Investigation 4: Solubility and Thermodynamics

Focus Questions: *How, mathematically, does temperature effect the equilibrium constant (Ksp)? How can experimental data for the solubility of a salt be used to determine the thermodynamic parameters of a reaction?*

Pre-lab reading

Chemistry; and Atoms-Focused Approach: Section 16.8

Primers:

Using the balance
Volumetric glassware use – General

Safety and Waste Disposal

- Eye protection should be worn at all times.
- Dispose of all solutions in properly labeled waste containers.

Background

The dissociation that occurs when potassium nitrate, a strong electrolyte, dissolves in water can be represented by equation 1

$$KNO_{3(s)} + H_2O_{(l)} \rightleftharpoons K^+_{(aq)} + NO_3^-{}_{(aq)} \qquad (1)$$

When solid potassium nitrate crystallizes from a saturated solution of the salt (the reverse process in the above equation), the system is at equilibrium. Since 1 mole of the dissolved salt will produce 1 mole each of potassium ions and nitrate ions, the equilibrium constant, K, for the dissociation reaction is equal to the square of the solubility (*s*, in moles/liter) of the salt at that temperature (equation 2).

$$K = [K^+][NO_3^-] = (s)(s) = s^2 \qquad (2)$$

The equilibrium constant and the absolute temperature (T) at which the equilibrium constant was determined can be used to determine the ΔG of the reaction using equation 3,

$$\Delta G = -RT\ln K \qquad (3)$$

where R is the gas constant. Since

$$\Delta G = \Delta H - T\Delta S \qquad (4)$$

where ΔH is the enthalpy change and ΔS is the entropy change for the reaction, the two expressions for ΔG found in equations 3 and 4 can be set equal (equation 5).

$$-RT\ln K = \Delta H - T\Delta S \qquad (5)$$

Rearranging equation 5 gives

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (6)$$

In this experiment, values of K will be determined experimentally for various temperatures (T). By plotting lnK versus 1/T, ΔH and ΔS for the reaction can be determined (equation 6).

Procedure

Transfer about 10 grams (be sure to record the precise mass!) of potassium nitrate to a clean 50 mL graduated cylinder from which all plastic support and guard pieces have been removed. Add about 8 mL of DI water and heat the graduated cylinder by clamping it in a hot water bath made from a 600 mL beaker. Stir CAREFULLY with a thermometer until the KNO_3 has dissolved. Remove the thermometer and record the volume of the potassium nitrate solution (using the correct number of significant figures).

Remove the graduated cylinder from the water bath and stir the contents slowly and CAREFULLY with the thermometer while the solution cools. Record the temperature at which crystals first appear.

Add 2 to 3 mL of DI water to the graduated cylinder and warm the mixture in the hot water bath with stirring until the solid has completely dissolved. Remove the thermometer and record the volume of the solution. Remove the graduated cylinder from the water bath and stir the contents slowly and CAREFULLY with the thermometer while the solution cools. Record the temperature at which crystals first appear.

Repeat, adding additional 2 mL portions of DI water, dissolving the solid with in a water bath with stirring, and cooling to crystallize the solid until a crystallization temperature near room temperature is reached. If necessary, the solution may be placed in a cool water bath (NOT an ice bath) to hasten cooling.

References

Atkins, P.; Jones, L. “Chemical Principles: The Quest for Insight”, 6th ed.; Freeman: New York. **2013**.

Silberman, R. G. *J. Chem. Educ*. **1996**, *73*, 426-7.