Thermodynamics of Solubility: Graphical Determination of ΔH and ΔS

Objectives: To determine the thermodynamic values of ΔH and ΔS for the dissolution of a salt in aqueous solution

Materials: Potassium chloride (KCl): distilled water

Equipment: 25 x 250-mm test tube with 2-hole rubber stopper; thermometer; glass or wire stirring rod; iron rings and ring stand assembly (see Figure 1); ceramic-centered gauze heating pad; 400-mL beaker; Bunsen burner

Safety: Some inorganic salts/solutions are irritants. All samples and solutions should be handled carefully. Hot glassware should be handled with care. Eye goggles and appropriate lab attire should be worn at all times in the lab.

Waste disposal: Salt solutions should be placed in the inorganic waste container provided in the fume hood.

INTRODUCTION

The amount of solute that will dissolve in water depends on many factors, including temperature and the nature of the solute and solvent (i.e., molecular vs. ionic, polar vs. non-polar). **Salts**, such as table salt (sodium chloride), are ionic compounds consisting of cations and anions; ionic compounds are usually soluble in water, but the extent of solubility will vary from one salt to another. The dissolution process can be expressed as an equilibrium, in which the dissolved ions are in equilibrium with undissolved solid in a **saturated solution**. For example, the dissolution of a sparingly soluble salt, CaF_2 can be represented as

$$CaF_2(s) \leftrightarrow Ca^{2+}(aq) + 2F^-(aq) \qquad\qquad K_{sp} = [Ca^{2+}][F^-]^2$$

where the bidirectional arrow indicates an equilibrium between products and reactants, and K_{sp} is the equilibrium constant for the solubility equilibrium. Although K_{sp} is more commonly used to represent equilibria of sparingly soluble salts, similar expressions can be used to represent the solubility of more soluble ionic compounds.

Many factors affect the solubility of a salt in aqueous solution. One of the major factors is the attractive forces between the ions in the solid salt compared to the attractive forces between the ions and the polar solvent, water. The energy of attraction between the ionic particles in the solid state is called the crystal lattice energy (E_{CL}), and is related to both the size and the charge on the ions. In order for the ions to dissolve in solution, these attractive forces must be overcome, an endothermic process which requires an input of energy equal to E_{CL}. The energy of attraction between the ions and the polar solvent is called the enthalpy of solvation ($\Delta H_{solvation}$) and is

typically exothermic. Whether or not the overall dissolution process is endothermic or exothermic depends on the relative magnitudes of the lattice energy and the enthalpy of solvation.

$$\Delta H_{solution} = \Delta H_{solvation} + (-E_{CL}) \tag{1}$$

If the overall enthalpy of solution is exothermic, dissolution is energetically favorable. However, enthalpy is not the only factor involved in the process. The entropy change (ΔS) associated with the dissolution of a substance also plays a vital role. Entropy is related to the number of microstates in a chemical system, or the number of ways that energy can be distributed. In the solid state, ions are locked into a rigid configuration within the crystal lattice, and the number of microstates available to a given ion is limited. When dissolved in solution, the solvated ions can occupy a nearly infinite array of microstates, so the entropy of the ions in solution is much greater than the entropy of ions in the solid state. Therefore, the dissolution process is typically entropically favored.

The combination of enthalpy and entropy will determine the relative position of the solubility equilibrium:

$$-RT \ln (K_{sp}) = \Delta H_{solution} - T\Delta S_{solution} \tag{2}$$

If we rearrange Eq. 2 to isolate the ln (K_{sp}) term, we obtain:

$$ln (K_{sp}) = \frac{\Delta H}{R}\left(\frac{1}{T}\right) - \frac{\Delta S}{R} \tag{3}$$

Equation (3) takes the form of a straight line equation, $y = mx + b$, which provides us with a method to estimate the values of ΔH and ΔS. More specifically, if we can determine the value of K_{sp} for a given solubility equilibrium at multiple temperatures, we can plot ln (K_{sp}) vs. $1/T$ (in Kelvin) to obtain a line with slope = $\Delta H/R$ and an intercept = $\Delta S/R$. The first step in this method requires the calculation of K_{sp} at multiple temperatures.

Since K_{sp} is related to the concentrations of dissolved ions, we can calculate K_{sp} if we can measure the concentrations of the ions in solution. There are multiple methods to do so. Consider, for example, the K_{sp} equilibrium of CaF_2 presented in the beginning of the Introduction. The F^- ion acts like a base in solution, and so its concentration can be determined by titration with a standard acid solution. If aliquots of saturated CaF_2 solutions at various temperatures are obtained and titrated, the value of K_{sp} can be calculated at each temperature.

Another approach is to determine the **saturation temperature** of a solution in which the concentrations of ions are known. The simplest way to obtain the saturation temperature is to add a known amount of salt to a given volume of water, and heat up the solution. When all the salt is dissolved the system is no longer in equilibrium (remember, equilibrium requires that both solid and dissolved ions be present simultaneously), but the concentration of dissolved salt is known. If the solution is now allowed to cool, at some point solid crystals will begin to form and the solution establishes an equilibrium. The temperature at which solid crystals start to form is the

saturation temperature for that concentration of ions, and the K_{sp} for the solubility equilibrium at the saturation temperature can be calculated from the ion concentrations.

This approach is illustrated in Example 1.

Example 1. A student dissolves 5.10 g of KNO₃ in 3.50 mL of water in a test tube and stirs until the solution is saturated. The student then immerses the test tube in a hot water bath at 80 ºC and stirs until all the undissolved salt is dissolved in solution.

The student then removes the test tube from the water bath and, while stirring, monitors the temperature of the solution as it cools. When the temperature of the solution reaches 63 ºC, crystals of salt begin to form in the solution. Calculate the value of K_{sp} for the dissolution of KNO₃ at this temperature.

Solution: The dissolution equilibrium for KNO₃ can be written as:

$$KNO_3(s) \leftrightarrow K^+(aq) + NO_3^-(aq) \qquad\qquad K_{sp} = [K^+][NO_3^-]$$

The solution contains 5.10 g of KNO₃ in 3.50 mL of water when crystals start to form at 63 ºC. We can convert the mass of KNO₃ to moles to obtain the following concentrations:

$$[K^+] = [NO_3^-] = \left(\frac{5.10g\ KNO_3}{101.0\ g/mol}\right)\left(\frac{1}{3.50\ mL}\right)\left(\frac{1000\ mL}{L}\right) = 14.43\ M$$

From the concentrations of K^+ and NO_3^- we can calculate at the saturation temperature (63 ºC) for this solution concentration:

$$K_{sp} = [K^+][NO_3^-] = (14.43)^2 = 208.2$$

The large value of K_{sp} for the solution in Example 1 is consistent for a salt that is readily soluble. If the same procedure is repeated with solutions of different concentrations, we can determine the saturation temperatures for each concentration and the value of K_{sp} at each temperature. With this information we can obtain a plot of ln (K_{sp}) vs. 1/T.

In this exercise you will examine the effect of temperature on the solubility of potassium chloride, KCl. You will observe how solubility changes with temperature and use this information to calculate the value of the equilibrium constant for the solubility equilibrium, plot ln (K_{sp}) vs. 1/T, and calculate the value of ΔH and ΔS for the dissolution of KCl.

Pre-Lab Questions

1.   What factors determine the solubility of a salt in water? Explain.

2.   A student is evaluating the solubility potassium chlorate ($KClO_3$; MW = 122.5 g/mol) at various temperatures. She dissolves 2.50 g of $KClO_3$ in a total volume of 7.5 mL of water.

   a.   Calculate the concentration of $KClO_3$ in this solution in g/100 mL.

   b. Calculate the concentration of $KClO_3$ in this solution in mol/L.

   c. The student heats the solution up to 80°C, and then removes the test tube containing the salt solution from the hot water bath. Crystals of $KClO_3$ appear at 74°C. Calculate the value of K_{sp} for $KClO_3$ at this temperature.

PROCEDURE

1. Obtain a test tube and stopper, and assemble the apparatus illustrated in Figure 1.

   NOTE: If the thermometer and stirring rod are not already inserted in the rubber stopper, insert them carefully. Apply a small amount of glycerine or other lubricant to the stopper holes. Grasp the thermometer or glass rod with a cloth or paper towel, and carefully insert into the stopper hole using a twisting motion while applying gentle pressure. Excessive force may result in breakage and possible injury. Fill the 400-mL beaker with approximately 300 mL of water, and place on the wire gauze pad as illustrated in Figure 1.

2. Place the clamp assembly holding the test tube and stopper on the ring stand, but do not lower it into the beaker at this time.
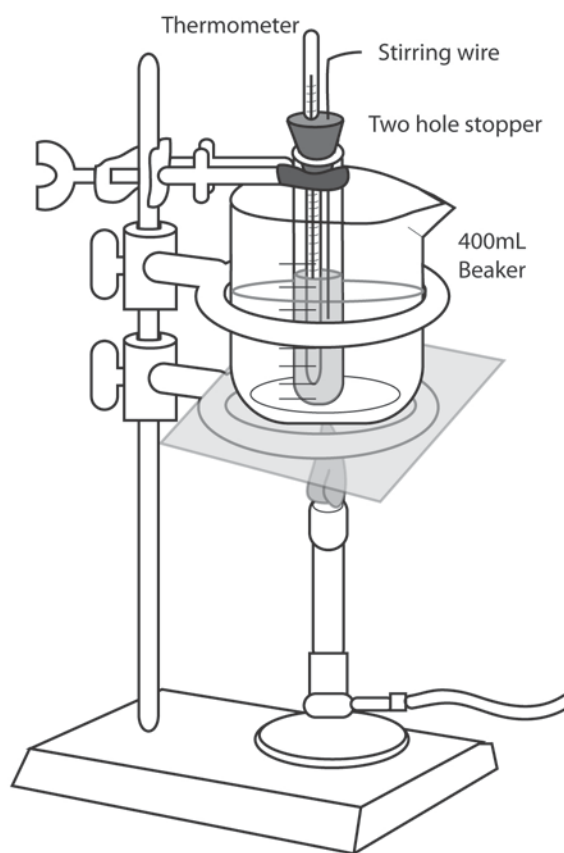
Figure 1. Apparatus for determining saturation temps of salt solutions.

3. Light the Bunsen burner and place it below the wire gauze pad to being heating the water in the beaker. Use a second thermometer to monitor the temperature of the water in the beaker. While the water is heating, prepare the original solution of your unknown salt.

I.   Determining the Saturation Temperature of Original Salt Solution

4. Obtain approximately 5 g of KCl on a piece of weighing paper or weighing boat. Weigh the sample + paper and record this mass on your Data Sheet to the nearest mg.

5. Carefully transfer <u>all</u> of your sample to your test tube. Reweigh the weighing paper or boat, and record this weight on your Data Sheet to the nearest mg.

6. Fill a clean 50-mL buret with distilled water. Dispense 10.00 mL of distilled water from the buret into the test tube containing your unknown sample. Record the actual volume of water added to your test tube to the nearest 0.01 mL.

7. Replace the rubber stopper with thermometer and stirring rod in the test tube. Be sure the thermometer bulb is about 1 cm above the bottom of the test tube.

8. When the temperature of the water in the beaker is about 80°C, proceed to step 10.

9. Clamp the test tube to the ring stand using a utility clamp, and lower the test tube assembly into the hot water bath until the level of water in the test tube is aligned with the level of water in the beaker. Secure the utility clamp to the ring stand.

10. Stir the mixture in the test tube by slowly moving the stirring rod up and down in the solution. Continue mixing and heating the test tube and contents to 80°C.

11. If the salt sample is not completely dissolved when the temperature of the solution has reached 80°C, remove the test tube from the hot water bath and add 0.50 mL of distilled water to your test tube. Record on your Data Sheet the exact total volume of water added to the test tube.

12. Reheat the test tube and contents in the hot water bath to 80°C while stirring carefully.

13. If necessary, repeat steps 12 and 13 until your salt sample is completely dissolved in solution at 80°C.

14. After the salt has completely dissolved, loosen the clamp holding the test tube to the ring stand and lift the test tube out of the hot water bath. Reclamp the test tube in a different position so the test tube and contents are no longer immersed in the hot water bath.

15. Continue to stir the solution in the test tube while monitoring the temperature of the solution in the test tube.

16. Carefully observe the solution while it cools. Note the temperature at which the salt begins to recrystallize from solution. This is the saturation temperature for your original salt solution. Record this temperature on your Data Sheet. If you are in doubt about the saturation temperature, reheat your solution to 80°C and repeat steps 16–18.

II. Determining the Saturation Temperature of Diluted Salt Solutions

17. Add 1.00 mL of distilled water from the buret to the solution in your test tube. As before, record the exact total volume of water added to your test tube.

18. Replace the test tube in the hot water bath and heat it while stirring until all the salt crystals have dissolved into solution.

19. Remove the test tube from the hot water bath and allow the solution to cool while stirring. Note the temperature at which salt crystals begin to form. Record the saturation temperature for your diluted salt solution on your Data Sheet.

20. Repeat Steps 18–20 until you have obtained saturation data for at least five different solution concentrations. If the saturation temperature falls below room temperature, replace the hot water bath with an ice bath. .

CALCULATIONS

1. Calculate the solubility of the KCl (in grams of salt per 100 mL of water) at the original saturation temperature. Record this solubility on your Data Sheet.

2. Recalculate the solubility of each of your diluted salt solutions, and record these solubilities along with the observed saturation temperatures on your Data Sheet.

3. Prepare a solubility-temperature curve for your salt.

4. From the solubility at each temperature, calculate the concentration of KCl in each of the trials and enter these values in the Data Table. (KCl = 74.55 g/mol)

5. From the concentration of KCl at each saturation temperature, calculate the value of K_{sp} and $\ln (K_{sp})$ for each temperature. ($K_{sp} = [K^+][Cl^-]$)

6. Plot $\ln (K_{sp})$ vs. $1/T$. Remember to convert saturation temperatures to Kelvin before calculating $1/T$. It is recommended that the data be plotted using a spreadsheet program such as MS Excel, from which a regression line or trend line equation can be calculated to obtain the slope and intercept values.

7. Use the slope and intercept to calculate ΔH and ΔS for the dissolution of KCl.

Data Sheet

I.   Determining the Saturation Temperature of the Original Salt Solution

Mass of weigh paper + sample (g)   _____

Mass of weigh paper (g)   _____

Mass of sample (g)*   _____

Total volume of water added (mL)   _____

Saturation temperature (^{o}C)   _____

Solubility (g salt/100 mL water)   _____

II.   Determining the Saturation Temperature of Diluted Salt Solutions

Total volume of original solution (mL): _____

Volume of water added (mL)	Total volume of diluted solution (mL)	Saturation Temperature (^{o}C)	Solubility (g salt/100 mL H$_2$O)

III.   Calculation of K$_{sp}$

Solubility (g/100 mL)	Concentration (mol/L)	Saturation T (Kelvin)	1/T	K$_{sp}$	ln (K$_{sp}$)

Trend line equation: _____ ΔH = _____ ΔS = _____

Post-Lab Questions

1. While transferring the weighed salt to the test tube in this experiment, a student accidently spilled some of their sample. How will this salt loss affect the salt solubilities calculated by this student? Will they be too high, too low, or unaffected? Explain.

2. It is important to keep the test tube closed to avoid evaporation of water while heating the salt solution.

    (a) Briefly explain how a loss of water by evaporation would affect the initial calculation of the solubility of your salt.

    (b) How would this affect your calculated value of K_{sp}?

    (c) Assuming that the loss of water by evaporation affected all subsequent calculated concentrations in the same manner, how would this ultimately affect the values of ΔH and ΔS obtained by graphical analysis.

3. Explain the chemical significance of the entropy change for dissolution of a salt.