Experiment 446.0

STATISTICAL TREATMENT OF DATA

Introduction

A major theme of laboratory work is the meaning of data. For example, one might wish to answer the question: "Is a gas ideal?" Although this question sounds simple, the answer may not always be straightforward. To show that a gas is ideal, one must show that the ratio,

$$\frac{PV}{T} = \text{constant}, \tag{0.1}$$

does not depend on the conditions of measurement, where P is the pressure, V is the volume, and T is the absolute temperature. So, to demonstrate that a gas is ideal, one must make a series of simultaneous independent measurements of the three parameters under a wide variety of conditions, construct the ratio for each set of conditions, and determine whether it is truly independent of conditions. If so, one may safely say that the material obeys the ideal-gas law over the range of conditions investigated. This seemingly-obvious discussion neglects an important, inherent property of scientific measurements. The measured values of the parameters P, V, and T are not generally known infinitely precisely. The ratio cannot be known with infinite precision for any particular set of conditions, and this uncertainty in the value of the ratio puts a limit on the confidence with which one may state that a gas obeys the ideal-gas law.

Every experimental measurement contains uncertainty. For example, one could have used as an example the measurement of the height of a liquid in a capillary or the measurement of the voltage of an electrochemical cell. In these cases and all others, the measurement has uncertainty, and the uncertainty limits the ability of the researcher to say that two numbers are identical. The problem arises from many sources, *e.g.* care in reading scales, experimental design, and limitations of the instruments we use in the laboratory. [1] Even with the greatest care and planning, though, there is still uncertainty in every measurement. An example is given by an equation derived from the Stokes-Einstein law:

$$\frac{D\eta}{T} = \text{constant}, \tag{0.2}$$

where D is the diffusion coefficient, η is the viscosity coefficient and T is the absolute temperature. One may ask whether this equation holds for water. The self-diffusion coefficient and viscosity coefficient of water as a function of temperature have been measured independently, and reported in papers in the literature. The results are shown in Figure 1, where the ratio on the left side is plotted as a function of the temperature (in degrees Celsius). If equation (0.2) applies, then the result should be a horizontal line. The error bars are based on the

[1] Many students assume, wrongly, that instrumental measurements are automatically "correct", or at least reliable. This is not always the case. Calibration may change as conditions change. Instrumental fluctuations may occur due to changes in electric voltage. Many other effects may conspire to disrupt the measurement. In this laboratory, we take care to ensure that, if used properly, the instruments will produce reliable, accurate results on known materials.

reported uncertainty in the determinations of the diffusion coefficients and viscosity coefficients. From this plot, it is clear that the equation is valid within some limits, but it appears that there may be a slight decrease of this "constant" with temperature in this range. The limitation on determining whether there is a real variation results from the fact that each value has some uncertainty due to the uncertainty in the reported measurements of the diffusion coefficient and viscosity. This example illustrates the importance of knowing the uncertainty in a measurement when one is testing relationships. Careful investigations have shown that the Stokes-Einstein equation is only approximately true.

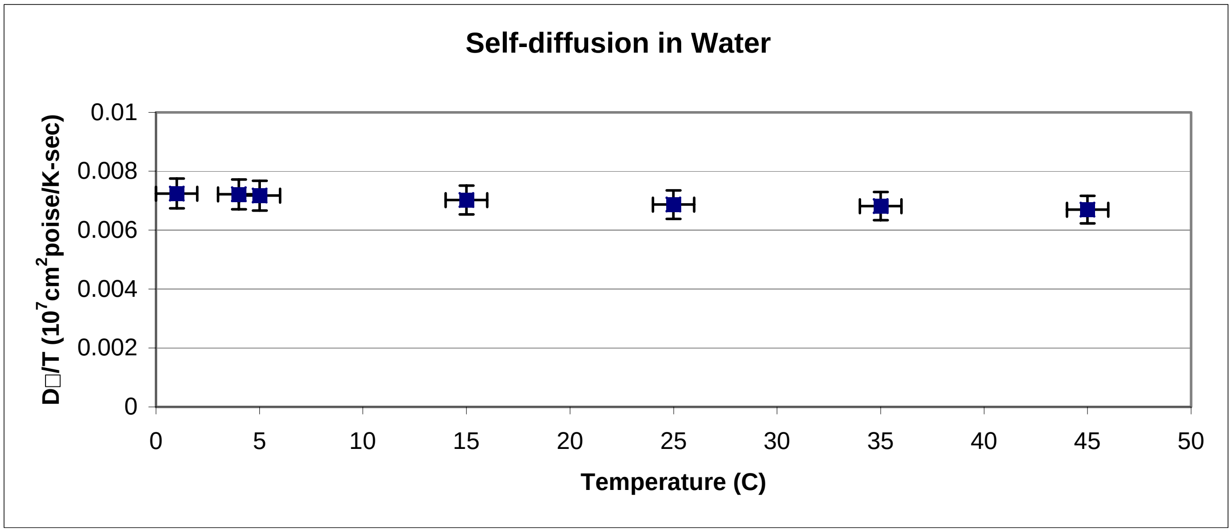

Figure 0.1. The ratio of equation (0.2) as a function of the temperature of determination.

Within reasonable limits, uncertainty can be analyzed and specified, and it is important that **every reported measurement include an associated uncertainty**. In a document at the Website, there is an extended discussion of uncertainty in measurements and its propagation in calculations. You should read this document carefully before you begin analysis of data. If you have questions about how to analyze uncertainty, ask your laboratory instructor or your professor.

There are three contributions to uncertainty in measurements: (1) limitation of resolution; (2) systematic deviations; and (3) random deviations. The first contribution is determined by the ability to read scales or the number of digits given by a digital device. The second sort of uncertainty is the result of some correctible problem, *e.g.* the miscalibration of a scale or voltmeter that causes a consistent error in the scale reading, or reading a scale from an angle that produces a different value. These are, in principle, correctible or reconcilable errors. Usually these are not a major factor in a properly designed experiment, although they may require one to carry out corrections to the measurements.[2] You must be careful in making measurements in the laboratory that you do not introduce this form of error into your results.

[2] There are many sources of systematic error. For example, in the measurement of temperature with a thermometer, one must take into account the amount of the thermometer exposed to the bath at the temperature and the part that is not. This is called a "stem correction" and factors that must be applied to correct the temperature are reported in the *Handbook of Chemistry and Physics*. This is usually a tiny fraction of a degree, but for extremely precise work, it is essential to include this correction to the temperature measurement. In other applications such as voltage

The third kind of uncertainty is inherent to all measurements and must be estimated. It is due to random effects in the system.[3] The means to estimate this sort of uncertainty is by repeated measurement of the same quality on identical systems. The statistical analysis of supposedly identical measurement sets is described in the write-up on uncertainty at the Website.

Experiment

You are to work independently of other students on this particular experiment and turn in an independent report, although you may discuss problems with other. Your laboratory instructor will assign you a set of data taken from various measurements made in the Department of Chemistry and Biochemistry by students like yourself. The sets of data are:

Coated chocolate candies: http://www.udel.edu/pchem/C446/Experiments/Chocolate.pdf
Coated peanut-butter candies: http://www.udel.edu/pchem/C446/Experiments/PeanutButter.pdf
Crispy coated candies: http://www.udel.edu/pchem/C446/Experiments/Crispy.pdf
Quarters: http://www.udel.edu/pchem/C446/Experiments/Quarter.pdf
Solution: http://www.udel.edu/pchem/C446/Experiments/Normality.pdf

The first four are measurements of the weights of various items. The last is a measurement of the normality of HCl solutions. For each set of data, you are to assume that the data are subject only to random error or random variation of a process. The data are of two different types: (a) sets of single measurements on single objects (in this case, candies or quarters) taken from a collection of similar objects; and (b) sets of repeated measurements on a single material (in this case, a standard HCl solution). In (a), one examines the consistency of making the candies (or quarters). In (b), you determine how precisely the solution's concentration is known.

It is convenient to use a program like EXCEL to carry out the calculations. If you have not used a program of this sort before, ask your laboratory instructor or your professor for help. This is an experiment like all others. As such, the report for this experiment is like the report for any other experiment. It should be in the proper format, have a careful explanation of the way the calculations were carried out. It should include the results, and answers to the discussion questions. It should be neat (Type your reports!), orderly, and organized. It is important to know and express numbers properly; use the proper number of significant figures at all times.

Calculations

1. For the set of data you are assigned (whether it be candy, quarters, or concentration), calculate the average and the standard deviation of each subset. Report these in a table.
2. Using critical t-values for 95% confidence from the student t-test, report the uncertainty in each average calculated in part 1. You may include these in the table.
3. Answer the following question: Does the process by which the candies of different color (or quarters of different states) are made yield subsets that are different in average weight? To answer this question scientifically, carry out a significance test. Find the square root of the pooled variance of each set of two colors (*e.g.* red and orange) by the following formula:

---

measurement in a temperature bath, one sometimes must account for the difference in resistivity of wires as a function of temperature to correct for systematic error in the voltage measurement.

[3] To notice random effects, the resolution of the experiment must be sufficient to detect the variations that result from them. Thus, if the resolution of a particular voltmeter is 1 millivolt and the maximum random deviation is 0.001 millivolt, a measurement with the voltmeter will not detect the effects of random variation of the voltage.

$$\sigma_{12} = \left[\frac{(N_1 - 1)\sigma_1^2 + (N_2 - 1)\sigma_2^2}{N_1 + N_2 - 2} \right]^{1/2}, \qquad (0.2)$$

where σ_j is the standard deviation of the j^{th} set (color or state) and N_j is the number of measurements in that subset. Next, calculate the standard deviation of the difference of the two means (averages) from this:

$$\sigma_D = \sigma_{12}\sqrt{\frac{N_1 + N_2}{N_1 N_2}}. \qquad (0.3)$$

Using the number of degrees of freedom of the total set, N_1+N_2-2, obtain the critical t-factor at 95% confidence. Compare the product of $t_c\sigma_D$ to the difference of the two average values. If the difference of the two averages is larger than this product, one would say the two averages are significantly different from each other. If the difference of the averages is less than this value, they are not significantly different from each other. Do this for **each pair** of subsets (either colors of candy or state quarters) in your data set. This answers the question of whether, on average, the subsets are distinguishable.

4. Whether or not the results of part 3 show that the subsets are different, pool **all of your data** on candy (or quarters) into a single set for this step. (a) Calculate the average and standard deviation of this set. (b) Make a frequency plot by the following process: choose a convenient step size, Δw.[4] The steps determine bins centered at $n\Delta w$ away from the average, as shown in Figure 2. Each bin is of width Δw and is centered at $\bar{w} \pm n\Delta w$.

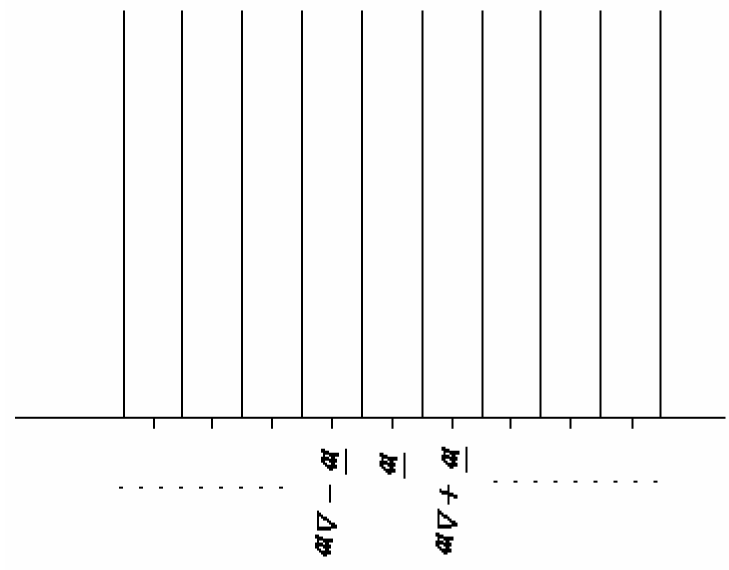

Figure 0.2. Bins for a frequency plot.

Count the number of times a measurement in the range of a bin. Do this for every bin. When you finish, you should have a table of number of measurements versus a weight $\bar{w} + n\Delta w$, where n is an integer. These data produce a frequency plot, essentially a stick plot that shows

[4] The choice of step size depends on the data. It is desirable to create bins of data with width Δw that contain several measurements, so the step size should not be too small. On the other hand, it should represent the distribution of data, so the step size should not be too large. You might wish to try several different sizes before doing a lot of work.

the distribution of measurements about the average. (If your bins are too large, the distribution you produce will have one or a few bins containing measurements, with the rest having zero; if the bins you choose are too small, all of the bins will have either 0 or 1 measurement. Either of these situations is not proper; so you may have to redo this parsing of the information by choosing a different bin width. A proper frequency plot shows a reasonable shape that gives the viewer an idea of how the measurements are distributed.

5. On the frequency plot, include a representation of a Gaussian function having the same average weight and same standard deviation as the data. Choose this Gaussian so that it emulates the frequency plot.[5]

Discussion Questions

1. Explain accuracy and precision.
2. Why is the Gaussian function used so widely in analyzing the uncertainty in data?

---

[5] To make this look right, you have to choose the amplitude of the Gaussian, and you may have to calculate more points than just one per bin. The easiest way to do this is with a program like Excel, with a procedure in which you calculate the Gaussian at several hundred points and plot it. This requires you to specify an amplitude; start with the value of the frequency in the average bin and vary it until the Gaussian seems to "fit" the data. This is a Gaussian for which half of the points fall (randomly) outside the Gaussian and half of the points fall inside the Gaussian.