. The most common is to use a dye molecule that changes color at different pH. I have shown two examples in class:

Phenolphthalein was the indicator used in the experiment in which two students blew CO₂ into water to acidify the solution. Phenolphthalein turns from clear below pH 8 to pinkish purple above pH 8 as the two protons shown on the OH groups are removed



colorless below pH 8 when protonated



























pinkish purple above pH 8 when deprotonated

Bromthymol Blue was the indicator used in all our titrations including the indicator tee-shirt demo. Bromthymol blue turns from blue in basic solution above pH 7 to yellow in acid solutions below pH 7.

There are many other pH indicators that can be used depending on the specific pH at which a titration changes color—examples of them and their pH region of color change are shown in the table below. We shouldn't be surprised about the variety--

indicators are just acids and their conjugate bases that happen to be colorful. Note that we assume that indicators are present in such small concentrations that we don't correct for them in our calculation on unknown concentrations.

TABLE 11.3 Indicator Color Changes*

Indicator	Color of acid form	pH range of color change	pK_{In}	Color of base form		
thymol blue	red	1.2 to 2.8	1.7	yellow		
methyl orange	red	3.2 to 4.4	3.4	yellow		
bromophenol blue	yellow	3.0 to 4.6	3.9	blue		
bromocresol green	yellow	3.8 to 5.4	4.7	blue		
methyl red	red	4.8 to 6.0	5.0	yellow		
litmus	red	5.0 to 8.0	6.5	blue		
bromothymol blue	yellow	6.0 to 7.6	7.1	blue		
phenol red	yellow	6.6 to 8.0	7.9	red		
thymol blue	yellow	8.0 to 9.6	8.9	blue		
phenolphthalein	colorless	8.2 to 10.0	9.4	pink		
alizarin yellow R	yellow	10.1 to 12.0	11.2	red		
alizarin	red	11.0 to 12.4	11.7	purple		

*The colors of the acid and base forms shown on the right are only a symbolic representation of the actual colors.

Modern America—the pH meter. Only losers like me use indicators any more. After all, there are pH meters that cost close to nothing that can be used to follow the pH over the entire range of a titration. A photo of such a device is shown below. Note that a pH meter takes advantage of electrochemical principles to measure the H^+ concentration. We will learn about this right after spring break. I know you are suddenly considering not staying those extra days and missing my first lecture on electrochemistry now.



Sample calculation to show how a titration works (high school chemistry time.)

Now that we have a way to know when

$$M_1V_1 = M_2V_2$$

We can see how someone might actually learn something from a titration.

Problem: Harold has an unknown acid in solution. He places a 10 ml aliquot of it into a flask along with some bromthymol blue. The solution turns a bright yellow color. Harold carefully titrates the aliquot with 20 ml of 0.5M KOH until suddenly a slightly greenish tinge indicating the color change to blue is observed. What is the concentration of the unknown acid?

$$M_1 = M_2V_2 / V_1 = (20 \text{ ml})(0.5\text{M}) / (10\text{ml}) = 1.0 \text{ M}$$

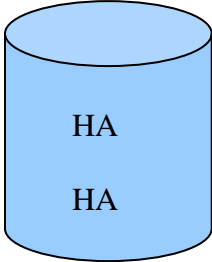
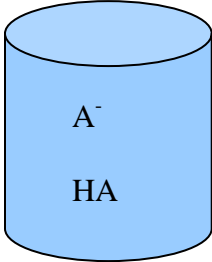
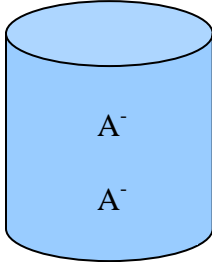
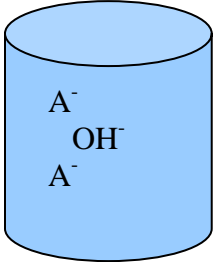
Harold is very pleased, and frankly quite startled that he can do this calculation in his head. What were the chances?

Now in principle this is high school chemistry in action, so it is the last time I do this kind of problem, but I show it to set the table for :

Modeling the Acid Base Titration Curve.

The real reason that titrations are so exciting is that they are a great way to see every kind of acid base calculation play out over the course of a single titration.

Consider the titration of a 2 moles of a weak acid with strong base. Note that as the OH⁻ is added, the post-neutralization result is four distinct regions each defined by a different calculation of pH.

Titrate:	0 moles of OH ⁻ added	1 mole of OH ⁻ added	2 moles of OH ⁻ added	3 moles of OH ⁻ added
				
Type of solution:	Weak acid	buffer	weak base	strong base
Type of calculation:	$H^+ = (K_{a1}C_a)^{0.5}$	$H^+ = K_{a1}C_a / C_b$	$OH^- = (K_w / K_{a3}C_b)^{0.5}$	$OH^- = C_b$

Note that over the course of the titration we cover pretty much every kind of simple acid base reaction there is.

So what does an acid base titration curve look like?

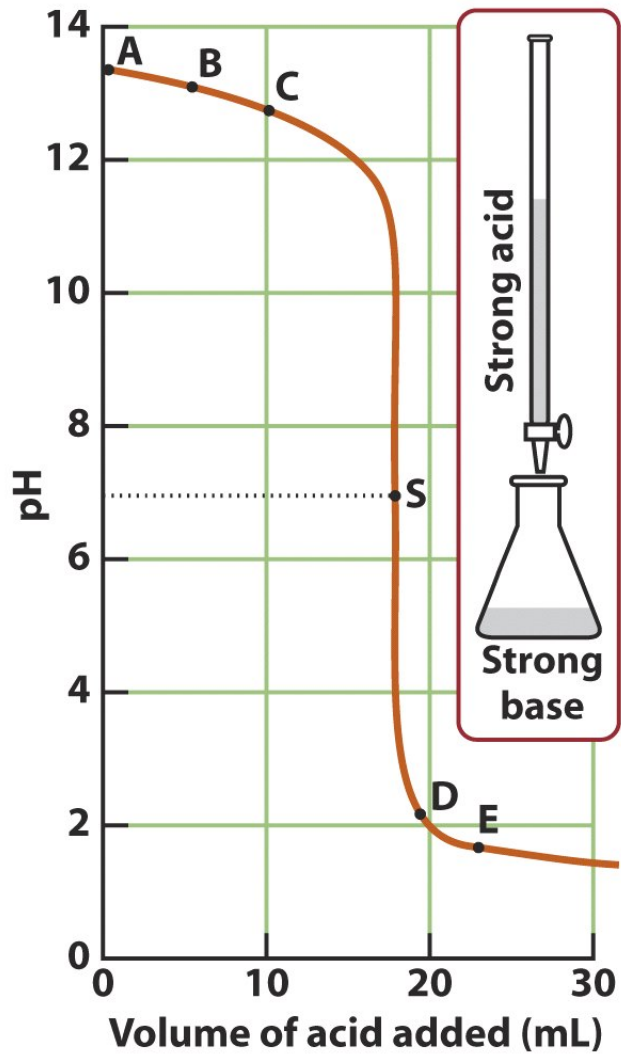
They fall in four general categories for monoprotic acids and bases.

- Strong acids titrated with strong bases (SA/SB)
- Strong bases titrated with strong acids (SB/SA)
- Weak acids titrated with strong bases (WA/SB)
- Weak bases titrated with strong acids (WB/SA)

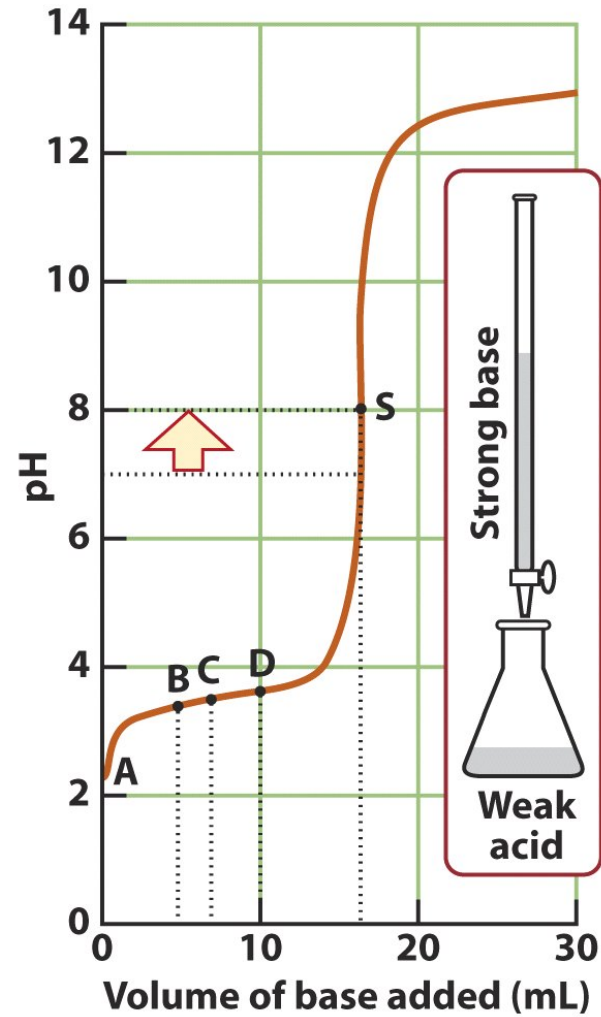
Note that the titrant is always strong and that a neutralization process always occurs. We don't titrate with weak acids and bases because weak acids and bases don't react!!

First we look at the strong versus strong cases:

Strong base titrated with strong acid



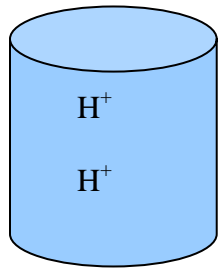
Strong acid titrated with strong base



What do we notice on the curves for strong titrating strong?

- Most importantly, there are only three kinds of solutions

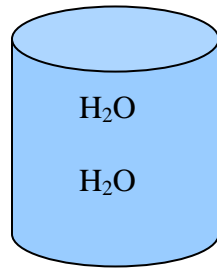
Excess strong acid



$$\text{pH} < 7$$

$$\text{H}^+ = C_a$$

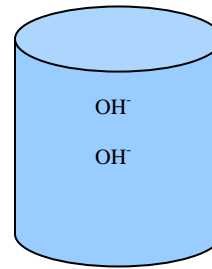
water



$$\text{pH} = 7$$

$$K_w$$

excess strong base



$$\text{pH} > 7$$

$$\text{OH}^- = C_b$$

- The curves are mirror images of each other. The only difference is that when you start with strong base you start at high pH and when you start with strong acid you start at low pH.
- You use the simple neutralization reaction $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$ to determine what is left with which to calculate
- Except under dilute conditions, the pH or pOH is determined by the analytical concentration of C_a or C_b . In the region between pH 6 and 8, where the inflection point occurs, the K_w term is significant and you have a “dilute strong acid or base” case.
- At the equivalence point, the pH must be 7 at 25°C because there is equal H^+ and OH^-

Sample calculation of strong acid with strong base:

50 ml of 0.1 M HCl is titrated with 0, 10, 25 and 50 ml of 0.2 M KOH. What is the pH at each new volume?

Answer: Note that after stripping away the spectators, this is simply a $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$ neutralization. Before the endpoint it will result in a $\text{H}^+ = C_a$ calculation and past pH 7 it will result in a $\text{OH}^- = C_b$ calculation.

- 0 ml added. No neutralization. $C_a = 0.1 \text{ M}$ so $\text{pH} = 1$
- 10 ml added. Neutralization results in .003 moles of H^+ in a volume of $50 + 20 = 70 \text{ ml}$. So $C_a = 0.042 \text{ M}$ and $\text{pH} = 1.4$
- 25 ml added. Neutralization results in .005 moles of H_2O , which when added to 55.4 M water means nothing. $\text{pH} = 7$ at the equivalence point for a strong acid/strong base titration.
- 50 ml added. Neutralization results in .005 moles of excess OH^- in a new volume of 100 ml. So $C_b = 0.05 \text{ M}$, $\text{pOH} = 1.3$ and $\text{pH} = 12.7$.

Modeling the Weak Acid/Strong Base or Weak Base/Strong Acid case.

There are many parallels between the weak acid or base titration and the strong acid or base titration, so it always pays to start by remembering what is the same and what is different.

The same:

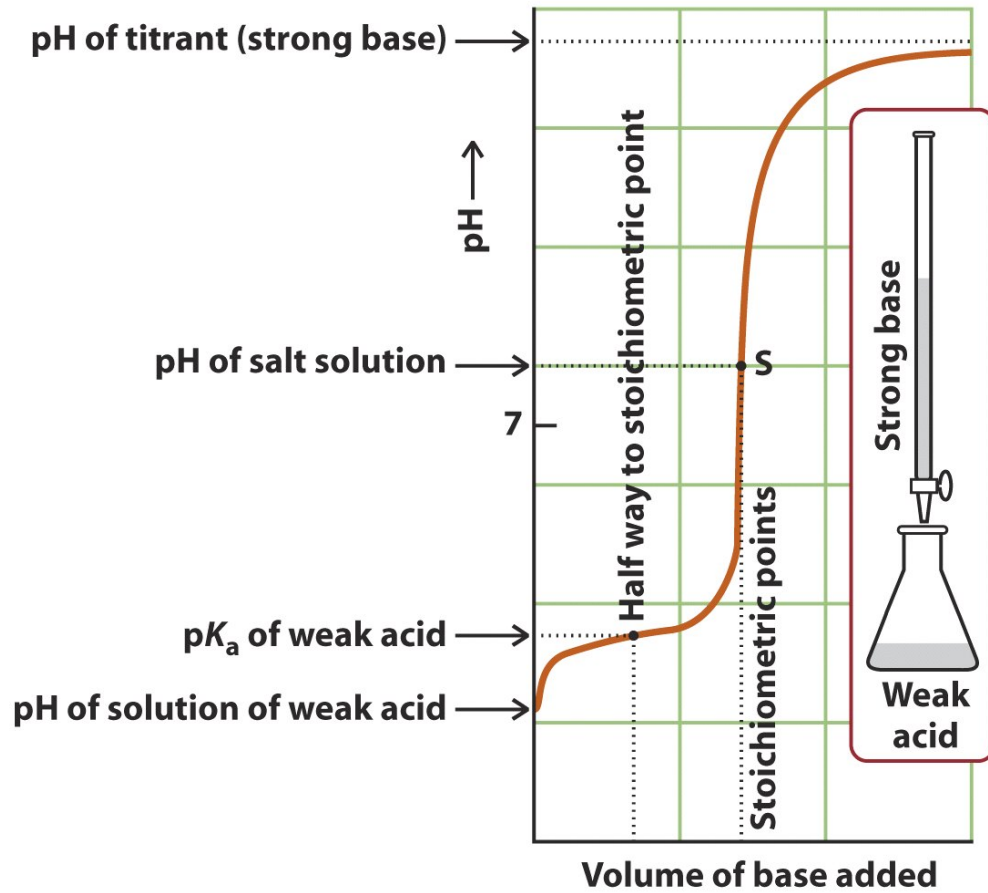
- The general shapes are similar with regions of relative flatness and regions of steep curve around the equivalence point.
- Weak bases and weak acid titrations with the same magnitude K value (like both K_a and K_b values being 10^{-10}) will produce curves that are mirror images turned upside down.

Different:

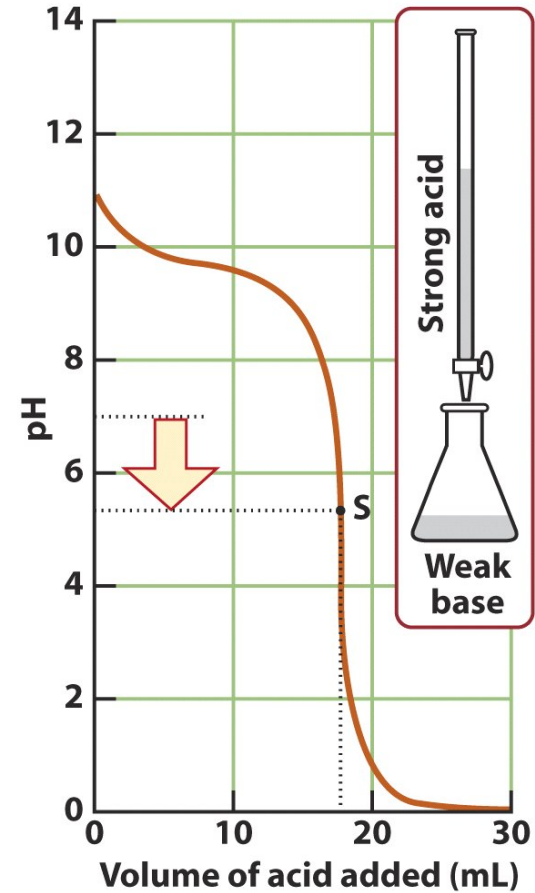
- The equivalence point is not $\text{pH} = 7$ but rather is determined by the pK value of the weak acid or base
- A true buffer region exists before the equivalence point that is centered around where the $\text{pH} = \text{pK}_a$ or the $\text{pOH} = \text{pK}_b$

Now we look at the weak versus strong cases:

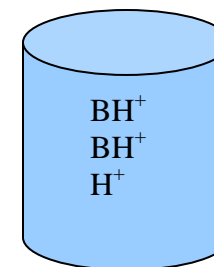
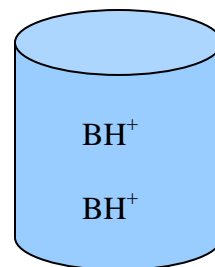
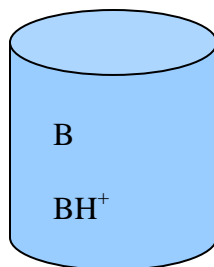
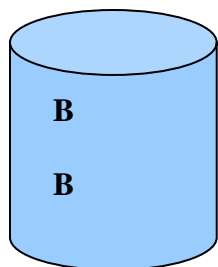
weak acid titrated with strong base



weak base titrated with strong acid



Note that there are four distinct regions in the monoprotic weak acid or base titration. They are shown here for the weak base titration with a strong acid. The beakers for the weak acid with strong base were presented in the introduction.



Type of solution:	Weak base	buffer	weak acid	strong acid excess
Type of calculation:	$\text{OH}^- = (\text{K}_b \text{C}_b)^{0.5}$	$\text{OH}^- = \text{K}_b \text{C}_b / \text{C}_a$	$\text{H}^+ = (\text{K}_w / \text{K}_b \text{C}_a)^{0.5}$	$\text{H}^+ = \text{C}_a$

A few points to reemphasize:

Weak acid titration curves have two very famous regions always asked about on exams:

- the end point where conversion from weak acid to weak base or weak base to weak acid occurs—the pH is NOT 7 at the equivalence point. It is the pH determine for the conjugate acid or base that is generated—**at the equivalence point, titration of a weak base will produce a weak acid with a pH < 7 and titration of a weak acid will produce a weak base with a pH > 7**
- the buffer region of a weak acid or base titration is formed when the first drop of strong acid or base is added and continues until the equivalence point is reached. Half way to the equivalence point, the half of the initial concentration is converted and $\text{C}_a = \text{C}_b$. **So half way to the equivalence point, the $\text{H}^+ = \text{K}_a$ ($\text{pH} = \text{pK}_a$) or the $\text{OH}^- = \text{K}_b$ ($\text{pOH} = \text{pK}_b$)**

Also note that titrations are just neutralization reactions. Follow the six steps for general acid/base calculations and you will get the right answer. Those six steps will always include knowing the neutralization reaction and using it to react the H^+ or OH^- that are added to solution. Examples of this are shown in the table below.

TABLE 11.2 Summary of Weak Acid and Weak Base Titration Equilibria

Point in titration	Primary species	Proton transfer equilibrium	Related Toolbox
1 Weak acid HA titrated with strong base			
initial	HA	$\text{HA}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$	10.1
buffer region	HA, A ⁻	$\text{HA}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$	11.2
stoichiometric point	A ⁻	$\text{A}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HA}(\text{aq}) + \text{OH}^-(\text{aq})$	10.2
<i>(Note: This is a solution of a salt with a basic anion.)</i>			
2a Electrically neutral weak base B titrated with strong acid			
initial	B	$\text{B}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HB}^+(\text{aq}) + \text{OH}^-(\text{aq})$	10.2
buffer region	B, HB ⁺	$\text{B}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HB}^+(\text{aq}) + \text{OH}^-(\text{aq})$	11.2
stoichiometric point	HB ⁺	$\text{HB}^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{B}(\text{aq})$	10.1
<i>(Note: This is a solution of a salt with an acidic anion.)</i>			
2b Weak base anion A⁻ titrated with strong acid			
initial	A ⁻	$\text{A}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HA}(\text{aq}) + \text{OH}^-(\text{aq})$	10.2
buffer region	A ⁻ , HA	$\text{A}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HA}(\text{aq}) + \text{OH}^-(\text{aq})$	11.2
stoichiometric point	HA	$\text{HA}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$	10.1
<i>(Note: This is a solution of a weak acid.)</i>			

Calculations involving weak acid or base titrations.

Honestly, these calculations are all you have been doing in this class since we started. Titration calculations will either result in:

weak acid
 weak base
 buffer
 strong acid
 strong base

calculations. So there really isn't any reason to repeat the examples. The ONLY difference is that the word "titrate" replaces the words "added to" or "mixed with."

Example. 100 ml of 0.1 M acetic acid **is mixed with** 200 ml of 0.1 M NaOH. What is the pH?

Example. 100 ml of 0.1 M acetic acid **is titrated with** 200 ml of 0.1 M NaOH. What is the pH?

These two examples are exactly the same problem. In both cases you apply the eight steps for an acid/base titration to get the result.