

## Ye Olde Chem 112 Entropy Experiment

### I. Introduction

Entropy is one of the most important quantities discussed in Chemistry 102. It is also one of the most perplexing in all of science for a variety of reasons. First, entropy is ordinarily thought about as the measure of the "randomness" of a chemical system. But this definition begs several questions. What precisely is meant by the word "randomness". If randomness is indeed a property of molecules, how does one measure it? What units should one attach to "randomness"?

Second, entropy is a confusing concept because it really cannot be measured directly like, say, pH. There are no entropy meters to be found in science laboratories. One can really only measure entropy *indirectly* via other physical quantities. And even then, one can typically only measure entropy changes.

Thirdly, entropy confuses folks because it comes in more than one flavor. The vanilla flavor is *thermodynamic*: changes in thermodynamic entropy are equal to the heat received by a system divided by the temperature at which the heat is received, i.e.

$$\Delta S_{\text{thermo}} = \frac{Q_{\text{rec}}}{T} \quad (1)$$

**Equation (1)** tells us that to measure a change in thermodynamic entropy, one must really measure two quantities, namely  $Q_{\text{rec}}$  and  $T$ .

The chocolate flavor of entropy is *statistical*. There are several relevant formulae here. At heart all of them connect with the individual states of a chemical system.

The purpose of this lab to gain experience regarding entropy of both flavors via observations and measurements. Statistical entropy is the more complicated and nuanced flavor. So we will really look at only one facet with additional ones addressed in advanced chemistry courses.

### II. A Few Key Ideas About Entropy

(1) Both flavors of entropy have units of energy divided by absolute temperature. Thus entropy changes (again, both flavors) are measured and recorded in units of joules per degree Kelvin, calories per Kelvin, or liter-atmospheres per Kelvin.

Note that there is some *deja vu* regarding this subject. The gas constant  $R$  has units of energy per mole per Kelvin:  $R \approx 8.31 \text{ joules/mole-K} \approx 0.082 \text{ liter-atmospheres/mole-K}$ .  $R$  is thus sometimes referred to as the "molar entropy constant".

Yet there is a cousin of  $R$ , namely Boltzmann's constant  $k_B$ :

$$\begin{aligned}
 k_B &= R / N_{\text{Avogadro}} & (2) \\
 &= 8.31 \text{ (joules/mole-K)} \times \frac{1 \text{ mole}}{6.02 \times 10^{23}} \\
 &= 1.38 \times 10^{-23} \text{ joules/Kelvin}
 \end{aligned}$$

Boltzmann's constant is sometimes referred to as the "entropy constant". Not incidentally, Mr. Boltzmann's famous constant appears on Mr. Boltzmann's gravestone. Entropy was that important to him!

(2) Physically speaking, entropy is a measure of one's information about a system. A high-entropy system is one in which little is known about the states of the molecules. A low-entropy system is one for which a great deal is known about the molecules. The systems with maximum entropy are ones in which virtually nothing is known about the molecular states. The minimum entropy is in effect when virtually everything is known about the molecules.

The take-home point is that there is a close connection between entropy and information. For most people, information offers a more accessible idea than "randomness". Thus to increase one's information about a system means to decrease the system entropy. By contrast, if the entropy of a system is increased, it can only mean that there has somehow been a loss of information about the system.

(3) There are several ways to modify the entropy of a system. A few are listed as follows:

(a) Adding heat increases the entropy; cooling a system decreases its entropy. This applies to solids, liquids, and gases.

(b) Increasing the volume of a system increases the entropy; compressing a system reduces the entropy. This also applies to solids, liquids, and gases alike.

(c) Mixing chemical components together, for example salt and water, increases the entropy. Unmixing the components, say, by distillation or chromatography, reduces the system entropy.

(4) To increase the thermodynamic entropy of any system is child's play. All one has to do is add heat. To reduce the entropy of a system and thus gain information, however, can be tricky business.

***Very Important Take-Home Idea: Information is not free. Rather it costs work to reduce the entropy of a system and thereby gain information about it.***

The above tells us that there are close family ties between work, heat, entropy, and temperature. As stated earlier, entropy cannot be measured directly. But one can get a handle on  $\Delta S_{\text{thermo}}$  and  $\Delta S_{\text{statistical}}$  via combinations of heat, work, and temperature measurements. We will get a taste of such measurements in this lab.

(5) Here is another very important idea. A system whose entropy increases spontaneously (i.e. on its own) provides a solid gold opportunity for obtaining useful work. If one is sufficiently clever, one can obtain useful work from a system undergoing a spontaneous change. If one is not clever, or elects to squander the opportunity, the amount of energy available for work is converted sooner or later into heat.

The above few sentences are a nutshell version of the second law of thermodynamics. The first law is all about energy and its conservation as discussed in Chem 101. The second law is really about entropy. Not incidentally, the third law of thermodynamics is also about entropy. Entropy is weird because it falls on a short list of non-conserved quantities.

(6) Here is one last important but subtle idea. Entropy is a state function. This means that to measure its changes, a chemist need only compare the final and initial states. The details of the intermediate states are really of no consequence. If a chemist takes a batch of molecules from some **State A** to **State B**, the entropy change is the same no matter what path is selected. This is an important concept with consequences in everyday life.

### III. Experiment

#### A. Changes in Thermodynamic Entropy Due to Heat

Adding heat to any system, for example a flask of water, raises its temperature. The heat--the added amount plus the heat already there--is stored as random motion of the molecules. The increased motion brings with it a loss of information about the position of each molecule. And as stated in **Section II**, an increase in the entropy means a loss of information about the system.

For the first experiment, we will measure the thermodynamic entropy changes incurred by liquid water during heating. To begin, add approximately 200 grams of tap water to a clean 250 mL Erlenmeyer flask. Measure the initial temperature which will be referred to as  $T_i$ .

Now use a hotplate to heat the water slowly so that the temperature is raised by 5 degrees Centigrade--close enough is good enough. Let the temperature at this point be referred to as  $T_f$ .

As we saw in **Section II**, the change in thermodynamic entropy equals the heat received by a system divided by the temperature at which it is received. The heat received by 1.00 gram of water is given rather precisely by the following formula:

$$h_{H_2O} = 1.00874 \times (T_f - T_i) - (0.7067 / 2) \times 10^{-3} \times (T_f^2 - T_i^2) + (15.93 / 3) \times 10^{-6} \times (T_f^3 - T_i^3) \\ - (83.8 / 4) \times 10^{-9} \times (T_f^4 - T_i^4)$$

So the heat received by  $m$  grams of water from  $T_i$  to  $T_f$  is just  $m \times h_{H_2O}$ . Note that in all of the

above calculations,  $T_i$  and  $T_f$  have units of degrees Centigrade and  $h_{H_2O}$  has units of calories/gram.

For this heating process, calculate  $m \times h_{H_2O}$ . Then convert  $T_i$  from degrees Centigrade to degrees Kelvin.

The thermodynamic entropy change  $\Delta S$  will then be approximated by the following:

$$\Delta S \approx \frac{m \times h_{H_2O}}{T_i(K)} \quad (3)$$

The calculation is confusing because  $T_i$  in the numerator is in degrees Centigrade whereas in the denominator it is measured in degrees Kelvin.

***Perform this heating procedure six times in succession. Let  $T_f$  of the previous trial become  $T_i$  of the succeeding trial. Use the six data points to construct a high-quality, well-labeled graph of  $\Delta S$  versus  $T_i(K)$ . Describe qualitatively how  $\Delta S$  depends on the temperature. What mathematical function describes such a dependence?***

## **B. Changes in Thermodynamic Entropy Due to Volume Changes**

Reducing the volume of any system, for example, the air inside a flask, compresses the gas and lowers its entropy. The reduced volume brings with it an increase in information about the position of each air molecule. A decrease in the system entropy means a gain in information about the system. The new information, however, is not free. It must be purchased and paid for via supplied work.

In this section of the lab, we will measure the thermodynamic entropy changes incurred by air during compression. Please take a half-dram vial and measure the temperature of the room air. This will be the temperature at which the air will receive work generously supplied by each student.

Refer to the barometer in the room in order to learn the air pressure. Convert the pressure value to atmosphere units. Convert the temperature to Kelvin units.

Now use the ideal gas law to compute the number of moles and the number of grams of air inside the vial. To a decent approximation, the air is 79% nitrogen, 20% oxygen, and 1% argon. We will ignore the room humidity and carbon dioxide exhaled by all of the occupants.

Now insert a rolled, softened cork firmly into the flask. Then push the cork down approximately 2 millimeters so as to compress the air. Carefully mark the position located by the bottom edge of the cork using either a grease pencil or transparent tape. This is position #1.

Then push the cork down another 2 millimeters so as to compress the air a little more. Again mark the position of the bottom edge of the cork. This marks position #2.

Repeat this step one last time so as to record a position #3.

Now remove the cork. Add liquid water to a level specified by each position. Determine the mass of the water. Use the density of the water, approximately 1.0 grams per mL, to compute the volume of the vial in mL at each position:

$$\text{Volume} = \frac{\text{mass}}{\text{density}} \quad (4)$$

Convert each volume value to liters. Then use the ideal gas law to compute the air pressure for each position in atmospheres.

With each compression step, the thermodynamic entropy of the air decreased because of the added work  $-p\Delta V$ . Each entropy change  $\Delta S$  can be approximated given by the formula:

$$\Delta S \approx \frac{\text{initial pressure} \times (V_{\text{final}} - V_{\text{initial}})}{T} \quad (5)$$

*There are three data points to obtain: values of  $\Delta S$  due to three successive compressions of air at constant temperature. Plot the three data points to yield a graph of  $\Delta S$  versus initial volume. Describe qualitatively how  $\Delta S$  depends on the volume. Is there a mathematical function which describes the dependence?*

### C. Changes in Statistical Entropy Due to Component Separation

Separating the individual components of a mixture, for example a liquid solution, increases one's information about the system. The increase in information means a decrease in the system entropy. Information is never free but rather costs work. This is the essential truth regarding all entropy measurements.

In this phase of the lab, we will use work to purchase information and reduce the entropy for a mixture of dyes. Intriguingly, we will trick nature into buying the information for us. We will be freeloaders of Nature's generosity. It is a good and much-appreciated deal for us.

Please use scissors to cut four strips of chromatography paper. Each strip should be approximately 3 inches by 5 inches. Then use a black felt marker to make four separate "dots" along a line one inch away from the 3-inch edge of each strip. The dots should be about 1 cm apart. Then fill a 250 mL beaker with 1 cm of liquid water.

For trial #1, hold one of sheets upright with the dot pattern toward the bottom. Slowly allow

the bottom of the sheet to dip into the water. The water will begin to rise, driven by capillary action of the paper. Please hold the sheet steady as the Rock of Gibraltar! Do not allow the edge to lose contact with the water!

When the water level reaches the row of black dots, start timing via a stopwatch.

In trial #1, allow the water to flow past the dots for 1.5 minutes. Then remove the sheet entirely and carefully set it aside.

Trial #2 follows the same procedure, only the water is allowed to flow for 2.5 minutes beyond the black dots.

Trial #3 follows the same procedure, only the water is allowed to flow for 6.00 minutes beyond the black dots.

Trial #4 follows the same procedure yet again, only the water is allowed to flow for 9 minutes beyond the dots.

On each strip there will appear four ink smears featuring blue, red, and yellow colors. Each trial thus had the following effect. Water was lifted to a certain height  $h$  at the cost of work generously supplied by Mr. Paper on behalf of Ms. Nature. By shelling out this work, Mr. Paper separated the black mixture of blue, red, and yellow dyes into their individual components. Information was purchased and the entropy was reduced.

Now measure the total length of each ink smear in centimeters. This is quantity  $L_{\text{total}}$ .

Then measure the individual lengths of the blue, red, and yellow smears in centimeter units. These are quantities  $L_{\text{blue}}$ ,  $L_{\text{red}}$ , and  $L_{\text{yellow}}$ .

For each smear, compute the fractions:

$$X_{\text{blue}} = L_{\text{blue}} / L_{\text{total}} \quad (6A)$$

$$X_{\text{red}} = L_{\text{red}} / L_{\text{total}} \quad (6B)$$

$$X_{\text{yellow}} = L_{\text{yellow}} / L_{\text{total}} \quad (6C)$$

Now compute the change in statistical entropy for each smear:

$$\Delta S = k_B ( - X_{\text{blue}} \ln X_{\text{blue}} - X_{\text{red}} \ln X_{\text{red}} - X_{\text{yellow}} \ln X_{\text{yellow}} ) \quad (7)$$

There are four smears on each chromatography sheet. For each sheet please compute the average

change in the statistical entropy.

*There are four data points to obtain: values of  $\Delta S$  due to water lifted through the paper. Plot the four data points to yield a graph of  $\Delta S$  versus time in minutes. Describe qualitatively how  $\Delta S$  depends on the time. Is there a time at which the entropy no longer changes? Or in other words, is there a point at which spending more of Mr. Paper's work buys no new information?*

#### **D. Using Spontaneous Entropy Increases to Obtain Mechanical Work**

In **Section II** we saw that spontaneous increases in a system's entropy can be used to obtain useful work. This principle is exploited all of the time everywhere. Gasoline burns spontaneously in air; Detroit uses the resulting entropy increase to make automobiles run. Many redox reactions take place spontaneously. The entropy increases here are the driving forces in batteries: entropy increases are used to start cars and make iPods, calculators, and pacemakers run. Entropy changes make virtually everything operate--bacteria and us included.

*Very Important!! Please read and understand all of the following steps before carrying them out!! Make sure your safety glasses are on at all times!!*

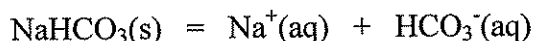
Weigh the softened cork used in experiment **IIIB**. Convert the mass in grams to kilograms.

Weigh out 3 grams of solid sodium bicarbonate ( $\text{NaHCO}_3(\text{s})$ ).

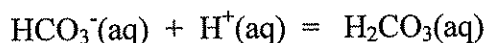
Add 1 mL of the 0.85 molar acetic acid solution to the half-dram vial used in **IIIB**.

Place the vial on the lab bench. Add the sodium bicarbonate quickly and insert the vial firmly in the flask. The following sequence of steps will then take place.

The solid material will mix spontaneously with the aqueous acid solution according to the reaction:



The weak base will then react spontaneously with the hydrogen ions in solution:



The weak acid (carbonic acid) will then spontaneously generate aqueous carbon dioxide gas and liquid water:



Some of the dissolved carbon dioxide will pass spontaneously from the liquid to the gas phase:



The gas pressure inside the vial will then increase---yes, spontaneously! The increased pressure will then cause the cork to pop out of the container and be lifted to a height  $h$  above the container. Many steps are involved, but the gist is that a series of spontaneous processes are exploited in order to obtain work, in this case, lifting an object against the force of gravity.

The numerous steps make the experiment complicated, so we can only get a decent handle on *part* of the entropy increase. Thus, please compute the mole fraction of sodium ions in solution  $X_{\text{Na}^+(\text{aq})}$ . Do likewise for the bicarbonate ions and water molecules to obtain  $X_{\text{HCO}_3^-(\text{aq})}$  and  $X_{\text{H}_2\text{O}(\text{liq})}$ . Now compute the entropy change using:

$$\Delta S = -n_{\text{Na}^+(\text{aq})} R \ln X_{\text{Na}^+(\text{aq})} - n_{\text{HCO}_3^-(\text{aq})} R \ln X_{\text{HCO}_3^-(\text{aq})} - n_{\text{H}_2\text{O}(\text{liq})} R \ln X_{\text{H}_2\text{O}(\text{liq})} \quad (8)$$

In the above formula, the "n" refer to number of moles for each component. Use  $R = 8.31$  joules/mole-K as the entropy constant value.

The work performed via the spontaneous entropy increase is:

$$\text{work} = m \times g \times h \quad (9)$$

Here  $m$  is the cork mass in kilograms.  $g$  is the acceleration due to gravity = 9.8 meters/second<sup>2</sup>, and  $h$  is the height to which the cork rises.

***Measure this height  $h$  in meters and the flight time in seconds. The preceding formula will then yield the quantity of work performed as measured in joules. Then compute the ratio  $\lambda = (\text{work performed} / \Delta S)$ . The teams of students who obtain the highest  $\lambda$ -value have converted an entropy increase to work with the greatest efficiency. Who are these illustrious and accomplished teams? What factors in the procedure and its execution enhance  $\lambda$ ? What factors diminish  $\lambda$ ?***

***Please compute the ratio  $\mu = \text{work performed} / \text{flight time}$ . The teams who obtain the highest  $\mu$ -values have converted entropy changes to work with the highest power. Who are these teams?***

## E. Using Spontaneous Entropy Increases to Obtain Useful Electrical Work

Redox reactions take place inside batteries spontaneously. Let us construct a simple wet cell



battery, use it to perform work, and measure the entropy increase along the way.

Take one lemon or lime. Cut an incision carefully with a razor blade. Measure the interior temperature using a thermometer.

Remove the thermometer and insert a copper strip into the incision.

Insert a nail approximately 3 cm from the copper strip.

Use a voltmeter to measure the direct current (DC) voltage over a one minute period. In so doing, record the voltage at ten second intervals.

Compute the average voltage. This is information received by each student and paid for using the electrical work generously supplied by Mr. Lemon or Ms. Lime.

The voltmeter draws approximately 0.1 microamps of current. Thus compute the entropy increase inside the lemon or lime as follows:

$$\begin{aligned}\Delta S &= \frac{\text{Average Voltage} \times 0.1 \times 10^{-6} \text{ amperes} \times 60 \text{ seconds}}{\text{Temperature (K)}} \\ &= \text{joules per Kelvin}\end{aligned}$$

***Record the entropy change in joules per Kelvin. What factors enhance its value? What factors detract from it?***

#### **IV. Data Sheet**

Please complete the data sheet supplied in the handout. Please hand the data sheet to the lab assistant before leaving.

#### **V. Lab Report**

Please write a lab report according to the following outline.

**I. Introduction:** As always, this should address briefly the purpose and significance of the experiment.

**II. Equipment and Procedure:** This should describe the materials and steps required of the experiment.

**III. Results:** This section should contain the results of the five separate experiments in concise table and graph form. Where graphs are involved, careful attention should be given to units and the labeling of axes.

**IV. Discussion:** Please use this section to address the questions posed for each experiment in

### Section III.

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#### Pre-Lab Exercises

- (1) The specific heat of water is about 1 calorie per gram per degree Kelvin. A chemist heats 100 grams of water from temperature 25 C to temperature 26 C. What is the approximate change in the water's entropy? (Answer: +0.34 calories per Kelvin)
- (2) A chemist prepares a 250 mL flask with 1.00 atm of air at a room temperature of 294 K. The chemist compresses the air to a volume of 245 mL. What is the approximate change in the entropy? (Answer:  $-1.7 \times 10^{-5}$  liter-atmospheres per Kelvin)
- (3) A chemist uses paper chromatography to separate the components of black ink. In the experiment, the chemist obtains a total smear length of 10.0 cm, a red smear length of 2.00 cm, a yellow smear length of 4.00 cm, and a blue smear of length 4.00 cm. What is the approximate change in the entropy. (Answer:  $-1.5 \times 10^{-23}$  joules per Kelvin)
- (4) A chemist mixes sodium bicarbonate with acetic acid. The resulting CO<sub>2</sub> gas causes a 30 gram stopper to rise 2 feet above a flask. What is the approximate amount of work performed? (Answer: + 0.18 joules)

## **Ye Olde Entropy Data Sheet**

1. In the first part of the experiment, water was heated six times. What is the total change in the entropy in calories per Kelvin?
2. In the second part of the experiment, air was compressed three successive times. What is the total change in the entropy in liter-atmospheres per Kelvin?
3. The third part of the experiment involved paper chromatography. Which paper strip showed the greatest entropy change? What was that change?
4. In the fourth phase of the experiment, how many joules of work were obtained?
5. In the final phase of the experiment, what was the change in the entropy in joules per Kelvin?