Error Analysis

by R. D. Poshusta

EINSTEIN'S MAXIM
If you cannot measure it, you cannot know it.
A. Einstein
POSHUSTA'S CORROLARY
That applies to errors too.
R. D. Poshusta

References

Experiments in Physical Chemistry, Shoemaker, Garland, and Nibler [McGraw-Hill, 5th Ed., 1996]

Data Reduction and Error Analysis for the Physical Sciences, P. R. Bevington [McGraw-Hill, 1969]

Introduction

There are three steps in error analysis of most experiments. The first, propagation of errors, can be performed even before the experiment is performed. The second, measuring the errors, is done during the experiment. And the third, comparison with accepted values, is performed after the experiment is completed. For this discussion we suppose that an experimental procedure exists that uses a variety of instruments to measure several quantities, x_1, x_2... x_n, and that these quantities enter a computation or formula, $F(x_1, x_2... x_n)$ that yields the ultimate desired value or objective of the experiment. Errors can be associated with each measurement or instrument, with the procedure, and with the value F. The primary purpose of error analysis is to determine **the confidence** that should be placed in the F-value.

EXAMPLE

Consider the example experiment for measuring the heat of vaporization of water. The procedure consists in measuring the equilibrium boiling temperature of water at several values of atmospheric pressure. The apparatus consists of a boiling flask and thermometer below a refluxing condenser and a manometer all of which can be partially evaluated and sealed from the laboratory atmosphere. Then two measurements are made repeatedly: temperature T_i and corresponding pressure P_i for trials i=1, 2... N. The desired quantity is the heat of vaporization given by $\Delta H = -R \dfrac{\partial \ln(P / P^0)}{\partial(1 / T)}$, where P^0 is the standard pressure (say, 1 atmosphere). The data values $\{T_i, P_i\}$ are to be used to compute ΔH as well as to determine the uncertainty in ΔH.

The first step will be to make a least squares fit of a straight line to a plot of ln (P/P^0) versus 1/T. The slope, *a*, of this fit will enter the calculation: ΔH = -R *a*. Of course the slope is a function of all data points and it will be required to find the errors in *a* due to errors in measuring temperatures and pressures.

A. Propagation of Errors

The purpose of this step is to **estimate** the highest precision that can be achieved with a given experiment design. In fact, it is a good idea to perform this step as part of designing the experimental approach. By propagation of errors you can answer important questions about the precision of F:

1. "Which measurement or instrument introduces the largest error?"

2. "Which instrument should be replaced first with a more precise one?"

3. "Are some instrument readings or procedural steps more critical than others?"

4. "Is this experimental design adequate for the required precision in F?"

The fundamental formula for propagating errors is this:

$$\delta F^2 = \left(\frac{\partial F}{\partial x_1}\right)^2 \delta x_1{}^2 + \left(\frac{\partial F}{\partial x_2}\right)^2 \delta x_2{}^2 + \ldots + \left(\frac{\partial F}{\partial x_n}\right)^2 \delta x_n{}^2$$

Where δF is the uncertainty or error in the computed quantity F, δx_i is the uncertainty in the measurement

of x_i, and $\dfrac{\partial F}{\partial x_i}$ is the partial of $F(x_1, x_2, ;x_n)$ with respect to x_i.

In words, the uncertainty in the value of F is the sum of terms that contain the uncertainties in the component measurements and the rate of change of F with respect to those components. The terms are squared to avoid accidental cancellation of errors when some partial derivatives are negative.

A similar formula, for the relative errors, sometimes simplifies the propagation of errors: The simplification occurs **if F is a product or quotient of the x_i values**; then the propagation formula reduces to:

$$\left(\frac{\delta F}{F}\right)^2 = \left(\frac{\delta x_1}{x_1}\right)^2 + \left(\frac{\delta x_2}{x_2}\right)^2 + \ldots + \left(\frac{\delta x_2}{x_2}\right)^2$$

In words, **if F is a product or quotient of the x_i values**; then the square of the relative error in F is the sum of the squares of relative errors of each component measurement.

EXAMPLE

Since the uncertainty in ΔH is $\delta\Delta H = R\,\delta a$, we examine the uncertainty in the slope of $\ln(P/P^0)$ versus $1/T$. First we can reasonably assume that the slope can be determined from only two data pairs (P_i, T_i) and (P_1, T_1); we will find the uncertainty in slope from the uncertainty in pressure and temperature at these two data points. Further, it is reasonable to assume both points contribute the same amount to the uncertainty: $\delta\Delta H = 2 R\,\delta a_i$. Here δa_i is the uncertainty in the slope due to data pair (P_i, T_i). To estimate δa_i, we suppose that the

slope is given by $\quad a = \dfrac{\ln(P_i / P^0) - \ln(P_1 / P^0)}{1/T_i - 1/T_1}$, where (P_1, T_1) is any other data pair.

Then $\quad \delta a_i{}^2 = \left(\dfrac{1/P_i}{1/T_i - 1/T_1}\right)^2 \delta P_i^2 + \left(\dfrac{T_i^2}{(T_i - T_1)^2}\right)^2 \delta T_i^2$

Now suppose that temperature is read to a precision of $\delta T \sim 0.01$ (the thermometer is marked in 0.05 increments and we interpolate by eye to one fifth of this), and suppose that pressure is read to a precision of $\delta P \sim 0.02$ torr. Let us take (P_1, T_1) near the high temperature limit: (760 torr, 373K), and take (P_i, T_i) near the low temperature: (17 torr, 298K). These are only estimates, but that is all we require for δa. By substituting into the previous formula we find $\delta a_i \sim 0.16K$, $a \sim -5500$ K, and hence $\delta\Delta H \sim 2\ (R\ 0.16K)$. In MKS units this is $\delta\Delta H \sim 3$ joule mole^{-1}. If the instrument errors are the only errors, we should expect a precision of about 3 joule/mole; other sources of error can increase this uncertainty.

Further, the contribution of the pressure term to δa is only 0.04 torr while that of the temperature term is 0.16K. Hence, the precision of ΔH can be increased by using a thermometer that can be read to a precision $\delta T = 0.001K$ but improving the pressure measurements alone will not significantly increase the precision.

The instruments selected for this experimental design will yield heats of vaporization with precision of about 3 joule/mole. For water, ΔH_{vap} is about 40 kJ/mole so that the uncertainty will be only about 0.1 ppt or 0.01%.

B. Measuring Errors

Now we come to the step in which the errors are actually <u>measured</u>. Without this we do not really know how big the errors are (Einstein's maxim). We have an estimate of the precision that can be achieved using the instruments described above, but there may be additional errors that we have not accounted for. Hence we will use the data from the experiment to obtain an experimental measure of errors from all sources. For this we rely on statistical analysis of repeated measurements.

Mean and Standard Deviation

When the same quantity is measured several times, we use the standard deviation from the mean as a measure of its precision (error). Truly random errors will cause a "normal"; distribution of measured values and ~60% of these values will lie within one standard deviation from the mean. With only a few measurements we cannot know that the distribution is "normal" but we usually assume it is.

Definition: For a set of N measurements $\{a_1, a_2... a_N\}$, the mean and standard deviation are:

$$\bar{a} = \frac{1}{N}\sum_{i=1}^{N} a_i \quad \text{and} \quad \sigma_a = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(a_i - \bar{a})^2}$$. Note that standard deviation is not defined if only

one measurement exists; we measure errors by <u>repeating</u> the measurement. Note also that the σ_a measures the "width" of the distribution of values about the average.

Least squares fitting

See also, *Experiments in Physical Chemistry*, by Shoemaker, Garland, and Nibler [McGraw-Hill, 5th Ed., 1996] appendix XXII.

In many experiments it is the relationship between two variables that is sought. In our example, we seek the slope of ln (P) versus 1/T. In such cases the data consists of pairs $(x_i, y_i, i = 1, 2... N)$ and these pairs (also called data points) are fit to a "model function" in a form y=f(x). The conventional way to do this is to minimize the squared deviation between the model and the data. Namely, we adjust the function f(x) until the quantity χ^2 is minimum:

$$\chi^2 = \frac{\sum_{i=1}^{N}(y_i - f(x_i))^2}{N-m}.$$

Here N is the number of data points, and m is the number of fitting parameters in f(x).

In a linear least squares fit the model function is f(x) = ax + b and the slope, a, and intercept, b, are varied to minimize χ^2; there are m=2 fitting parameters. Clearly, the statistical information contained in the data set can be used to extract the uncertainties of the fitting parameters. References will show how these uncertainties are computed.

For linear least squares fitting one may use the slope and intercept functions of MathCad. Uncertainties of the slope and intercept can be calculated as shown in the MathCAD file scicomp/datanal/lstsq_1.mcd.

EXAMPLE

The following are data for the boiling temperature and total pressure for water obtained in a heat of vaporization experiment.

P/torr	T/C
23.8	25.0
31.8	30.0
55.3	40.0
68.3	44.0

118.0	55.0
196.1	66.0
277.2	74.0
369.7	81.0
400.6	83.0

A linear least squares fit of ln (P/760 torr) versus 1/T gave a slope of -5.162 10^3 K and hence ΔHvap = 42.916 kJ/mole at the average temperature 328K. From the calculated uncertainty of the slope, that of the heat of vaporization is found: $\delta\Delta$Hvap ~ 6 joule/mole. Then the result of the experiment should be reported: ΔHvap (328K) = 42.916±0.006 kJ/mole. For the details of the calculations, see scicomp/datanal/water.mcd.

C. Comparison and Discussion of Errors

Finally, you should search for literature values or accepted values to compare with your measurements. This constitutes the third leg of a complete error analysis.

A complete discussion will include

1. The deviation between this experimental value and the accepted value. Try to account for this difference. Is it because the experiment was not performed at the same conditions as the accepted value? Is the difference significant (in view of the uncertainties)?

2. A comparison of the estimated errors due to propagation of error with the measured error(s). If the latter are much larger than the former, can you find additional sources of error to explain the difference?

3. Suggestions to improve the precision and accuracy of the experiment. What changes in the instruments or procedure can reasonably be made to improve the measurements? [Be able to defend your suggestions.]

EXAMPLE

The accepted heat of vaporization of water is 40.656 kJ/mole at 373KC and 44.016 kJ/mole at 298K [Atkins, Physical Chemistry, page C5]. Our result is ΔHvap (328K) = 42.916; 0.006 kJ/mole. Assuming a linear variation of ΔH with T, our result lies 291 joule/mole higher than the interpolated value.

The measured uncertainty in ΔH is 6 joule/mole and the estimate from propagation of errors is ~ 3 joule/mole. This close agreement indicates there are no significant errors aside from those inherent in reading the thermometer and manometer. The measured value is somewhat larger than the propagation estimate; this might be due to additional errors in the experiment roughly the same size as from the propagation analysis, or it might be due to the approximations incorporated into the estimates for propagation of errors. One source of error not included in propagation of errors is the possibility that the boiling liquid is not quite in equilibrium with its vapor.

Our value, ΔH$_{vap}$ (328K) = 42.916±0.006 kJ/mole, is higher (~50 times the measured uncertainty in ΔH$_{vap}$) than the interpolated accepted value. This suggests a systematic error. We cannot tell from the present evidence whether the measurement is in error or the interpolation method is wrong. Some possible avenues for investigation include:
(1) correct the vapor pressure for the presence of applied pressure (from the atmosphere) as described by Atkins (page 193), and (2) improve the interpolation by using an expression for the temperature induced change in ΔH$_{vap}$ (328K) = ΔH$_{vap}$ (298K) + ΔCp (328K-298K).