

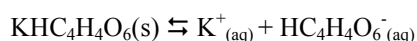
# 4 Equilibrium Constants and Thermodynamics

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## DISCUSSION

- **Determine the equilibrium constant for a reaction at various temperatures by measuring equilibrium concentrations.**
- **Titrate a weak acid with a strong base.**
- **Calculate thermodynamic quantities from the variation of the equilibrium constant with temperature.**

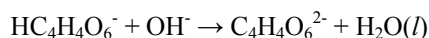
In this experiment, you will measure how much potassium bitartrate (also known as cream of tartar or potassium hydrogen tartrate) dissolves in water, according to the following dissociation reaction:



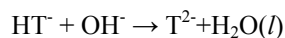
The ion  $\text{HC}_4\text{H}_4\text{O}_6^-$  is called the bitartrate ion. For convenience, it will be abbreviated as  $\text{HT}^-$ . Since potassium bitartrate (KHT) is only moderately soluble, just a little of it, mixed in water, will cause the above reaction to reach equilibrium. The equilibrium constant is given by this equation:

$$K = \frac{[\text{K}^+][\text{HC}_4\text{H}_4\text{O}_6^-]}{1} = [\text{K}^+][\text{HC}_4\text{H}_4\text{O}_6^-]$$

At equilibrium, the concentration of bitartrate ions equals the concentration of potassium ions in solution. Thus, measuring one or the other gives you sufficient information to calculate  $K$ . You will find the concentration of bitartrate ions by taking advantage to the fact that bitartrate is a weak acid and is neutralized by a strong base, shown with the following chemical equation:



or with abbreviations for the chemical species,



At room temperature and again at ice-water temperature, you will determine the equilibrium bitartrate concentration by titrating the solution with  $\text{NaOH}(\text{aq})$  of known concentration.

Then, knowing the equilibrium constant at those two different temperatures, you will calculate the thermodynamic quantities,  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$ , for the expression below:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K$$

From the previous expression, you can derive the following:

$$\ln K = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T} \right) + \frac{\Delta S^\circ}{R},$$

which is in the form  $y = mx + b$ , the equation of a straight line. Thus, you will plot  $\ln K$  ( $y$ ) versus  $1/T$  ( $x$ ) for the two temperatures, find the *slope* ( $m$ ) and the *intercept* ( $b$ ) of the line drawn through the data points, and obtain the thermodynamic quantities from

$$\begin{aligned} \Delta H^\circ &= -R \cdot \text{slope} \\ &\text{and} \\ \Delta S^\circ &= R \cdot \text{intercept}, \end{aligned}$$

where  $R = 8.3145 \times 10^{-3} \frac{\text{kJ}}{\text{mol} \cdot \text{K}}$ .

## PROCEDURE

## A. Measurements at Room Temperature

- If you miss the end-point, add a little KHT (instead of NaOH) to return the proper faint color. In doing this, remember to remeasure and again record the final buret reading of the KHT solution.

1. Measure out about 0.7 grams of solid potassium bitartrate, and place it in one of the larger plastic bottles at your work station. Add about 100 mL of distilled water, cap the bottle, and with your finger firmly over the cap, shake the contents of the bottle for at least 5 minutes. For the titration, you will use a NaOH solution that is approximately 0.05 M. The actual concentration of this NaOH solution will be given to you. Record the actual NaOH concentration on the report sheet.

2. When the potassium bitartrate mixture has been shaken for the necessary amount of time, record its Celsius temperature to the nearest degree.

Filter about half of the mixture (using the instructions in the following paragraph) and reserve the remainder for the second part of the experiment.

With a needle-less syringe, draw up a whole syringeful of bitartrate mixture. Install the filter cap on the syringe, and push the liquid out through the filter and into one of the small, dry, plastic bottles at your work station. Repeat as necessary until the requisite amount is filtered.

Do at least two titrations according to Steps 3-6 below:

Drain the water from one of two burets at the work station, and rinse the buret several times with small portions of NaOH solution. Discard the washings. Close the stopcock, and fill the buret with NaOH(aq) to above the zero mark. Open the stopcock, and be sure solution fills the buret tip completely. Add more solution to the buret until the level is slightly below the zero mark.

3. Read this volume to the nearest 0.01 mL, and record it as the initial NaOH buret reading.

Drain the water from the second buret. Rinse this buret with several small portions of the filtered potassium bitartrate solution, and then fill the buret. Be sure the buret tip is filled with solution and the buret is filled close to the zero mark.

4. Record the initial KHT buret reading to the nearest 0.01 mL.

5. If this is the first trial, drain about 5 mL of KHT solution into a clean 50 mL erlenmeyer flask. Record the final buret reading to the

nearest 0.01 mL. Add one drop of phenolphthalein to the flask.

6. Titrate with NaOH until the solution in the flask is just barely pink for at least 30 seconds. Record the final NaOH buret reading. Now that the first trial is complete, it is worthwhile to estimate the maximum amount of KHT solution that could have been used without having to use more than 10 mL of NaOH. For example, if 4 mL of NaOH was required to titrate the 5 mL of KHT during the first trial, 8-9 mL of KHT should be used in the future trials, if 6 mL of NaOH was required to titrate the 5 mL of KHT, 7-8 mL of KHT should be used in the future trials. The reason for doing this is that maximizing the volumes used during the titration minimizes the percent error associated with reading the burets during the titration.

7. Calculate the volume of KHT solution used.

8. Calculate the volume of NaOH(aq) used.

9. Calculate the number of moles of NaOH.

10. Calculate the moles of  $\text{HT}^-$ .

11. Calculate the molarity of  $\text{HT}^-$ .

12. Obtain the equilibrium constant by squaring the molarity of  $\text{HT}^-$ .

13. When all trials have been completed, calculate the average equilibrium constant. Discard the potassium bitartrate solution from the buret. Also discard the *filtered* potassium bitartrate solution you have been using.

## B. Measurements at Ice Temperature

14. Place the bottle containing the unfiltered potassium bitartrate mixture in an ice bath. Shake the bottle often. After about 10 minutes, measure the Celsius temperature of the mixture to the nearest degree.

Filter the cold mixture a little at a time, and collect the solution in the other small *dry* plastic bottle at your work station. Keep the unfiltered solution in the ice bath in order to keep it cold. After enough of the solution has been filtered, rinse the buret that had contained potassium bitartrate with some of this new solution. Fill the buret with it.

15-25. Repeat Steps 3-12 using the cold solution. When the titrations have been completed, discard all solutions, and rinse out the bottles. Rinse and fill the burets with distilled water.

**C. Determination of  
Thermodynamic Quantities**

26. For each of the two experimental temperatures, calculate the natural logarithm of the equilibrium constant.
27. Calculate the Kelvin temperatures.
28. Calculate  $1/T$ , using the Kelvin temperatures.
29. Use your calculator to obtain the slope of the line through the two values of  $\ln K$  versus  $1/T$ .
30. Obtain the intercept.
31. Calculate  $\Delta H^\circ$ .
32. Calculate  $\Delta S^\circ$ .
33. Calculate  $\Delta G^\circ$  at 298 K from the relation,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ .

# 4 Equilibrium and Thermodynamics

Name \_\_\_\_\_  
 Section \_\_\_\_\_ Locker \_\_\_\_\_  
 Instructor \_\_\_\_\_

## Measurements at Room Temperature

1. Concentration of standard NaOH(aq)	
2. Temperature of mixture	

	Trial #1	Trial #2	Trial #3
3. Initial NaOH buret reading			
4. Initial KHT buret reading			
5. Final KHT buret reading			
6. Final NaOH buret reading			
7. Volume of KHT solution used			
8. Volume of NaOH solution used			
9. Moles of NaOH			
10. Moles of HT <sup>-</sup>			
11. Molarity of HT <sup>-</sup>			
12. Equilibrium constant			
13. Average equilibrium constant			

## CALCULATIONS

## B. Measurements at Ice Temperature

	Trial #1	Trial #2	Trial #3
14. Temperature of mixture			
15. Initial NaOH buret reading			
16. Initial KHT buret reading			
17. Final KHT buret reading			
18. Final NaOH buret reading			
19. Volume of KHT solution used			
20. Volume of NaOH solution used			
21. Moles of NaOH			
22. Moles of HT <sup>-</sup>			
23. Molarity of HT			
24. Equilibrium constant			
25. Average equilibrium constant			

**CALCULATIONS**

## C. Determination of Thermodynamic Quantities

	Room Temperature	Ice Temperature
26. $\ln K$		
27. Kelvin temperature		
28. $1/T$		

**CALCULATIONS**

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29. Slope of the line (with units)	
30. Intercept of the line	
31. $\Delta H^\circ$ (with units)	
32. $\Delta S^\circ$ (with units)	
33. $\Delta G^\circ$ at 298 K (with units)	

**CALCULATIONS**

**APPLICATION OF PRINCIPLES**

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1. Why is the equilibrium constant for the reaction,  $\text{KHT}(s) \rightleftharpoons \text{K}^+ + \text{HT}^-$ , equal to the square of the bitartrate concentration?

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2. Is the sign of  $\Delta S$  what you would expect for a solid dissolving in water and breaking into ions? Explain your answer.