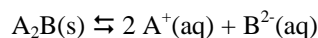


When man tries to imagine Paradise on earth, the immediate result is a very respectable Hell.  
--Paul Claudel

## The Thermodynamics of Solubility Equilibrium

In addition to the homogeneous equilibrium you have investigated in earlier experiments, an important heterogeneous equilibrium exists for many salts and their solutions. At some point as solute concentration is increased the solubility limit at a given temperature is reached. We say the solution is "saturated". Typically some undissolved solute will remain in the mixture and thus the potential for equilibrium between the solid phase and the dissolved solute in solution exists. For a hypothetical salt  $A_2B$ , the solubility equilibrium and equilibrium constant are expressed as:



$$K_c = [A^+]^2[B^{2-}]$$

The amount of  $A_2B$  that dissolves is the "solubility" which can be expressed in any convenient units--here moles/Litre or Molarity is useful. From the reaction above you can see that this amount is the same as the amount of  $B^{2-}$  ion that enters the solution. Thus if we use the letter  $s$  to represent the solubility of  $A_2B$ , we can rewrite the equilibrium constant as:

$$K_c = (2s)^2s$$

Notice that the quantity  $2s$  is substituted for  $[A^+]$ . This maintains the stoichiometric relationship with  $[B^{2-}]$  while allowing the use of a single variable. Because the equilibrium constant is expressed as the product (as in multiplication) of solubilities, it is generally called the "solubility product constant" and given the symbol  $K_{sp}$ .

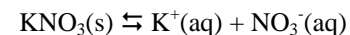
Typically when we speak about  $K_{sp}$  values we are interested in very slightly soluble salts--the kinds of compounds you learned as "insoluble" in your solubility rules. But the quantity can be calculated for *any* salt as long as you have solubility data. **However, determining  $K_{sp}$  values from simple experiments in which solubility is measured almost never yields accurate results, even for very insoluble compounds.** The reasons for this are complex and have to do with ion interactions which occur in all but the most dilute of solutions. In other words, there are "ideal" solutions (the kind we talk about) and "real" solutions (the kind we steer clear of) just as there are ideal and real gases.

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Adapted from: Solubility and Thermodynamics: An Introductory Experiment, Robert G. Silberman, *J. Chem. Educ.*, 1996, vol. 73, No. 5, p. 426

For the purposes of this experiment we will ignore the effects of ion interaction. In fact, we will be using a very soluble salt,  $KNO_3$ , because it has characteristics that make it easy to work with, it's inexpensive, relatively harmless as used, and easily recovered for reuse.

The equilibrium established in a saturated solution of  $KNO_3$  may be represented as:



As with all equilibria, the relative amounts of products and reactants at a given temperature are determined by the "tension" between the tendency toward maximum entropy and the tendency toward minimum energy. In this experiment you will first determine the solubility of potassium nitrate at a variety of temperatures and then use the solubility to calculate the " $K_{sp}$ " of the salt. Recall the relationship between the equilibrium constant and the free energy change,  $\Delta G^\circ$ :

$$\Delta G^\circ = -RT \ln K$$

where  $R = 8.31 \text{ J/mol}\cdot\text{K}$  and  $T$  is the temperature in Kelvin. So you can determine the free energy change at each temperature from the  $K_{sp}$  at each temperature.

The *sign* of the enthalpy change ( $\Delta H$ ) should be clear from the solubility behavior (i.e., whether more or less dissolves at higher temperatures) but the value of  $\Delta H$  can also be determined from the value of the  $K_{sp}$ . It is known that over small temperature ranges,  $K$  and  $\Delta H$  are related as follows:

$$\ln K = -\frac{\Delta H}{R} \frac{1}{T} + C$$

$$y = m x + b$$

So a plot of the natural logs of the values of  $K_{sp}$  vs.  $1/T$  (in Kelvin) will yield a nearly straight line with slope =  $-\Delta H/R$  (again,  $R = 8.31 \text{ J/mol}\cdot\text{K}$ ).

And, of course, once you know  $\Delta G$  and  $\Delta H$ , you can determine  $\Delta S$  at each temperature. Again, it should be clear what the *sign* of the entropy change will be considering the process.

To summarize: you will determine the solubility of  $KNO_3$  in water at different temperatures and use this information to calculate the " $K_{sp}$ " of the salt. From the  $K_{sp}$  you will determine the free energy change, enthalpy change and entropy change for this process and compare them to the values calculated from tables in your text.

### Preparing to experiment

You will be provided with the following materials:

1. solid  $\text{KNO}_3$  (use about 3 g)
2. a temperature probe
3. a boiling water bath

Design an experiment to determine the temperature at which  $\text{KNO}_3$  becomes insoluble in water (to start, add distilled water to the 4 mL mark with the solid already in the cylinder), gradually diluting the solution by 3 additions of 1 mL each and repeating the measurements. [see **Technique**]

**BE SURE TO BRING YOUR TI-83/84 CALCULATOR TO CLASS FOR THIS EXPERIMENT. YOU WILL ALSO NEED A COPY OF THE HCHEM.83G FILES IN YOUR CALCULATOR MEMORY.**

### Pre-lab take-home quiz

These questions should be answered on a separate sheet of paper to be turned in on the day you do this experiment.

1. The solubility of  $\text{ZnS}$  at  $25^\circ\text{C}$  is  $3.5 \times 10^{-12}$  M. What is the  $K_{\text{sp}}$  for  $\text{ZnS}$ ? What is  $\Delta G^\circ$  at  $25^\circ\text{C}$ ?
2. The  $K_{\text{sp}}$  for  $\text{Ag}_2\text{S}$  is  $4.1 \times 10^{-52}$ . What is  $[\text{Ag}^+]$  in a saturated solution of  $\text{Ag}_2\text{S}$ ?
3. The  $K_{\text{sp}}$  for  $\text{Ag}_2\text{CrO}_4$  is  $9.0 \times 10^{-12}$ . If 200 mL of 0.0050 M  $\text{AgNO}_3$  is combined with 300 mL of 0.0020 M  $\text{K}_2\text{CrO}_4$ , will a precipitate form?

### Technique

#### 1. Determining the solubility

In order to determine the solubility in moles/Litre you need to know the moles of solute (easy) and the volume of the solution. To make this second piece of information easier to get, you can do the experiment in your 10 mL graduated cylinder (remove the plastic base before heating). The initial volume can be read directly from the cylinder *once the solid has dissolved* (stir in the hot water). Each 1 mL addition thereafter will increase the volume, but again you should record the volume only after redissolving the solid in the hot water bath.

Try to minimize the amount of time the cylinder spends in the hot water, i.e., don't leave it there any longer than needed to dissolve the solid. Otherwise you will spend a lot of time waiting for the solution to cool before crystals form. Always keep the solution stirred and record the first temperature that crystals become visible. Experience seems to indicate that the falling temperature levels off a little as crystallization occurs. *Be careful not to lose solid as you remove the thermometer probe from the cylinder to add more water.*

**KEEP THE THERMOMETER PROBE CABLE AWAY FROM THE HOTPLATE!!!!!!!!!!**

#### 2. Recycling the $\text{KNO}_3$

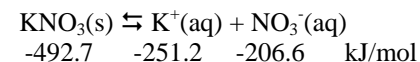
After you have your four readings, pour your solution into the beaker indicated by your instructor. The water can be evaporated and the potassium nitrate reused.

### The Chemicals

**Potassium nitrate** is commonly known as "saltpeter". It is a colorless, odorless solid with a saline, pungent taste. It is used in fireworks, pickling brines, the manufacture of glass, matches, gunpowder, freezing mixtures and candle wicks.

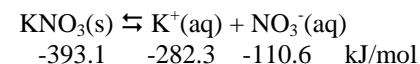
### Analysis

1. Use the mass of  $\text{KNO}_3$  and the measured volumes of the various mixtures to calculate the Molarities (solubilities) for each of the four trials.
2. Plot a graph of the solubility of  $\text{KNO}_3$  (in mole/L) vs. the temperature. What does this graph suggest about the sign of  $\Delta H$  for this process? Explain.
3. Use the calculated solubilities to determine the " $K_{\text{sp}}$ " for potassium nitrate at the four temperatures measured. Then plot a graph as described in the introduction to determine the value of  $\Delta H$  for this process. The  $\Delta H_f^\circ$  values for the process are given below.



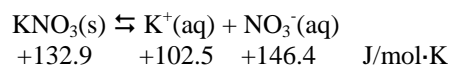
Calculate  $\Delta H_{\text{rxn}}$  from them. Explain any disagreement.

4. Calculate the free energy change for this process at each of the four temperatures measured, using your " $K_{\text{sp}}$ " values from #3. The  $\Delta G_f^\circ$  values for the process are given below:



Calculate  $\Delta G_{\text{rxn}}$  from them. Explain any disagreement.

5. Use the experimental values of  $\Delta G$  and  $\Delta H$  to calculate  $\Delta S$  at each of the four temperatures. The  $S^\circ$  values for the process are given below:



Calculate  $\Delta S_{\text{rxn}}$  from them. Explain any disagreement. How does the sign on  $\Delta S$  "fit" this process? Is this process entropy or enthalpy driven--or both? Explain.

### Now the "truth"

You already know that we choose to assume gases behave ideally because it greatly simplifies ordinary work in the lab and some of the mathematics that goes along with it. The same is true about solutions. What you have learned about the equilibrium in saturated solutions is true enough, but what you have not been told is that ions, even in rather dilute solutions, can clump together in groups, or establish quite large hydration spheres with water, etc. In other words, sometimes the actual concentration of "ions" in a solution is difficult to determine by simple experimental means.

The most accurate determinations of  $K_{\text{sp}}$  are done by examining successively more dilute solutions in light of a mathematical model of "real" solutions. When this is done and the ion concentration is extrapolated to zero, the "official"  $K_{\text{sp}}$  or what is sometimes call the thermodynamic  $K_{\text{sp}}$  is found. This value *should* come close to the value you would get if you found  $\Delta G^\circ$  for the process and then used the expression  $\Delta G^\circ = -RT \ln K_{\text{sp}}$  to determine the  $K_{\text{sp}}$ . This often results in disagreements between ordinary experimental values and calculated values related by factors of 10 or 100!!!!

**MORAL:** Basic solubility and  $K_{\text{sp}}$  concepts are deceptively simple and not meant to be strictly mathematical.