

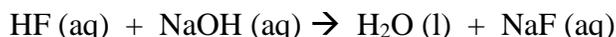
You are encouraged to carefully read the following sections in Tro (2<sup>nd</sup> ed.) to prepare for this experiment: Sec 4.8, pp 158-159 (Acid/Base Titrations), Sec 16.4, pp 729-43 (Titrations and pH Curves).

**Objectives:** You will be able to: (1) determine the hydrogen ion concentration of a weak acid via titration against a strong base, (2) calculate the pH of a weak acid / strong base titration at the endpoint of a titration, (3) evaluate a pH titration curve and determine the pH of a weak acid / strong base titration at the equivalence point, (4) use the molar solubility, as determined from the hydrogen ion concentration, to determine the  $K_{sp}$  of an ionic compound.

**Background:**

**pH:** In an acid-base titration, a solution of unknown concentration is reacted with a **standard** solution of known concentration. The progress of the reaction is monitored using a pH meter or an indicator. When an indicator is used, the titration continues until the indicator changes color to signal the endpoint of the titration. The **endpoint** occurs in the first drops past the equivalence point. The **equivalence point** is the point at which the number of moles of base is stoichiometrically equivalent to the number of moles of acid. Stoichiometric determination of the hydrogen (hydronium) concentration can be used to calculate the initial pH and the pH at the endpoint of the titration.

To see how this data can be used, follow the titration of hydrofluoric acid against sodium hydroxide below.



If 35 mL of HF required 25 mL of 0.250 M NaOH to reach the pink phenolphthalein endpoint, what is the concentration of HF? At this point simply determine the concentration of the HF stoichiometrically.

$$[\text{HF}] = 0.0250 \text{ L NaOH} \times \frac{0.250 \text{ mol NaOH}}{1 \text{ L NaOH}} \times \frac{1 \text{ mol HF}}{1 \text{ mol NaOH}} \times \frac{1}{0.0350 \text{ L HF}} = 0.179 \text{ M}$$

0.179 M HF is equal to the concentration of the weak acid at the start of the titration. To determine the pH at the start of the titration, we will use this information, the  $K_a$  of HF, an ICE table for the dissociation of HF in water, and  $\text{pH} = -\log [\text{H}_3\text{O}^+]$

	HF (aq) + H <sub>2</sub> O (l)	H <sub>3</sub> O <sup>+</sup> (aq) + F <sup>-</sup> (aq)	$K_a = 3.5 \times 10^{-4}$
<b>Initial Conc.</b>	0.179	0	0
<b>Change in Conc.</b>	-x	+x	+x
<b>Equilibrium Conc.</b>	0.179 - x	x	x

$$3.5 \times 10^{-4} = K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)(x)}{0.179-x}$$

Now solve for  $x$  using the quadratic equation and you get  $x = [\text{H}_3\text{O}^+] = 0.00774 \text{ M}$ . Plugging that into the pH equation, you find the initial pH of the solution is 2.11.

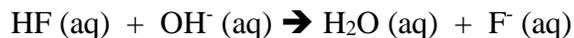
At the equivalence point (endpoint in this experiment since the initial concentration of acid was based off of the endpoint) all of the weak acid will have reacted with the strong base to form the conjugate weak

base as can be seen in the table below. The concentrations of the weak acid and the strong base that react are:

$$[\text{HF}] = (0.179 \text{ M HF})(0.0350 \text{ L}) / (0.0600 \text{ L}) = 0.104 \text{ M HF}$$

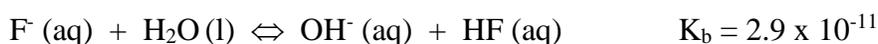
$$[\text{OH}^-] = (0.250 \text{ M OH})(0.0250 \text{ L}) / (0.0600 \text{ L}) = 0.104 \text{ M OH}^-$$

*Note: You must take into account the dilution from the presence of both solutions.*



	HF	OH <sup>-</sup>	F <sup>-</sup>
Before reaction	0.104	0.104	0
reaction changes	-0.104	-0.104	+0.104
After reaction	0	0	0.104

So, the reaction that determines the pH of the solution at the equivalence point is actually the interaction of the product weak base in water. An ICE table can be used to figure out the concentrations of the reactants and products at equilibrium.

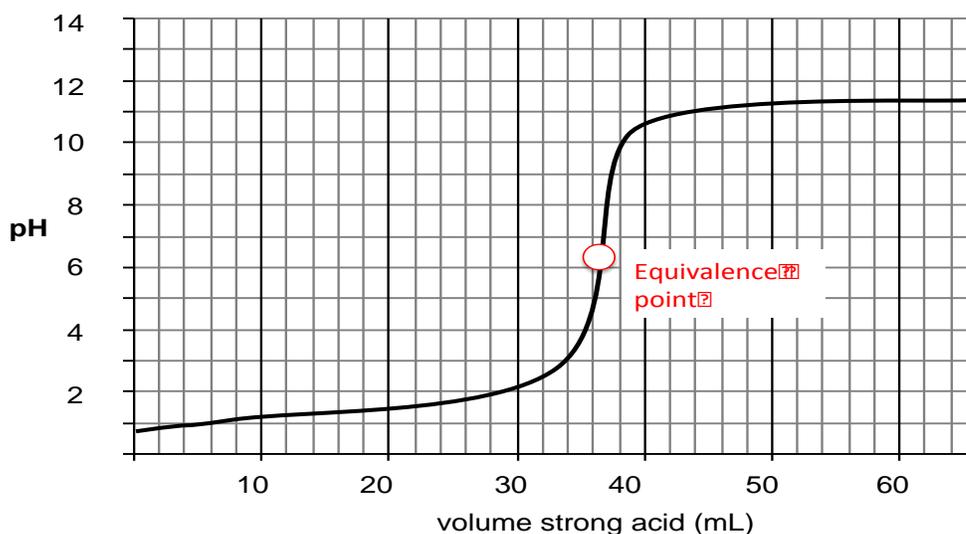


	F <sup>-</sup>	HF	OH <sup>-</sup>
Initial Conc.	0.104	0	0
Change in Conc.	-x	+x	+x
Equilibrium Conc.	0.104-x	x	x

$$2.9 \times 10^{-11} = K_b = \frac{[\text{OH}^-][\text{HF}]}{[\text{F}^-]} = \frac{(x)(x)}{0.104-x}$$

Solve for  $x$  using the quadratic equation and you get  $x = [\text{OH}^-] = 1.7 \times 10^{-6} \text{ M}$ . Plugging that into the equation  $\text{pOH} = -\log [\text{OH}^-]$ , you find the pOH of the solution is 5.77. Finally, using the equation  $14 = \text{pH} + \text{pOH}$ , you find that the  $\text{pH} = 8.23$ .

The second method of following the progress of the reaction is to evaluate the pH throughout the titration. A plot of pH versus titrant results in a **titration curve**. The equivalence point occurs in the middle of the steepest part of the curve, the inflection point of the curve.

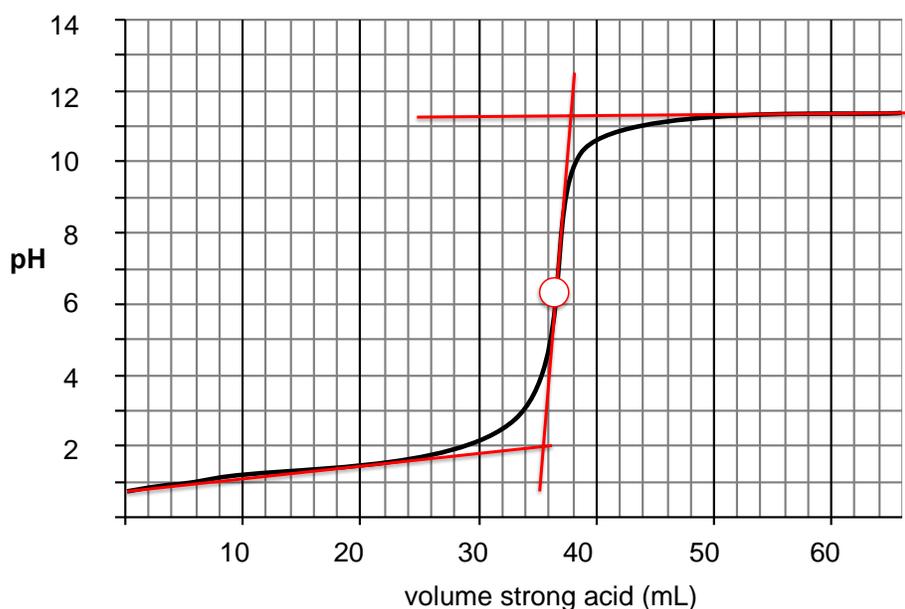


Graph 1: Titration Curve of a Strong Acid with a Strong Base

The titration of a strong acid versus a strong base results in three regions. In the region prior to the equivalence point the pH is determined by the concentration of the excess strong acid. In the region following the equivalence point the concentration of the excess strong base will determine the pH of the solution. The pH at the equivalence point will be 7.00.

The titration of a weak acid versus a strong base differs from that described above in two ways. First the region prior to the equivalence point is due to the pH of a buffer that results from the presence of a weak acid and its conjugate base. Secondly, the region surrounding the equivalence point will be less steep than that for a strong acid/strong base titration and the pH at the equivalence point will be dependent on the concentration of the conjugate base of the original weak acid. The pH at the equivalence point can be determined geometrically from a pH graph using the following steps.

1. Using a ruler, draw lines that follow the flat horizontal parts of the curve (figure below).
2. Draw a line that follows the flat, more vertical part of the curve.
3. Using a ruler, measure the distance between the top intersection and the bottom intersection.
4. The geometric center of this distance is the pH at the equivalence point.



## Titration of a Saturated Potassium Hydrogen Tartrate (KHT) Solution Against Standardized NaOH

### Preparation of the Saturated KHT Solution for Titration

1. Gather:
  - a. 2 125-mL Erlenmeyer flasks (washed and rinsed with and distilled water)
  - b. 1 400-mL Beaker (washed and rinsed with distilled water)
  - c. 1 Funnel (washed and dried)
  - d. 1 25-mL Volumetric Pipet (washed)
  - e. Pipet filling pump
  - f. Stirring Rod (washed and dried)
  - g. 1 piece of Filter Paper
  - h. 1 250-mL Erlenmeyer flask (washed and dried)
2. Mass 2.8 g of KHT
3. Transfer the KHT into a clean 400-ml beaker
4. Add distilled water to the KHT in the beaker until the level reaches the 200 mL mark on the beaker.
5. Stir the solution with a stir rod for approximately 20 min to ensure saturation.
6. Filter your mixture into the 250 mL Erlenmeyer flask. (The filtrate that passes through the filter *must be* clear.)
7. Rinse a 25 mL volumetric flask once with a small portion of your clear filtrate. Draw some into the volumetric pipet to do this.
8. Using the volumetric pipet, transfer 25-ml of the saturated KHT solution into a 125-mL Erlenmeyer Flask and record on the data sheet as Volume of  $\text{HT}^-$  solution to the 0.01 mL.
9. Repeat 1 more time into the additional 125-mL flask and then a final sample into the 250 mL beaker (for use later during the pH titration).
10. Add two drops of phenolphthalein indicator to each of the saturated KHT solutions in the 125-mL Erlenmeyer flasks

### Preparation of the Standard NaOH Solution for Titration

Remember standardized NaOH is valuable and time consuming to make. Take only what you need from the bottle, and be certain the stock bottle is tightly sealed after you use it.

11. Rinse the buret with a small portion (~5 mL) of the NaOH solution, discard this rinse.
12. Fill the buret with NaOH and be certain no air bubbles exist in the tip of the buret. These will be blown out when the buret is full and the stopcock is opened. Discard this small bit of solution.

### Preparation of the pH meter.

Be careful never to touch the pH-sensitive circuit of the pH meter with anything but water, aqueous solutions or

13. Rinse the sensor of the pH meter with distilled water and blot it dry with a Kimwipe.
14. Add pH 7 standard to the sensor.
15. Press the calibrate button with the cap off the pH meter.
16. Wait until the pH meter stops blinking and reads 7.00. (If this doesn't happen see your instructor.)
17. Rinse the sensor with distilled water and dry with a Kimwipe.

## Titration

18. Record the indicated molarity of the standardized NaOH solution from the bottle ( $\approx 0.05$  M) onto your data sheet.
19. Record the initial buret reading on your Data sheet to the nearest 0.01 ml.
20. Titrate the solution with the standardized NaOH solution until the light pink end point persists for at least 30 s.
21. Record the final buret reading on your data sheet to the nearest 0.01 ml.
22. Using a plastic dropper, cover the pH sensor of the pH meter with a drop of your final solution.
23. Record the pH in the top portion of your data sheet
24. Rinse the pH sensor with distilled water and dry with a Kimwipe
25. Refill your buret with additional NaOH
26. Repeat these steps the second sample.

## **pH Curve for the Titration of Saturated Potassium Hydrogen Tartrate (KHT) Solution Against Standardized NaOH**

### pH Curve Titration

27. You will use the third 25 mL sample in the 250 mL beaker for this titration.
28. Measure the initial pH of the saturated solution by placing the sensor down into the solution. Record the pH on your data sheet for 0 mL of added base.  
NOTE: Be certain to prevent the beaker from tipping over. Hold the sensor always; never stand it alone in the beaker.
29. Rinse the sensor with distilled water and dry with a Kimwipe.
30. Add 1 mL NaOH to the beaker mixture. Swirl the contents to ensure complete reaction.
31. Again measure the pH of this new mixture by setting the sensor back into the reaction mixture.
32. Record the pH and total volume of NaOH added on your data sheet.
33. Repeat the steps of adding NaOH and measuring the pH until you have added 20 mL of NaOH to your KHT solution.



# Results and Conclusions

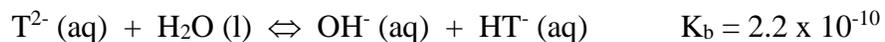
## Titration:

1. Calculate the molarity of  $\text{HT}^-$  from your two best runs.
  - a. Run 1
  
  
  
  
  
  
  
  
  
  
  - b. Run 2
  
2. Calculate the average molarity of  $\text{HT}^-$  from your two best runs.
  
3. The average molarity of  $\text{HT}^-$  equals the acid's initial concentration. Determine the pH of the solution prior to the titration if the  $K_a = 4.6 \times 10^{-5}$  for  $\text{HT}^-$ .



4. Calculate the concentration of tartrate ( $\text{T}^{2-}$ ) at the endpoint using your ICE chart information from question 3.

5. Calculate the pH of the solution at the endpoint.



6. Compare the pH of the endpoint recorded in your data sheet to that calculated in question 5.?

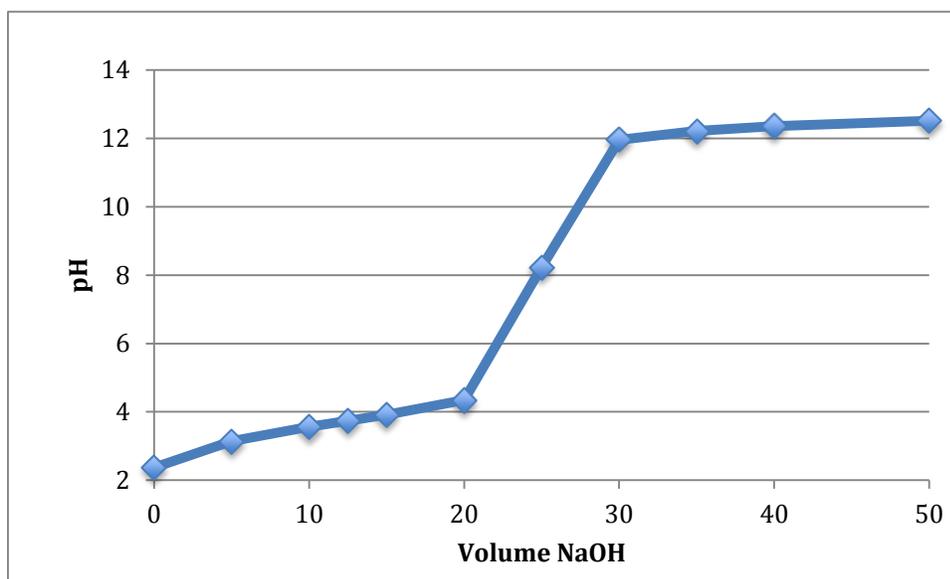
7. Graph, using excel, a pH curve for the titration of  $\text{HT}^{-}$  against  $\text{NaOH}$ . Label the initial pH, buffer region, equivalence point, and excess base regions on your graph.

8. What is the pH at the equivalence point according to the pH curve?

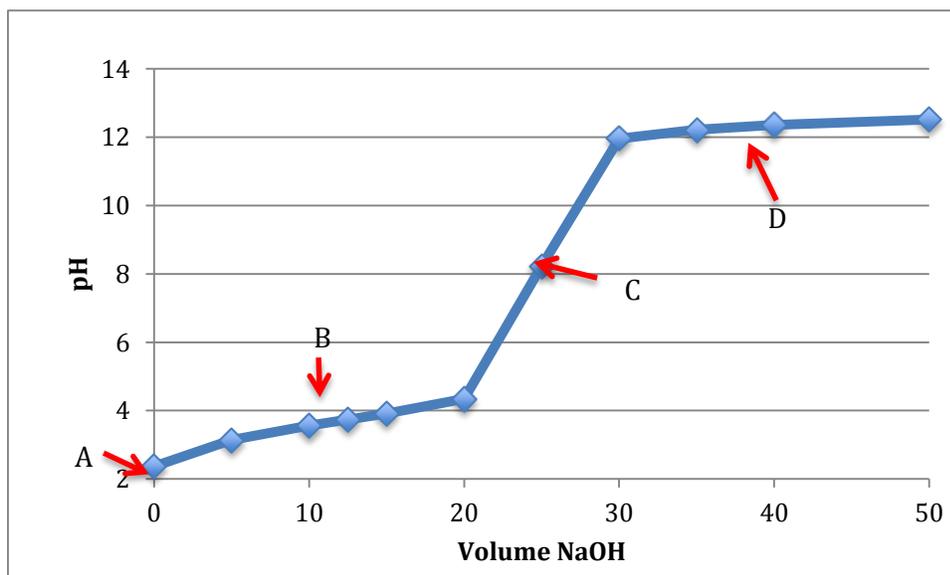
9. Compare the pH at the equivalence point calculated in question 5 to the pH determined in from the pH curve?

# Pre-Lab Questions

1. Why are strong acids or bases used as titrants and never weak acids or bases?
2. Label the weak acid/strong base pH curve below with the following points.
  - a. Initial pH
  - b. Buffer region
  - c. Half-equivalence point
  - d. Equivalence point
  - e. Excess strong base



3. Consider the points marked on the figure below (A, B, C, D) for a weak acid (abbrev. HA)/strong base pH titration.



Complete the following table by identifying the one of the four species ( $\text{HA}$ ,  $\text{A}^-$ ,  $\text{H}_3\text{O}^+$ ,  $\text{OH}^-$ ) that is most concentrated, the one that is least concentrated, and any pairs that have nearly equal concentration in the mixture at that point. The first entry is provided for you.

Point on curve	Highest concentration	Lowest concentration	Nearly Equal Concentrations
A	HA		
B			
C			
D			

4. Consider the titration of 20.0 mL 0.120 M  $\text{HC}_2\text{H}_3\text{O}_2$  against 0.150 M KOH.

a. What is the initial pH of the solution? ( $\text{HC}_2\text{H}_3\text{O}_2$   $K_a = 1.8 \times 10^{-5}$ )

b. What is the pH after 16 mL (equivalence point) of 0.150 M KOH has been added to the solution. ( $\text{C}_2\text{H}_3\text{O}_2^-$   $K_b = 5.6 \times 10^{-10}$ )