THE THERMODYNAMICS OF POTASSIUM NITRATE DISSOLVING IN WATER

OBJECTIVE
In this experiment, the changes in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) of the potassium nitrate (KNO₃) dissolving reaction will be determined by measuring the equilibrium constant (K_{sp}) at different temperatures.

SAFETY
Fill in NFPA diamond for KNO₃:
Color in each of the small diamonds with the appropriate color and label its meaning (e.g., reactivity). Write the number for each as is pertains to KNO₃.

Other:

BACKGROUND
1. Solubility product constant (Ksp) (Textbook Sec. 12.2, pp. 310-315; Video: Bozeman: https://youtu.be/KVZ_KS45rVg)

The solubility product constant (Ksp) indicates how soluble a compound is in a solution (generally water). The higher Ksp (>1), the more soluble the compound. When Ksp = 1, the concentrations of compound and ions are equal. For example, the Ksp for KNO₃ at 25°C is 5.22, 30 g KNO₃ dissolves in 100 g H₂O compared with insoluble seashells (CaCO₃), the Ksp is 3.3 x 10⁻⁹ (1.3 x 10⁻¹⁰ g/100 mL).

A dynamic equilibrium will be established in a saturated KNO₃ solution in water:

\[
\text{KNO}_3 (s) \rightleftharpoons K^+ (aq) + NO_3^- (aq)
\]  

[Eq. 1]

Because the concentrations of solids do not change, so only the aqueous and gaseous phases are considered in the Ksp equation. Thus the equilibrium constant K_{sp} (also called solubility constant) of this reversible reaction can be defined:

\[
K_{sp} = [K^+] [NO_3^-]
\]  

[Eq. 2]

[K⁺] = molar concentration (mol/L)
reaction coefficient = powers of concentration

N.B.
- Ksp has no units.
- Because the solubility of KNO₃ changes when the temperature (T) changes, the Ksp is a function of the temperature.

1 http://faculty.uca.edu/kdooley/kno3_ksp_v010814__1_.pdf
2. Thermodynamics

<table>
<thead>
<tr>
<th>ΔH</th>
<th>ΔS</th>
<th>ΔG = ΔH – TΔS</th>
<th>Enthalpy</th>
<th>Entropy</th>
<th>Reaction Thermodynamically Favorable</th>
</tr>
</thead>
<tbody>
<tr>
<td>–</td>
<td>+</td>
<td>–</td>
<td>favored (exothermic)</td>
<td>favored (more random)</td>
<td>Forward: all temperatures</td>
</tr>
<tr>
<td>+</td>
<td>–</td>
<td>+</td>
<td>opposed</td>
<td>opposed</td>
<td>Opposite direction at all temperatures</td>
</tr>
<tr>
<td>–</td>
<td>+</td>
<td>+/-</td>
<td>favored</td>
<td>opposed</td>
<td>Forward: only at low temperatures</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
<td>+/-</td>
<td>opposed</td>
<td>favored</td>
<td>Forward: only at high temperatures</td>
</tr>
</tbody>
</table>

Three important thermodynamic parameters ΔG (free energy change), ΔH (enthalpy change) and ΔS (entropy change) can be used to obtain a better understanding of the dissolving process of KNO₃:

In this experiment for KNO₃ dissolving in water:
• ΔS is always positive since the randomness of the system increases
• ΔH is be positive if heat is added (endothermic), and negative if heat is released for KNO₃ dissolving in water (exothermic).
• ΔG is negative (thermodynamically favored) if ΔG is negative, but the opposite direction (dissolving is not thermodynamically favored) if ΔG is positive.

Several important equations will be used to determine these three parameters:
• ΔG = ΔH – TΔS
• ΔG = – R T ln(Ksp)
  Combining Eq. 3 & Eq. 4:
  • ΔH – TΔS = – R T ln(Ksp)
  [Eq. 5]
  For a reaction:
  \[ \ln(K_{sp}) = -\frac{\Delta H}{R} \left(\frac{1}{T}\right) + \frac{\Delta S}{R} \]
  [Eq. 6]
  \( y = mx + b \)

N.B., A plot of ln Ksp versus 1/T yields a straight line with a slope of –ΔH/R and a y-intercept of ΔS/R.
**Model - 1**

At 0°C, 1-L of KIO₃ (saturated) is prepared by dissolving 46.0 g KIO₃ in water. Determine the Ksp.

1. Balance equation:
   
   \[ \text{KIO}_3(s) \rightleftharpoons \text{K}^+(aq) + \text{IO}_3^-(aq) \]

2. Calculate [KIO₃]:
   
   \[
   \frac{46.0 \text{ g}}{1 \text{ L}} \times \frac{1 \text{ mol}}{214.0 \text{ g}} = 0.215 \text{ mol/L}
   \]

3. Calculate Ksp:
   
   \[ K_{sp} = [\text{K}^+] [\text{IO}_3^-] \]
   
   \[ K_{sp} = (0.215) (0.215) = 0.0462 \]

**Model - 2**

Determine ΔG at STP based on Ksp = 0.0462. (Use Eq. 4).

\[
\Delta G = -(R)(T)(\ln K_{sp})
\]

\[
\Delta G = -(8.314 \text{ J/K·mol})(0^\circ \text{C} + 273)(\ln 0.0462) = 6980 \text{ J/mol}
\]

(ΔG is negative so reaction is thermodynamically favored. In other words, KIO₃ is soluble in water at 0°C.)
Model – 3

Determine $\Delta H$ and $\Delta S$ from the following data:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$1/T$ (K$^{-1}$)</th>
<th>$K_{sp}$</th>
<th>$\ln K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>0.00366</td>
<td>0.0462</td>
<td>-3.07</td>
</tr>
<tr>
<td>293</td>
<td>0.00341</td>
<td>0.143</td>
<td>-1.94</td>
</tr>
<tr>
<td>373</td>
<td>0.00268</td>
<td>2.28</td>
<td>-0.824</td>
</tr>
</tbody>
</table>

1. Determine $\Delta H$ & $\Delta S$ (Use Eq. 6)

\[ y = -\frac{\Delta H}{R} \left(\frac{1}{T}\right) + \frac{\Delta S}{R} = -2120 \left(\frac{1}{T}\right) + 4.945 \quad (R^2 = 0.9241) \]

- $\Delta H$ is derived from the slope: $-2120 \text{ K} = -\frac{\Delta H}{R} = -\frac{\Delta H}{8.314 \text{ J/} \text{K} \cdot \text{mol}}$

\[ \Rightarrow \Delta H = (2120 \text{ K})(8.314 \text{ J/} \text{K} \cdot \text{mol}) \quad \Rightarrow \Delta H = 1.763 \times 10^4 \text{ J/mol} \]

- $\Delta S$ is derived from the y-intercept: $4.945 = \frac{\Delta S}{R} = -\frac{\Delta S}{8.314 \text{ J/} \text{K} \cdot \text{mol}} \quad \Rightarrow \Delta S = 41.13 \text{ J/K-mol}$

- $\Delta G$ can also be derived from Eq. 3: $\Delta G = \Delta H - T\Delta S$

\[ \Rightarrow \Delta G = (1763 \text{ J/mol}) - (273 \text{K})(41.13 \text{ J/K-mol}) \quad \Rightarrow \Delta G = -9465 \text{ J/mol} \]

2. The dissolving of KIO$_3$ is endothermic by thermodynamically favored. Explain.

Dissolving KIO$_3$ requires energy and, if this were the only factor, the reaction would not be thermodynamically favored. However, what makes dissolving thermodynamically favored is the increase in entropy. The dispersion of the resulting ions throughout the water releases more energy than the enthalpy required to separate the ions.
**Pre-Lab**

1. How do you determine if the solution is saturated? Explain.

2. What is the equilibrium equation for the solubility constant of LiCl(s)?

3. What is the equation for the solubility product of LiCl?

4. Why isn’t LiCl(s) included in the equation?

   The solubility of LiCl in water at 20°C is 550.0 g/L.
   a. Calculate the molar concentrations of LiCl, Li⁺ and Cl⁻:

   b. Calculate Ksp for LiCl (20°C).

5. a. Fill in the below table for the solubility of NaF at different temperatures.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Ksp</th>
<th>Temp (K)</th>
<th>1/T (K⁻¹)</th>
<th>ln Ksp</th>
<th>ΔG (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.751</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.925</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>1.446</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
b. Plot $\ln K_{sp}$ as a function of $1/T$. Fit the data and determine the slope of the line.

\begin{equation}
Y = -654.31x + 2.1295 \quad R^2 = 0.9952
\end{equation}

\textbf{c. Calculate }$\Delta H$ and $\Delta S$.

$\Delta H$ is derived from the slope:

\[\Delta H = \frac{-654.31 \text{ K}}{8.314 \text{ J/K} \cdot \text{mol}} \Rightarrow \Delta H = 5.440 \times 10^3 \text{ J/mol}\]

$\Delta S$ is derived from the y-intercept:

\[\Delta S = \frac{2.2195 \text{ K}}{8.314 \text{ J/K} \cdot \text{mol}} \Rightarrow \Delta S = 18.25 \text{ J/mol}\]
**PROCEDURE**

1. Assemble a hot water bath. (Figure 1)

2. Measure ca. 20 g of KNO₃. Record the exact mass and transfer to a dry, clean 200-mL test tube.

3. Add 15 mL of d.i. water to the test tube. Cover with Parafilm.

4. Heat the tube in the water bath, stirring the mixture with a stir rod until all of the KNO₃ has dissolved.

5. Remove the test tube (using a test tube holder) and quickly dry the outside. Lift the thermometer and stirring rod until the thermometer bulb is just above the solution Mark and label the level of the solution in the test tube as “1”.

6. Let cool at room temperature. Record the temperature at which the first white crystal appears. This is the equilibrium temperature.

7. Add 5 mL of water to the test tube mixture.

8. Return the test tube to the hot water bath. Repeat heating and cooling (steps 4-7) for a total of four trials.

9. Dispose the KNO₃ solution into the waste container.
Name(s) ___________________________  Section _______  Date ________ 

DATA SHEET

1. Mass of KNO₃ (g) ________________  Moles of KNO₃ (mol) ________________

2. Calculation:

**Calculation of ΔG (kJ/mol) from K<sub>sp</sub>**

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
<th>Trial 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total volume (mL)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration (M) of [KNO₃] = [K⁺] = [NO₃⁻]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K&lt;sub&gt;sp&lt;/sub&gt; = [K⁺][NO₃⁻]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature(°C) when white crystal forms</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature(K) when white crystal forms</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔG = -RTlnK&lt;sub&gt;sp&lt;/sub&gt; (Eq. 3)</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

**Calculation of ΔH (kJ/mol) and ΔS (J/K•mol)**

<table>
<thead>
<tr>
<th>1/T (K⁻¹)</th>
<th>Linear fitting equation from the graph</th>
<th>R² value of the linear fitting</th>
<th>Slope of the line</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
</table>

**Calculation of ΔS (J/K•mol) (method 1 based on Equation 6)**

y intercept of the linear line

ΔS (J/K•mol)

**Calculation of ΔS (J/K•mol) (method 2 based on Equation 4 ΔG = ΔH – TΔS)**

ΔS (J/K•mol)

Average ΔS (J/K•mol)