Only a fool tests the depth
of the river with both feet
--Ashanti proverb

The Process of Solution

Like any other chemical or physical process, the dissolving of a solid in water involves some kind of eventual balance between enthalpy and entropy changes. You have already spent a good deal of time and effort committing the "solubility rules" to memory, but the actual processes behind dissolving are by no means as simple as a few rules. The fact that the rules seem to follow no obvious pattern is an indication that solubility is a fairly complex phenomenon.

It is, however, possible to arrive at an overview of the process which is relatively straightforward and general enough to explain most aspects of dissolving. To do so, the process of solution is broken down into three hypothetical "steps":

1. Solute particles separate from the solid mass
2. Solvent particles move apart to make room for the separated solute particles
3. Solvent and solute particles are attracted to one another

The first two steps *increase* the potential energy of the solute and solvent particles and are thus **endothermic**. The final step results in a *decrease* in potential energy for the particles and so is **exothermic**.

Taken together, these three enthalpy changes determine the sign and magnitude of the **heat of solution** (ΔH_{soln}), or the heat absorbed or released when a substance dissolves in a solvent (generally water). It is possible to estimate the relative magnitudes of each change and thus guesstimate at least the sign for ΔH_{soln} for many solutes. For example, an ionic solute requires considerable energy to break up (high +) and water, which is highly polar, requires a lot of energy to separate the water molecules in order to make "room" for the dissolved solute (another high +). But the resulting ions strongly attract polar water molecules, so the third energy change is a large negative number. This final effect tends to nearly cancel the first two so that heats of solution for ionic compounds in water tend to be rather small and can be either + or - .

The *entropy* changes associated with solids dissolving in water can also be considered. Certainly the first two steps in the process as listed above would be expected to increase the entropy as they both provide for increased freedom of movement for the solute and solvent particles (and thus more kinds of motions for energy dispersal). By its very nature, the last step yields a mixture in which modes of motion that were not possible in either pure component are now possible. Placing a molecule of A in a position where there formerly could only have been a molecule of B increases the entropy of the system *so there is generally an overall increase in entropy when a solid dissolves in water*.

From this brief discussion it would seem that the heat of solution depends mainly on the type and strength of the intermolecular forces and/or bonding operating in the mixture. In this investigation we will narrow the scope somewhat by examining *univalent* ionic compounds dissolving in water. A *univalent* compound is composed of ions with +1 and -1 charges. It might be helpful to recall that the strength of an ionic bond can be estimated by the electronegativity difference between the elements and that polar water molecules interact most strongly with very small ions rather than large ones (charges being equal).

To make the exercise somewhat more interesting, we will look at a *series* of compounds for periodic effects: NaCl, NaBr, NaI, and LiCl.

Preparing to experiment

You will be provided with the following materials:

1. a calorimeter w/cover and stirring bar
2. a thermometer probe
3. solid samples of NaCl, NaBr, NaI, LiCl (use about 1 g/15 g water)

Design an experiment to determine the heat of solution of each compound.

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 on next page]

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. List the compounds NaCl, NaBr and NaI in order of increasing bond strength and tell how you arrived at the list.

2. A sample of 2.50 g LiI is added to 75.0 mL of water initially at 21.0^{o}C. After stirring and dissolving, the temperature of the solution is 24.3^{o}C. Assume that the specific heat of the <u>solution</u> is 4.184 J/g^{o}C, the density is 1.00 g/mL, and the calorimeter constant is 40.0 J/^{o}C. Determine the heat of solution for LiI (ΔH_{soln}).

The chemicals

Sodium bromide is a white crystalline substance that absorbs water from the air slowly. It is used in photography and in medicine as a sedative.

Sodium iodide is white, odorless and deliquescent. It slowly turns brown when exposed to air due to oxidation that forms iodine. Its uses parallel those of potassium iodide. It is also used in medicine as an expectorant.

Lithium chloride is a very deliquescent solid with a sharp saline taste. It is used in the manufacture of mineral waters, in fireworks and in the soldering of aluminum. It has been used in medicine as a treatment for manic psychosis, and formerly as a salt-substitute for low sodium diets.

Analysis

[You may assume in your analysis that the average specific heat of each solution is 4.184 J/g^{o}C. Be careful in comparing enthalpy changes with different signs. A ΔH value of -50 kJ is *greater* than a ΔH value of +25 kJ. Remember, the sign simply indicates the direction of heat flow. Thus it is better to say things like “more exothermic” or “more negative” in comparing values rather than “larger” or “smaller”.]

1. Use your data to determine the heat gained or lost in each trial (be sure to include the calorimeter constant in your calculations; it was given in a previous experiment as 5.6 J/^{o}C).

2. Use your answers to #1 and the moles of each solid used to determine the molar heat of solution (ΔH_{soln}) in each case. Be sure to add an appropriate sign to each answer.

3. What is the trend in heat of solution for the sequence NaCl, NaBr, NaI? What factor(s) is/are probably most important here? (*hint*: think about the three factors that determine the heat of solution and then consider the strength of the bonds and sizes of the ions)

4. Explain how the heat of solution for LiCl fits into the picture based on your answer to #3.

5. For each solid, tell what is the driving force behind solution: enthalpy, entropy or both---and say WHY.

6. Predict the sign of ΔH_{soln} for KCl. Explain your prediction.