

Solubility and Thermodynamics of Potassium Nitrate

Cautions

Potassium Nitrate (KNO_3) is an oxidizer and skin irritant.

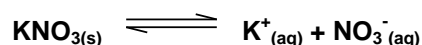
Open flames and hot water can cause burns.

Purpose

The purpose of this experiment is to measure the solubility of potassium nitrate as a function of temperature and use the data to calculate the equilibrium constant, enthalpy, entropy, and free energy of the dissolution reaction.

Introduction

When a salt dissolves in water it will dissociate into ions. In aqueous solution potassium nitrate (KNO_3) dissociates according to the following reaction.



Once a sufficient amount of K^+ and NO_3^- are in solution, the ions will recombine into solid potassium nitrate, KNO_3 . At this point a pair of ions will recombine for every pair that dissociates, and the concentrations of the ions in solution will remain constant. The reaction is said to be at equilibrium. The two-sided arrow indicates that the reaction is reversible and undissolved solid is in equilibrium with the dissolved ions. This is known as a saturated solution. The equilibrium constant expression, shown in equation (1), defines the equilibrium constant (K_{sp}) for KNO_3 dissolving in water.

$$K_{sp} = [\text{K}^+][\text{NO}_3^-] \quad (1)$$

The “sp” stands for the solubility product, and the brackets around the ions symbolize molar concentration (M or mol/L). The equilibrium constant is not only concerned with solubility but also is expressed as a product of the molar concentration of ions. The value for K_{sp} for a compound changes with the temperature.

Thermodynamics may be used to understand what energy changes occur when a salt dissolves in water. The energy difference between the solid salt and its dissolved ions is known as the enthalpy change (ΔH), and the relative disorder of the dissolved ions is an indication of the entropy change (ΔS). A positive enthalpy change will occur if heat must be added to dissolve the salt in water. The enthalpy change will be negative if the dissolution process releases heat. The entropy change for a solid salt dissolving in water should be positive because the dissolved ions possess more disorder than a solid salt molecule. The free energy change (ΔG) for a salt dissolving in water indicates whether the process will occur spontaneously. A negative free energy change implies that the salt will spontaneously dissolve in water while a positive free energy change indicates that the process is non-spontaneous. The Gibbs-Helmholtz equation, shown in equation (2), is a mathematical relationship between the changes in free energy, enthalpy, and entropy.

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

A mathematical relationship, shown in equation (3) also exists between the free energy change and the solubility equilibrium constant.

$$\Delta G = -RT \ln K_{sp} \quad (3)$$

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In equation (3), R is the gas constant (8.314 J/mol-K), and T is the temperature in Kelvin. The change in free energy for a reaction is dependant on temperature just as is the equilibrium constant. By substituting the equilibrium constant relationship in to the Gibbs-Helmholtz equation, equation (4) results.

$$-RT\ln K_{sp} = \Delta H - T\Delta S \quad (4)$$

By using algebra, it is possible to rearrange equation (4) into the form of a straight line as shown in equation (5).

$$\ln K_{SP} = -\left(\frac{\Delta H}{R}\right)\left(\frac{1}{T}\right) + \frac{\Delta S}{R} \quad (5)$$

By plotting $\ln K_{sp}$ versus $1/T$, the slope of the line is $-\Delta H/R$ and the y-intercept is $\Delta S/R$. By evaluating the temperature dependence of the solubility equilibrium constant, the enthalpy and entropy of dissolution can be determined.

Procedure

A. Preparing the Hot Water Bath

- A1. Place ~ 300 mL of tap water into a 600-mL beaker.
- A2. Place the beaker on a wire gauze using an iron support ring, and place a second iron ring around the beaker.
- A3. Begin heating the water and continue to Part B.

B. Sample Preparation

- B1. Weigh ~ 15 grams of KNO_3 and record the actual mass in Table 1 on the data sheet. Transfer the salt to a large test tube (25mm X 200 mm).
- B2. Use a graduated cylinder to add 15.0 mL of water to the test tube and mix the contents.
- B3. Observe whether the process is exothermic or endothermic.
- B4. Obtain a two-hole split stopper. (Make sure the stopper will fit in the opening of the test tube.)
- B5. Place a thermometer and looped **glass** stirrer inside the stopper.
- B6. Place the thermometer and stirrer inside the test tube with the stopper in the opening. Mix the solution.

C. Determining the Equilibrium Constant

- C1. Heat the test tube containing the KNO_3 in the boiling hot water bath while stirring until all the KNO_3 is dissolved. The solution should be clear and colorless.
- C2. Determine the volume of the KNO_3 solution.
 - i. Remove the thermometer and stirrer from the KNO_3 solution in the test tube.
 - ii. Fill another test tube with tap water until the volumes in both test tubes are equal.
 - iii. Measure the volume of tap water using a 100 mL graduated cylinder
 - iv. Record this volume in Table1 on the data sheet.
- C3. Remove the test tube containing the KNO_3 from the hot water bath and allow it to cool while stirring the solution slowly with the stirrer (**DO NOT** use the thermometer to stir the solution).
- C4. Record the temperature at the point when the **first** crystals appear. The solution will appear to be "snowing." The solution is at equilibrium when the first crystals begin to appear.
- C5. Add 5.0 mL of water to the test tube and reheat the mixture until all the solid KNO_3 has re-dissolved

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- C6. Determine and record the volume of the solution as you did in step **C2**. Do not assume the solution will only have increased by 5.0 mL.
- C7. Cool slowly while stirring and record the temperature at the point when the **first** crystals appear.
- C8. Repeat steps **C5** through **C7** adding 5.0 mL of water each time until a total of 6 sets of data have been obtained.

Disposal

Place the KNO_3 solution into the container labeled "KNO₃ Waste." For easier removal of the KNO_3 reheat the solution till the entire solid has re-dissolved.

Clean-Up

Wash all glassware with soap then rinse 3 times with tap water, and once with deionized water.

Put all borrowed items by in their original locations so that the next laboratory section will have all the needed items.

Calculations

1. Calculate the number of moles of KNO_3 and record in Table 1 on the data sheet.
2. Using the number of moles and volume, calculate the molar concentration of KNO_3 , K^+ , and NO_3^- . Record concentration in Table 1 on the data sheet.
3. Calculate the K_{sp} for each data set using equation (1). Record the values in Table 1 on the data sheet.
4. Convert all temperatures into Kelvin for each data set and record in Table 2 on the data sheet.
5. Determine the natural logarithm (\ln) of the K_{sp} at each temperature and record in Table 2 on the data sheet.
6. Calculate ΔG for each data set using equation (3) and record in Table 2 on the data sheet.
7. Calculate the reciprocal of each temperature ($1/T$) and record in Table 3 on the data sheet.
8. Using a spreadsheet program construct a graph with the y-axis being $\ln K_{\text{sp}}$ and the x-axis being $1/T$. Attach the graph to the data sheets.
9. Determine the best linear fit of the data using linear regression and record the slope of the line in Table 3 on the data sheet.
10. Calculate ΔH of the reaction by using the slope of the straight line from the graph and the value of R. Record the value in Table 3 on the data sheet.
11. Calculate ΔS of the reaction by using the y-intercept of the straight line from the graph and the value of R. Record the value in Table 4 on the data sheet.

NOTE: The following equations may be helpful for calculations 10 and 11.

$$y = mx + b$$
$$\ln K_{\text{sp}} = -\left(\frac{\Delta H}{R}\right)\left(\frac{1}{T}\right) + \left(\frac{\Delta S}{R}\right)$$

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Data Sheets

Name: _____

Lab Partner: _____

Table 1: Experimental Data and Determining K_{sp}

	Units	1	2	3	4	5	6
Mass of KNO_3							
Moles of KNO_3							
Total Volume							
Temperature when crystals appeared							
Molar Concentration of KNO_3							
Molar Concentration of K^+							
Molar Concentration of NO_3^-							
K_{sp}							

Table 2: Determining ΔG

	Units	1	2	3	4	5	6
Temperature	K						
$\ln K_{sp}$							
ΔG							

Solubility and Thermodynamics of Potassium Nitrate**Table 3: Determining ΔH**

	Units	1	2	3	4	5	6
1/Temperature	K^{-1}						
Slope of the straight line							
ΔH							

Table 4: Determining ΔS

	Unit	
ΔS		

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Calculations: *Show all sample calculations and remember to attach graphs and spreadsheet data.*

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Pre-lab Assignment

Name: _____

1. What is ΔG ? What does the sign of ΔG tell you about the spontaneity of a reaction?
2. In your own words, define entropy. What symbol is used to abbreviate change in entropy?
3. A student performs this lab exercise and records the following data. Use this data and the calculations instructions on page 3 to prepare a graph of the $\ln(K_{sp})$ vs $1/T$ and calculate the following values. Make sure to show all work, and attach the graph.

Trial #	Units	1	2	3	4	5	6
Temperature when crystals appeared	$^{\circ}\text{C}$	53.6	46.1	39.5	34.1	31.3	28.4
Molar Concentration of KNO_3	mol/L	6.35	5.36	4.69	4.05	3.66	3.3

K_{sp}							
$1/T$	K^{-1}						
$\ln K_{sp}$							

Slope: _____

Intercept: _____

 $\Delta H =$ _____ $\Delta S =$ _____