Men argue, Nature acts
--Voltaire

An Entropy-driven Reaction

According to the second law of thermodynamics, a process is spontaneous only if the entropy of the universe increases as it occurs. It's difficult enough to keep track of the entropy of your notebook, let alone the *universe*, and of course that is one reason why the quantity of **free energy** (ΔG^o) is so handy. It allows us to predict (based on thermodynamic data and a simple calculation) whether a process will be spontaneous without doing bookkeeping on the entropy changes occurring in the system and surroundings.

Still, the concept is fairly simple, and although entropy increase is the ultimate determining factor for reaction spontaneity, it is sometimes difficult to identify in our ordinary experience a process which is "entropy-driven" (i.e. is both endothermic and spontaneous). You will investigate such a process in this experiment.

Preparing to experiment

You will be provided with the following materials:

1. a calorimeter
2. $Na_2SO_4 \cdot 10\ H_2O$ (use about 1.00 g)
3. NH_4NO_3 (use about 0.60 g)
4. a temperature probe
5. a plastic stirring rod
6. a large test tube

Design an experiment to investigate the reaction between these two solids, using a test tube as a reaction vessel (a special top has been provided with the calorimeter that will allow you to place the test tube through the center hole). Use about 50 mL of water in the calorimeter. Measure the temperature change.

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.

Adapted from: A Cold Mixture of Sodium Sulfate Decahydrate and Ammonium Nitrate, Julie B. Ealy & James L. Ealy Jr., *Visualizing Chemistry*, ACS, 1995

Pre-lab take-home quiz

Answer these questions on a separate sheet of paper to be turned in on the day you do this experiment.

1. The reaction (not balanced) that takes place in the test tube between the solids is:

$$Na_2SO_4 \cdot 10\ H_2O(s) + NH_4NO_3(s) \rightarrow (NH_4)_2\ SO_4(aq) + \ NaNO_3(aq) + H_2O(\ell)$$

Balance the reaction.

2. Based on the suggested quantities given on the facing page, determine by calculation which substance will be the limiting reagent.

3. Thermodynamic data for the reaction is given below:

kJ/mol	$Na_2SO_4 \cdot 10\ H_2O$	NH_4NO_3	$(NH_4)_2SO_4$	$NaNO_3$	H_2O
ΔH^o_f	-4324	-365	-1173	-446	-286
ΔG^o_f	-3644	-184	-900	-372	-237

Calculate ΔH^o_{rxn}, ΔG^o_{rxn}, and ΔS^o_{rxn}. Write these values somewhere (in addition to on this assignment!) so you'll have them then you do the analysis of your data.

Technique

1. Reactions between solids

Most of the reactions we study in the lab occur in water solution or between gases. However, reactions *can* occur between solids and the change in this experiment is a good example. In order to achieve as complete a reaction as possible, *it is important to mix the solids thoroughly*. This is especially true if quantitative information is desired (as in this experiment where the enthalpy change is sought). You can best achieve this by using a stirring rod to mix the solids once the test tube has been inserted in the calorimeter.

The chemicals

Sodium sulfate decahydrate is a white crystalline solid also known as Glauber's salt after a 17th century alchemist who used it for a medicine. The salt is *efflorescent* (that means it spontaneously loses its water of hydration to the air if left uncovered--so don't). It is soluble in 1.5 parts of water and is used for standardizing dyes, in freezing mixtures and for dyeing and printing textiles.

Ammonium nitrate consists of odorless, deliquescent crystals (that means they gradually pick up water from the air if left uncovered---so don't). One gram dissolves in about 0.5 mL of water. It is used for making nitrous oxide (laughing gas), in freezing mixtures, explosives, matches, pyrotechnics and fertilizers. In historic times disastrous explosions have been attributed to ammonium nitrate (e.g., 1947 at Texas City), the most recent of which was the bombing of the Federal Building at Oklahoma City.

Analysis

These questions should be answered in your laboratory notebook following your observations.

1. Assuming that the density of water is 1.00 g/mL and the specific heat is 4.184 J/g^{o}C, use your data to determine the enthalpy change for the reaction *per mole of the limiting reagent*. Be sure to include the calorimeter constant in the calculations (5.0 J/^{o}C). Compare this to your calculated ΔH^{o}_{rxn} from the pre-lab quiz.

2. Based on the balanced equation would you expect the entropy of the system (ΔS_{sys}) to increase or decrease? Explain *briefly*.

3. Based on your data, does the entropy of the surroundings (ΔS_{surr}) increase or decrease during the reaction? Explain *briefly*.

4. Why is this reaction described as *entropy-driven*?

5. How does the entropy of the universe (ΔS_{univ}) change during the reaction? Explain how this is possible in light of your answers to 2 and 3.