# Acid/Base Titration and Solubility Equilibria

Many substances that involve ionic bonds are only partially soluble in water. Among such are most of the organic acids. These are mostly covalently bonded substances that possess one or more acidic hydrogens. Examples include citric acid from citrus fruits, uric acid which precipitates out in people with symptoms of gout and acetyl salicylic acid, otherwise known as aspirin.

The acid we will be examining in this lab is a salt of the diprotic acid, tartaric acid, $H_2C_4H_4O_6$, called potassium hydrogen tartrate, (KHT) which is an acid itself and has the formula, $KHC_4H_4O_6$. (MW = 188.18) This substance has a limited solubility in water shown by the equation:

$$KHC_4H_4O_6(s) \leftrightarrow K^+(aq) + HC_4H_4O_6^-(aq)$$
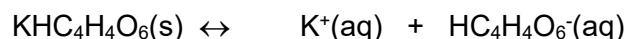
When the system is at equilibrium, it is said to be **saturated.** The equilibrium constant for this saturated solution involves the solubility of a solid, so is called the "solubility product" constant. Thus the equilibrium constant, K is written as K_{sp} and has the following expression for this equilibrium system:

$$K_{sp} = [K^+][HC_4H_4O_6^-] = [K^+][HT^-]$$

where the formula for hydrogen tartrate, $HC_4H_4O_6^-$ has been replaced by HT^- for brevity. Note that at equilibrium, the concentrations $[K^+]$ and $[HT^-]$ are the same!

Our objective is to measure the concentrations of these components in this system and then calculate the K_{sp} value. In order to do this, we need to be able to measure at least one of the items, K^+ or $HC_4H_4O_6^-$. We will take advantage of the fact that $HC_4H_4O_6^-$, is a weak acid and use the reaction between this substance and a strong base, sodium hydroxide in a laboratory method known as a **titration** in order to measure the amount in solution.

Acid-Base Titration:

An acid reacts with a base to form a salt and water. Thus, if we add NaOH, a strong base to a solution of HT^-, the following net ionic reaction occurs:

$$OH^- (aq) + HT^- (aq) \rightarrow H_2O (l) + T^{-2} (aq)$$
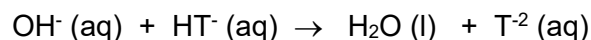
As Na^+ is a spectator ion, it was omitted from this reaction for clarity.

As can be seen from this balanced reaction, the hydroxide and HT^- react in a 1:1 mole ratio. Therefore, if we add just enough OH^- in order to react with the HT^- and if we know how many moles of OH^- were added, then we immediately know how many moles of HT^- we have in solution and we can proceed to calculate the molarity.

We will know how much OH⁻ is added by carefully measuring the amount we add using a **buret**, a long graduated cylinder with a stopcock on the end. We will also know the molarity of the NaOH solution we are adding. If we know the molarity and the volume, we then know the moles as:

$$M \times V = \text{moles}$$

The astute student might ask "How does one know when we've added enough NaOH?". Excellent question!! The answer is that we add an **indicator** to the acid solution. As NaOH is added to the HT^- solution, then as long as there are moles of HT^- present, the NaOH will react. The instant the all of the HT_- is reacted, we are at the **equivalence point**. The very next fraction of NaOH that is added will no longer have any more HT^- with which to react and will therefore remain in solution unreacted. To know when this has happened, we will put in a substance that will change color when excess NaOH is present. For the lab today, we will use **phenolphthalein** which is colorless as long as there is no excess NaOH present. The instant there is excess NaOH, the phenolphthalein reacts with it to change to a pink color. The moment pink appears, you are at the **endpoint** of the titration.

NOTE!! In order to turn pink, there must be excess NaOH present!! Thus by definition we are PAST the equivalence point!!

Here is where lab skill comes into play. Your goal is to produce an endpoint that has the lightest possible pink that you can barely see!!! The more faint the pink color, the more precise your results!!

The titration setup for this lab is illustrated here:
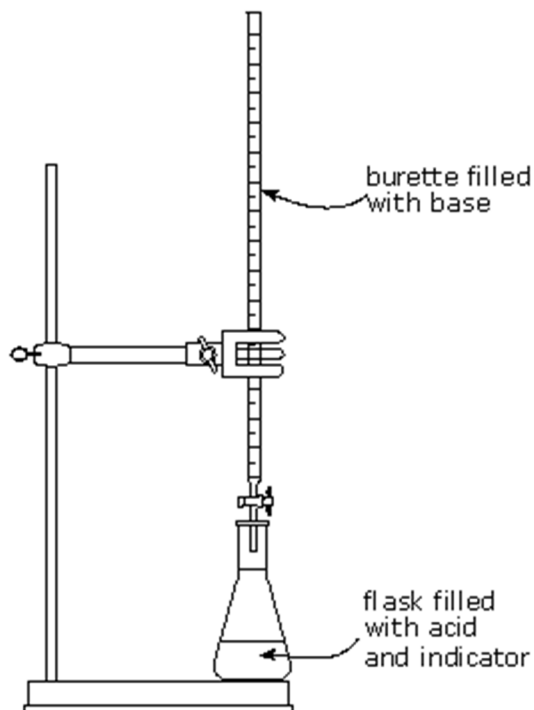
Example: The following is provided as a sample set of data and calculation.

A saturated solution of a low solubility acid HB (MW = 134.54) was prepared by mixing solid HB with deionized water overnight and allowing to sit undisturbed. A 25.00 mL sample of the liquid containing no solid material was collected using a 25.00 mL pipet and placed in a 125 mL Erlenmeyer flask along with 2 drops of phenolphthalein indicator.

A buret was cleaned and then rinsed with 0.01025 M NaOH solution. The initial volume of the NaOH was recorded to be 0.15 mL in the buret.

The titration was carried out to a light pink endpoint. The final volume of NaOH was 34.65 mL.

Calculate the solubility and solubility product, K_{sp}.

Volume of NaOH:

V_{NaOH} = Final Vol - Init Vol = 34.65 mL – 0.15 mL = 34.50 mL.

mMoles of NaOH:

mmoles NaOH = M_{NaOH} x V_{NaOH} = (0.01025 M)(34.50 mL) = 0.3536 mmol NaOH

mMoles of H⁺:

$$\text{mmoles } H^+ = 0.3536 \text{ mmol NaOH} \cdot \left(\frac{1 \text{ mmol } H^+}{1 \text{ mmol NaOH}} \right) = 0.3536 \text{ mmol } H^+$$

Molarilty of H⁺:

$$[H^+] = \frac{mmol \, H^+}{mL \, sample} = \frac{0.3536 \, mmol}{25.00 \, mL} = 0.01414 \, M \, H^+$$

Solubiilty:

$$Solubility, s = Molarity \, x \, MW = \left(\frac{0.01414 mol}{L} \right) \left(\frac{134.54 \, g}{mol} \right) = 1.903 \, g/L$$

Solubility Product, K_{sp}:

$$K_{sp} = [H^+][B^-] = (0.01414)(0.01414) = 2.00 \, x \, 10^{-4}$$

From the discussion, we see that the order of operations is this..

1.) Create a saturated solution of KHT.
2.) Remove the saturated solution from the top and filter, if necessary, to remove any solid material.
3.) Take a precisely measured portion of the saturated solution and place in an Erlenmeyer flask along with a drop in indicator.
4.) Add NaOH solution using the buret until a faint pink color persists.
5.) Calculate the moles of NaOH added which is equal to the moles of acid originally present.
6.) Using the volume of the acid sample and the moles, calculate the molarity, $[HT^-]$ which is equal to $[K^+]$.
7.) Calculate the solubility in g/100 mL and calculate the K_{sp}.

Pre-Lab Questions:

(See Lab Notebook pages 10-12)

1.) Consider each of the following and indicate the effect (higher or lower) of each of the following errors in the **calculation** of the K_{sp}. In each case explain why.

    a. Some solid material was not filtered out prior to titrating.

    b. An air bubble in the buret tip was not removed and comes out during the titration.

    c. The buret was not rinsed with NaOH prior to filling.

d. During the titration, water is added to wash down the sides of the flask thus diluting the acid solution.

2.) An experiment similar to the one performed was done in order to determine the K_{sp} of $Ba(OH)_2$. In this instance, a strong acid, HCl is placed in the buret and a titration performed. Using the data provided, complete the remaining entries in the table.

a. Write the solubility equation of $Ba(OH)_2(s)$ in water.

b. Write the K_{sp} expression for this equilibrium.

c. Write the reaction that occurs when HCl is added.

d. If phenolphthalein is used as an indicator, describe the appearance of the solution prior to and at the endpoint.

Data Table

Concentration of HCl Solution: 0.05020 M

$Ba(OH)_2$ Sample Volume   25.00 mL

Value	Titration Number		
	1	**2**	**3**
Initial Buret Volume(mL)	0.02	0.03	0.02
Final Buret Volume (mL)	39.71	39.86	39.75
Titration Volume (mL)	_____	_____	_____

Show all calculations on the reverse page.

Average Titration Volume (mL)   _____

mmoles of HCl (mmol)   _____

mmol OH^- (mmol)   _____

$[OH^-]$ (mol/L)   _____

$[Ba^{+2}]$ (mol/L)   _____

Solubility (g/L)   _____
($Ba(OH)_2$,MW = 171.35g/mol)

K_{sp} _____

Calculations: Show all neatly and completely for credit. Include units, annotation and correct significant figures.

(See Lab Notebook pages 10-12)

Laboratory Procedure:

1.) Ahead of time, a saturated solution of KHT has been prepared. Obtain a clean dry 100 mL beaker and take it to your instructor to obtain a clean sample. Take it back to you work area and cover with a watch glass.

2.) **If the sample contains any cloudiness, obtain a piece of filter paper and a funnel and filter the sample into another clean dry beaker. Fold the filter paper as indicated in the figure.**
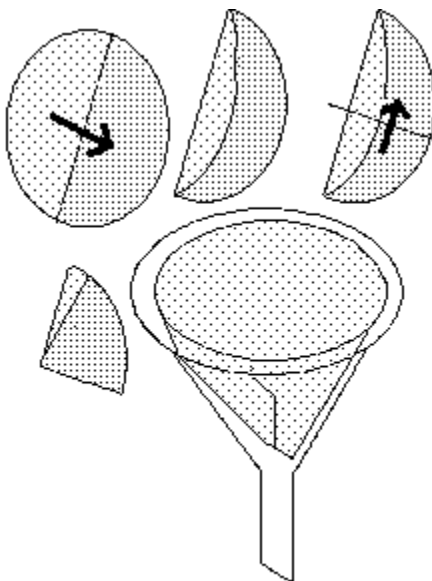
If any solid remains, then it will dissolve during the titration producing more acid. Thus more NaOH will be required and the Ksp will be calculated to be too large.

3.) Obtain a clean buret and rinse twice with 10 mL portions of deionized water. Discard the waste. Then rinse twice with 10 mL portions of your NaOH solution. If this isn't done, then the NaOH will be diluted by the remaining water in the buret. Be sure to run the solution through the buret tip to rinse out all the water. Attach to a ring stand using a buret clamp and fill to the top with a small funnel. (**CAUTION: NaOH is CAUSTIC!)**

4.) Using a discard beaker, open the stopcock fully for a moment and blow out any remaining air bubbles present. Tap the tip with your finger if needed. If the bubble comes out during the titration, then it will appear that more NaOH will have been added than is required. Close the stopcock and fill the buret to the top again. Record your initial volume.

5.) Obtain a clean dry 125 mL Erlenmeyer flask, 25.00 mL pipet and pipet pump. Rinse the pipet with some of the KHT solution. Draw your KHT solution up to the pipet mark

measuring to the bottom of the meniscus. Place the pipet over your Erlenmeyer flask and remove the pump allowing the liquid to flow. When the pipet is empty, touch the tip to the side of the flask to draw the last drop. **Do not blow out any remaining liquid.** Rinse down the sides of the flask with a small amount of deionized water.

6.) Obtain a stirring/hot plate and a magnetic stirring bar. Place the stirring/hot plate under the buret and the magnet in the acid solution. Add 2 drops of phenolphthalein solution and place in position on the stirring/hot plate under the buret. Make sure the heat is off and turn on the stirring until a gently stirring indicated by a light vortex in the solution is formed.

7.) Begin titrating by adding 0.5 to 1 mL portions of NaOH to the acid solution by quick twists of the stopcock. Continue this until a bit of pink begins to form at contact. Reduce the portions to 0.25 to 0.5 mL and continue.

   Occasionally rinse the sides of the flask with deionized water to wash any splashed material down into the solution.

   Rinsing with water will not introduce any error as it is the moles of acid present that determines the endpoint

8.) When the pink is beginning to persist for a longer time, start adding in small increments, 3-5 drops at a time. Continue this process reducing the additions until you are adding dropwise.

   Be careful at this point! You wish for the faintest possible pink you can perceive!!

   Hint: Add ½ and ¼ drops by slowly opening the stopcock until a ½ drop forms, then wash into the acid solution with deionized water.

9.) Continue to the faint pink endpoint and record the final volume.

   Refill the buret and repeat with a second sample. Calculate a % difference and if your results differ by more than 0.5 %, continue to a third trial.

   HINT: For repeat trials, you have a general idea of the titration volume. It should be identical for successive trials. Therefore, you may add NaOH initially until you get within 5-10 mL of the expected endpoint and continue carefully from that point.

Names:_____

Data Table

Concentration of NaOH Solution: _____ M

KHT Sample Volume   25.00 mL

Value	Titration Number		
	1	**2**	**3**
Initial Buret Volume(mL)	_____	_____	_____
Final Buret Volume (mL)	_____	_____	_____
Titration Volume (mL)	_____	_____	_____
Average Titration Volume (mL)	_____		
mmoles of NaOH (mmol)	_____		
mmol HT^- (mmol)	_____		
$[HT^-]$ (mol/L)	_____		
$[K^+]$ (mol/L)	_____		
Solubility (g/L)	_____		
K_{sp}	_____		

Calculations: Show all neatly and completely for credit. Include units, annotation and correct significant figures.

(See Lab Notebook pages 10-12)

Post-Lab Exercises:

1.) Would the calculated value for the K_{sp} in this experiment be too large or too small or unaffected by each of the following? Give your answer but you must explain for credit.

 a.) Some solid material was present in the titration sample.

 b.) Water was present in the Erlenmeyer flask prior to pipetting the 25.00 mL sample.

 c.) The saturated solution was prepared at a temperature of 30.0°C (Literature values for values are given at 25.0°C.)

 d.) Water was present in the buret prior to filing with the NaOH solution.

2.) Calcium hydroxide, $Ca(OH)_2$(s) has a low solubility in water. The hydroxide ion liberated can be titrated with a standardized HCl solution.

a.) Write the reaction for the dissolution of $Ca(OH)_2$(s) in water.

b.) Write the K_{sp} expression for the reaction in a.).

A saturated solution of $Ca(OH)_2$ was prepared and then filtered to remove the solid material. 25.00 mL of the supernatant liquid was then titrated three times with 0.01514 M HCl. The average titration volume was 38.83 mL.

c.) Compute the molar concentration of OH⁻ in the 25.00 mL aliquot sample.

d.) Compute the $[Ca^{+2}]$ concentration in the 25.00 mL aliquot sample.

e.) Using your K_{sp} expression, compute a value for the solubility product constant.