G. Experiment #7, Understanding and Explaining a Physical Chemistry Concept

Objectives:

1. Generate a written report on a physical chemistry topic that is scientifically and grammatically sound using mathematics.
2. Generate a written report on a physical chemistry topic (same one from objective #1) that is scientifically and grammatically sound using plain English only (general audience, non-chemists).
3. Understand the importance of knowing your audience when writing a technical/scientific paper.

Procedure:

For this lab, I want you to explain a difficult concept in physical chemistry. The concept should come from a part of the book we are covering this semester. I want you to explain it two ways: using the language of mathematics and using plain English. The mathematics explanation should be thorough enough to be easily followed (i.e. the major steps connecting equations should be clear), and should be based on first principles (such as the laws of thermodynamics). The plain English explanation, on the other hand, should be understandable by an educated person not in the field of chemistry, and should not rely on complicated mathematical terms (i.e. you shouldn't say "by taking the integral" or "wavefunction" or "partial derivative with respect to T") that a non-science major wouldn't understand. When making the plain English explanation, make sure that you motivate the discussion by telling why the particular idea is important.

You can choose whatever topic you want, but it should be cleared by me. This project should be typed entirely in Word including all equations. I don't want to set a firm limit on length, but will say that you want to take your time on this, really think about it, and focus on ways to explain your idea in a clear yet concise way. I give an outlined example below. I would expect you to go into greater detail then I have here.

<u>Explanation using the language of math</u>

In order to calculate practical entropies, a mathematical relationship between entropy and macroscopically measured thermodynamic properties is required. Knowing entropies is useful because entropy is a key factor in predicting whether a chemical reaction will occur. A key relationship that allows the calculation of changes in entropy is given in equation 1.

(1) $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$

Equation 1 can be shown to be true starting with the first law of thermodynamics, equations 2 & 3.

(2) $\Delta U = q + w$

(3) $dU = \delta q + \delta w$

For reversible processes, the change in heat (q), and work (w) can be expressed as equations 4 and 5, relying on the definition of entropy from the second law of thermodynamics and the definition of PV work.

(4) $dS = \frac{\delta q_{rev}}{T} \rightarrow \delta q_{rev} = TdS$

(5) $\delta w = -PdV$

Substituting into equation 3 yields equation 6.

(6) $dU = TdS - PdV$

Noting that U is a function of volume and temperature, it can be differentiated leading to equation 7.

(7) $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

Setting equations 6 and 7 equal to each other yields equation 8, which may be solved for dS as shown in equation 9.

(8) $TdS - PdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

(9) $dS = \frac{1}{T}\left[\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV\right]$

By recognizing the definition of heat capacity, equation 10, distributing the temperature term, and factoring out the delta V we arrive at equation 11.

(10) $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

(11) $dS = \frac{C_V}{T} dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV$

Noting that entropy, like internal energy, is a function of temperature and volume, it is instructive to compared equation 11 (repeated) with the derivative of entropy (equation 12).

(11) $dS = \frac{C_V}{T} dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV$

(12) $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

We see that the only way that both of these statements could be true is if equations 13 and 14 are true.

(13) $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \rightarrow ds = \frac{C_V}{T} dT$

(14) $\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]$

As was mentioned before, equation 13 is significant because the change in entropy between two temperatures can be calculated according to equation 15, allowing for the calculation of absolute entropies. Calculation of absolute entropy is possible if the temperature dependent heat capacity is known and by using the third law of thermodynamics which says that the entropy of a pure, perfect, crystalline substance at absolute zero is zero.

(15) $\Delta S = \int_0^{T_2} \frac{C_V(T)}{T} dT$

Explanation using plain English

We all know from practical experience in life that some things happen spontaneously while others do not. A marble placed on a sloping track will spontaneously roll. An ice cube placed on a warm side walk spontaneously melts. If windows are washed with vinegar, the acid in the vinegar spontaneously reacts with hard water minerals to clean the glass. A curious observer might ask why some things happen spontaneously, while others require work. A rock rolls freely down a hill, but requires work to push back up. Why?

Answering these types of questions strikes at the heart of a field of science concerned with the way energy is moved around called thermodynamics. The first law of thermodynamics, which was formulated based on the experiences of mankind since the dawn of recorded observations, says that energy cannot be created or destroyed. Also, experience has shown us that energy can be transferred in two ways: by doing work and by heating. If a person pushes a rock up a hill, that person is transferring their own energy stored within their bodies to the rock. Energy gained by work, can be given away as heat. The rock that was pushed up the hill could be allowed to slide down so that its energy is transferred in the form of heat from friction. Since energy cannot be created or destroyed, if something changes in energy then the total amount of energy change has to be equal to the amount of work that was done on it plus the amount of heat it took in or gave away.

A principle quality of our universe, observed over and over, is that things tend to spontaneously behave in a way that reduces their energy.

Hence, the rock rolls down a hill. Not up. However, a reduction in energy isn't the only motivation for something to happen spontaneously. The other factor is the amount of order. Again, from eons of observation we also know that things tend to become spontaneously disordered over time. If you have a beautifully organized Scrabble board, with several seven letter words – and whack it – then it spontaneously becomes disordered. The propensity to become disordered is another important factor in determining if something will happen. We just know intuitively that things don't spontaneously order themselves.

The problem with disorder is that while it makes perfect sense, it is really difficult to measure in cases where the objects being ordered or disordered are too small to see (like the size of molecules). Fortunately, there is a way to connect the amount of disorder of things too small to see with measurements that can be made in the laboratory. By carefully making measurements of pressure, temperature, and volume of gases under controlled conditions it can be shown that the amount of disorder of a gas is proportional to the amount of heat transferred to the gas divided by the temperature of the gas. This realization is part of what is known as the second law of thermodynamics, which says that the amount of disorder tends to increase until it is as messy as possible.

By combining the idea that change in disorder is the same as heat absorbed divided by temperature with the idea that change in energy is the amount of heat absorbed and the amount of work, we can also say that the change in energy of something is the change in disorder multiplied by temperature plus the amount of work, since heat absorbed and entropy are so intimately related…