

**OBJECTIVE**

The  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  of the potassium nitrate ( $\text{KNO}_3$ ) dissolving reaction will be determined by measuring the equilibrium constant ( $K_{\text{sp}}$ ) at different temperatures.

**BACKGROUND****1. Solubility product constant (see textbook:  $K_{\text{sp}}$ , Sec. 16.5, page 783; solution Sec. 12.3-12.4, page 551)**

In a saturated potassium nitrate ( $\text{KNO}_3$ ) solution in water ( $\text{H}_2\text{O}$ ), a dynamic equilibrium will be established and the reaction equation is shown in equation 1:



The equilibrium constant  $K_{\text{sp}}$  (also called the solubility product constant) of this reversible reaction can be defined in equation 2:

$$K_{\text{sp}} = [\text{K}^+][\text{NO}_3^-] \quad [\text{Eq. 2}]$$

where:

$[\text{K}^+] =$  molar concentration of  $\text{K}^+$  (mol/L)

$[\text{NO}_3^-] =$  molar concentration of  $\text{NO}_3^-$  (mol/L)

Because the solubility of  $\text{KNO}_3$  changes when the temperature ( $T$ ) changes, the  $K_{\text{sp}}$  is a function of the temperature.

**2. Thermodynamics (Textbook Section. 17.5, page 828; Section 17.9, p. 845; Figure 12.11, page 556)**

Three important thermodynamic parameters  $\Delta G$  (free energy change),  $\Delta H$  (enthalpy change) and  $\Delta S$  (entropy change) could be used to obtain a better understanding of the dissolving process of  $\text{KNO}_3$ :

- The  $\Delta S$  for  $\text{KNO}_3$  dissolving in water is always positive since the randomness of the system increases (Textbook Sec. 12.2, pp. 546-551).
- The  $\Delta H$  would be positive if heat needs to be provided for  $\text{KNO}_3$  to dissolve (endothermic), and negative if heat is released for  $\text{KNO}_3$  dissolving in water (exothermic).
- The  $\Delta G$  can be used to determine the spontaneity of the  $\text{KNO}_3$  dissolving process; a negative  $\Delta G$  means the process is spontaneous while positive  $\Delta G$  means the process is nonspontaneous.

Several important equations will be used to determine these three parameters:

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$$\Delta G = -RT \ln K_{\text{sp}} \quad R = 8.314 \text{ J/K}\cdot\text{mol} \quad [\text{Eq. 3}]$$

$T =$  temperature in Kelvin

Once the  $K_{\text{sp}}$  at a certain temperature is known, the  $\Delta G$  can be calculated by using Equation 3.

Equation 4 tells the relationship among the three parameters:

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$$\Delta G = \Delta H - T\Delta S \quad [\text{Eq. 4}]$$


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Equations 3 and 4 can be combined to obtain the Equation 5:

$$-RT\ln K_{sp} = \Delta H - T\Delta S \quad [\text{Eq. 5}]$$

Reorganization of Equation 5 yields Equation 6, which shows the linear relationship between  $\ln K_{sp}$  and  $1/T$ :

$$\ln K_{sp} = - \left( \frac{\Delta H}{R} \right) \left( \frac{1}{T} \right) + \frac{\Delta S}{R} \quad [\text{Eq. 6}]$$

Therefore, a plot of  $\ln K_{sp}$  versus  $1/T$  yields a straight line with a slope of  $-\Delta H/R$  and a y-intercept of  $\Delta S/R$ .

The second way to calculate the  $\Delta S$  is by using Equation 4. Once  $\Delta G$  and  $\Delta H$  are known from Equation 3 and the slope of the linear graph,  $\Delta S$  can be calculated with temperature in Kelvin.

### 3. Examples

**Example 1.** At  $0^\circ\text{C}$ , one liter of saturated  $\text{KIO}_3$  solution can be prepared by dissolving 46.0 g  $\text{KIO}_3$  in water. Determine the  $K_{sp}$  of  $\text{KIO}_3$  at  $0^\circ\text{C}$ .

*Step 1. Calculate the concentration of  $\text{KIO}_3$*

$$46.0 \text{ g} \times \frac{1 \text{ mol}}{214.0 \text{ g}} \times \frac{1}{1 \text{ L}} = 0.215 \text{ mol/L}$$

*Step 2. Calculate the  $K_{sp}$*

Equation 1 shows one mole of  $\text{KIO}_3$  will dissociate to one mole of  $\text{K}^+$  and one mole of  $\text{IO}_3^-$ , therefore both concentrations of  $\text{K}^+$  and  $\text{IO}_3^-$  are 0.215 mol/L.

$$K_{sp} = [\text{K}^+][\text{IO}_3^-] = 0.215 \times 0.215 = 0.0462$$

**Example 2.** Determine the  $\Delta G$  based on the  $K_{sp}$  from the Example 1. According to Equation 3:

$$\Delta G = -(8.314 \text{ J/K}\cdot\text{mol})(0^\circ\text{C} + 273 \text{ K})(\ln 0.0462) = 6.98 \times 10^3 \text{ J/mol}$$

**Example 3.** Determine the  $\Delta H$  and  $\Delta S$  based on the data from the following table.

Temperature (K)	$1/T$ ( $\text{K}^{-1}$ )	$K_{sp}$	$\ln K_{sp}$
273	0.00366	0.0462	-3.07
293	0.00341	0.143	-1.94
373	0.00268	2.28	-0.824

Plot  $\ln K_{sp}$  vs  $1/T$  and fit the data. The equation shows the slope and y-intercept as  $-2.12 \times 10^3$  and 4.945, respectively:

$$y = -2.12 \times 10^3 x + 4.945$$

$$R^2 = 0.9241$$

Therefore, based on Equation 6:

$$-2.12 \times 10^3 \text{ K} = -\frac{\Delta H}{R} = -\frac{\Delta H}{8.314 \text{ J/K}\cdot\text{mol}}$$

$$\Delta H = 2.12 \times 10^3 \text{ K} \times 8.314 \text{ J/K}\cdot\text{mol} = 1.76 \times 10^4 \text{ J/mol}$$

Since  $\Delta S/R$  is the y-intercept in Equation 6:

$$4.945 = \frac{\Delta S}{R} = \frac{\Delta S}{8.314 \text{ J/K}\cdot\text{mol}}$$

$$\Delta S = 4.945 \times 8.314 \text{ J/K}\cdot\text{mol} = 41.13 \text{ J/K}\cdot\text{mol}$$

**Example 4.** The second method to calculate  $\Delta S$  is from Equation 4. For instance, since the values  $\Delta G$  and  $\Delta H$  are available from the calculation of example 2 and 3, the  $\Delta S$  at  $0^\circ\text{C}$  can be calculated as the following:

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{17630 \text{ J/mol} - 6890 \text{ J/mol}}{273 \text{ K}} = 39.34 \text{ J/K}\cdot\text{mol}$$

## PROCEDURE

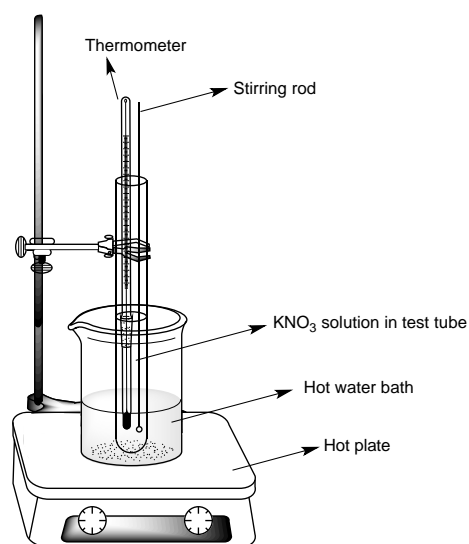
### Safety

- Wear departmentally-approved eyewear while doing this experiment.
- Do not ingest any solids or solutions as glassware may be contaminated with other chemicals.
- Clean any spilled  $\text{KNO}_3$  solid around the balance and  $\text{KNO}_3$  solution on the bench after you finish the lab.

### Chemical Hazards

$\text{KNO}_3$  – oxidant and irritant

1. Assemble a hot water bath for  $\text{KNO}_3$  dissolving as shown in Figure 1. Make sure there are no cracks in your beaker. Also, do not allow the hot plate's electrical cord to touch the hot surface.

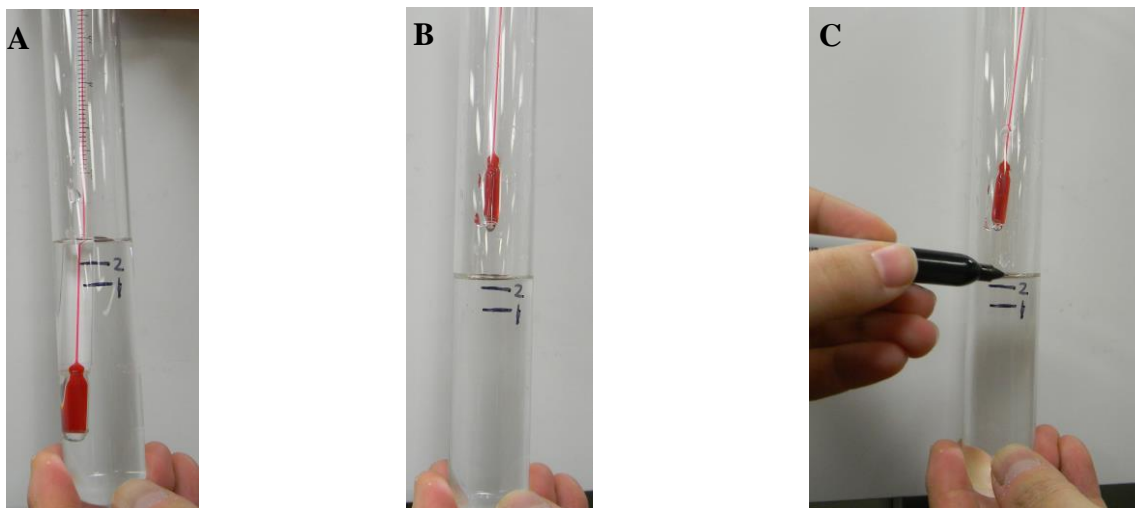


**Figure 1.** Setup for heating the  $\text{KNO}_3$  in test tube.

2. Weigh about 20 g of  $\text{KNO}_3$  to the nearest 0.001 g. Record the exact mass of  $\text{KNO}_3$  and transfer the compound to a dry clean 200 mL test tube.

3. Measure 15 mL of distilled water using a graduated cylinder and add it to the test tube with  $\text{KNO}_3$ . Heat the tube in water bath with the hot plate and stir the mixture with a metal wire rod until all of the  $\text{KNO}_3$  dissolves.

4. Remove the test tube from the hot water bath and use paper towel to dry the outer wall of the test tube quickly (Figure 2A). Lift the rubber stopper with the thermometer and stirring rod gently until the thermometer bulb stays right above the solution level (Figure 2B). **Note: Don't remove the rubber stopper with the thermometer completely from the test tube.**



**Figure 2.** Lift the thermometer and mark the  $\text{KNO}_3$  solution level (step 4 and 5).

5. Mark the solution level on the test tube with a sharpie and label it as **1** (Figure 2C). Replace the rubber stopper with the thermometer and let the test tube with  $\text{KNO}_3$  solution cool naturally while slowly stirring the solution.
6. Observe the  $\text{KNO}_3$  solution when it cools and record the temperature when the first white crystal appears. This will be the temperature for the equilibrium in Equation 1.
7. Add 5 mL of distilled water (with a graduated cylinder) to the test tube after you record the temperature. Put the test tube back to hot water bath and heat it until all  $\text{KNO}_3$  dissolves. Repeat steps 4, 5 and 6 to mark the solution level as **2** and record the equilibrium temperature.
8. Repeat step 7 two more times and collect the data for the 3rd and 4th trials.
9. After you finish all four trials, there should be four markers on the 200 mL test tube labeled as **1, 2, 3** and **4**. Determine the solution volumes at each mark. Add tap water to the tube up to the first mark. Pour this water into a 100 mL graduated cylinder and record the volume. Repeat the procedure for each of the remaining marks on the tube, and measure the remaining volumes.
10. When the experiment is finished, transfer the  $\text{KNO}_3$  solution into the waste container in the fume hood and clean the glassware by rinsing with tap water and then distilled water.

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**DATA SHEET**

1. Mass of KNO<sub>3</sub> (g) \_\_\_\_\_ Moles of KNO<sub>3</sub> (mol) \_\_\_\_\_

2. Calculation:

**Calculation of  $\Delta G$  (kJ/mol) from  $K_{sp}$**

	Trial 1	Trial 2	Trial 3	Trial 4
Total <u>measured</u> volume (mL)				
Concentration (M) of [KNO <sub>3</sub> ] = [K <sup>+</sup> ] = [NO <sub>3</sub> <sup>-</sup> ]				
$K_{sp} = [K^+][NO_3^-]$				
$\ln K_{sp}$				
Temperature (°C) when white crystals form				
Temperature (K) when white crystals form				
$\Delta G$ (in J/mol, Equation 3)				
$\Delta G$ (kJ/mol)				

**Calculation of  $\Delta H$  (kJ/mol) and  $\Delta S$  (J/K•mol)**

1/T (K <sup>-1</sup> )				
Linear fit equation from the graph				
R <sup>2</sup> value of the linear fit				
Slope of the line				
$\Delta H$ (kJ/mol)				

**Calculation of  $\Delta S$  (J/K•mol) (method 1 based on Equation 6)**

y-intercept of the line				
$\Delta S$ (J/K•mol)				

**Calculation of  $\Delta S$  (J/K•mol) (method 2 based on Equation 4  $\Delta G = \Delta H - T\Delta S$ )**

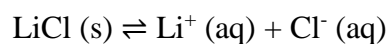
$\Delta S$ (J/K•mol)				
Average $\Delta S$ (J/K•mol)				

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**Pre-Lab Questions**

1. How do you determine whether a solution is saturated?

2. The equilibrium of a saturated LiCl aqueous solution is shown below:



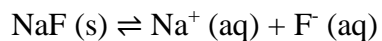
At 20.0 °C, the solubility of LiCl in water is 550.0 g/L.

(a) Calculate the molar concentration of LiCl.

(b) Calculate the molar concentration of  $\text{Li}^+$  and  $\text{Cl}^-$ .

(c) Calculate the  $K_{\text{sp}}$  for LiCl at 20.0 °C.

3. The equilibrium of a saturated NaF aqueous solution is shown below:



The following table shows the solubility of NaF at different temperatures.

Temp (°C)	$K_{\text{sp}}$	Temp (K)	$1/T$ ( $\text{K}^{-1}$ )	$\ln K_{\text{sp}}$	$\Delta G$ (J/mol)
0	0.751				
20	0.925				
100	1.446				

(a) Complete the entries in the table.

(b) Plot the  $\ln K_{\text{sp}}$  as a function of  $1/T$ . Fit the data and determine the slope of the line.

(c) Calculate the  $\Delta H$  and  $\Delta S$ .

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## Post-Lab Questions

1. Is the  $\text{KNO}_3$  dissolving process spontaneous or nonspontaneous? Please explain based on your data.

2. (a) Is the  $\text{KNO}_3$  dissolving process exothermic or endothermic? Please explain based on your data.

(b) Which picture (a or b) on page 553 (textbook) matches with your observation and calculation results on  $\Delta H$ ? Please explain based on your data.

(c) Figure 12.11 (page 556) shows the temperature-dependent solubility of  $\text{KNO}_3$ . Does your data match the trend of the curve?  $\text{Na}_2\text{SO}_4$  shows a different trend in solubility when temperature changes in Figure 12.11. What does it mean about  $\Delta H$ ?

3. Is your  $\Delta S$  for  $\text{KNO}_3$  positive or negative? What does it mean?

4. During the lab, each time when you add more water to the test tube, you have to wait longer time to get precipitation of  $\text{KNO}_3$ . Why?