

UNCERTAINTY, PRECISION AND ACCURACY

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Introduction

All experimental data have associated uncertainties that ultimately limit the conclusions one can make. For example, one may wish to determine if some parameter varies linearly as a second parameter is varied. Whether one can determine that the variation is a linear relationship from a particular set of data depends on how certain one is about the measured values of each of the two parameters. Uncertainty is a part of the experimental process, no matter how hard one tries to minimize it. Thus, it is important to express uncertainty clearly when giving experimental results. (In many cases, this quality of an experiment is called "error", but it is not "error" in the common sense of the word, so I prefer the word "uncertainty" for this quantity.)

Accuracy

When the value of a parameter is determined experimentally, one must make some assessment of the "correctness" of the determination. *Accuracy* is a measure of the agreement of a particular measurement with the "true" (or "accepted") value of the parameter under the conditions. Accuracy has a sign that indicates whether the experimentally measured value is high (+) or low (-), compared to the true value.

For example, suppose a measurement of a resistor gave a resistance of 6.83 ohms. If the resistor were purchased from an electronics supply store that

certified the resistor has a value of 6.80 ohms, then the accuracy of the measurement is

$$6.83 \text{ ohms} - 6.80 \text{ ohms} = + 0.03 \text{ ohms.}$$

Such a calculation gives the **absolute deviation** of the measurement. In this case, the measurement is said to be “high” relative to the accepted value. One may also define the **relative deviation** as

$$\frac{6.83 \text{ ohms} - 6.80 \text{ ohms}}{6.80 \text{ ohms}} = \frac{0.03}{6.80} = 0.0044 \quad (= 0.44\%)$$

A measure of the accuracy can only be determined if some prior knowledge of the true value is available.¹

Systematic Errors and Accuracy

The discrepancy between an accepted value of a parameter and an experimentally measured value results from deviations in the manner in which the measurement is carried out. No two measurements are exactly the same. Some deviations can be controlled and some cannot. Those that can, in principle, be controlled by careful adjustment of the experimental procedure are **systematic errors**. They definite values that can, in principle, be measured and corrected. Systematic errors are sometimes called **determinate errors**. The most common types error are instrumental error, operator error, and method error.

Such errors are often unidirectional, so they slant the result of the measurement. If that is the case, the experiment is said to have a **bias**. Systematic errors can be corrected only after the nature of the bias is identified. A common determinate error is an incorrectly calibrated instrument that systematically gives results that are either too high or too low. Recalibration of the apparatus should correct this kind of error. In this laboratory, many of the instruments are calibrated before one makes a determination of the value of some unknown parameter. Failure to calibrate the instrument properly is a major source of determinate error.

Indeterminate Errors and Precision

Were determinate error the only source of uncertainty in a measurement, the job of the experimenter would reduce to a sequence of operations to eliminate each source of determinate error, after which one would presumably measure the “accepted” value of some parameter. Measuring the parameter would always give the same number at each measurement. However, there are additional sources of variation that ultimately determine how “well” one may measure a quantity. These are **indeterminate errors** (also called **random errors**). They generally cannot be positively identified as their values from

¹ Determining “true values” of specific quantities is not easy. Different methods of measuring the same quantity usually give slightly different answers. There is a great deal of effort put into developing accepted values for certain properties that can be measured by a variety of experimenters to calibrate their measuring devices. Even standards change occasionally, when the situation warrants revision. For example, until 1948 the coulomb was defined as the quantity of electricity passing through a circuit to deposit 0.0011180 grams of silver from a solution of silver nitrate. Now the coulomb is defined as the quantity of electricity on the positive plate of a 1-farad capacitor subject to an electromotive force of one volt.

measurement to measurement vary randomly. Some are inherent to the way the experiment is set up; some are simply a result of the way nature acts. A good experiment reduces or eliminates systematic error and provides an estimate of the indeterminate error, expressed as uncertainty.

Consider a simple act such as weighing a sample. This may be carried out several times on a single sample, simply to be certain of the value. Suppose the object of an exercise is to create a sample that weighs 2.0000 grams. To be sure of this weight, the experimenter measures the weight in five repeated measurements. It is unlikely that the five weights will be exactly the same, as shown in the table.

Weight as Measured in Five Different Experiments				
2.0001 grams	2.0000 grams	1.9997 grams	1.9998 grams	2.0004 grams

The question is the following: is this sample 2.0000 grams? It seems that one measurement indicates this is the case. However, the other four measurements deviate from this value. The variation across the set of measurements produces some uncertainty about the weight. Any expression of the weight must include some indication of this uncertainty.

The uncertainty is a function of the type of sample, the conditions under which it is being weighed, the balance, and the person doing the weighing. Presuming there is no determinate error, one may state these measurements reflect something about the random error associated with the measurement of the weight.

As a first approximation, one could round these numbers to the nearest 0.001 gram, in which case each would be said to weigh 2.000 ± 0.001 grams. But this implies the weight is known only to the nearest milligram, a reduction in information about the sample's weight that may not be necessary.

The last digit contains some information. It shows that all of the five measurements fall between 1.9997 grams and 2.0004 grams. Thus, one could say that the actual value, based only on these measurements is 2.0000 ± 0.0004 grams. This gives a statement of the uncertainty by including the **range** of all values in the set.

The statements above are attempts to quantify a quality of the measurement. This quality is the **precision**. It is defined as the degree of agreement between replicate measurements of the same quantity. There is a distinction between precision and accuracy one should always make. Even if the measurement's precision is excellent, it may be inaccurate if a determinate error is present.

Quantifying Uncertainty Due to Random Variations

Uncertainty in experimental data caused by random fluctuations can be quantified. A report of the precision gives a measure of the "goodness" of a measurement. Knowledge of precision also makes possible comparison among repeated measurements or measures of the same quantity made by different techniques or different laboratories. Thus, one may decide, based on reported

precision, whether two measures of the same quantity (perhaps by two different techniques or by two different people) are identical **within the uncertainty of the experiment**.

Quantifying uncertainty can take many forms, from very simple analyses to sophisticated computer-based methods. In the end, the reported precision is a statement of the experimenter's best estimate of the range of values that should be considered identical to the reported value. Because this decision is somewhat subjective, several different analysts examining the same data may arrive at slightly different measures of precision. Nevertheless, there are some consistent ways of reporting uncertainty in an experimental result. Here are some measures of precision and, hence, uncertainty.

Average of a Finite Set

In repeated measurements of the same quantity, one obtains a set of values, as given above. Generally, unless one knows that one or several of the data are suspect (because of presumed determinate errors during those measurements), one must give equal weight to all measurements. Thus, the "best" value for the measurement is simply the **average over the set**. For example, the average of the weights in the table above is:

$$\langle w \rangle = \frac{1}{5}(2.0001 + 2.0000 + 1.9997 + 1.9998 + 2.0004) \text{ grams} = 2.0000 \text{ grams}$$

It would appear that a correct interpretation of the set of measurements is that the weight is, indeed, 2.0000 grams. The question one must answer in reporting of the results is, given the repeated measurements, how certain is this statement?

Range as a Measure of Precision

While working in the laboratory, one often wants some sense of the precision of a measurement that requires an easy calculation. For a series of measurements of a single parameter, it is reasonable to approximate the uncertainty crudely by the **range**, *i.e.* the difference between the maximum and minimum values of the set. For example, for the example set, the range is:

$$\text{range} = (2.0004 - 1.9997) \text{ gram} = 0.0007 \text{ gram}$$

For example, one might express the uncertainty as the half range of the set, so one would express the measurement above as

$$w = 2.0000 \pm 0.00035 \text{ grams}$$

Clearly, this gives a reasonable estimate of the uncertainty in this measurement.

Average Deviation as a Measure of Precision

A second quantity that can be easily estimated in the laboratory is the **average absolute deviation**. It is the average of the absolute deviations from the average:

$$\langle |\Delta w| \rangle = \frac{1}{N-1} \sum_i |\Delta w_i|$$

For the example, the average absolute deviation is:

$$\langle |\Delta w| \rangle = \frac{1}{4}(0.0001+0.0000+0.0003+0.0002+0.0004)\text{gram} = 0.00025\text{gram}$$

Thus one might express the result of the measurement as

$$w = 2.0000 \pm 0.0025 \text{ grams}$$

The average absolute deviation will usually be slightly smaller than the half range, but it is another reasonable estimate of uncertainty. Remember that the statement of uncertainty is a somewhat subjective process, so that different measures, provided they are clearly defined, of a single set may express uncertainty in slightly different ways.

Statistical Measures of Precision

If the variations from the average are truly randomly dispersed, then repeated measurements are represented by a **normal probability distribution**, a function that indicates the likelihood of finding a particular value in the set of measured values. When the width of this function is small compared to the average value, the average represents, relatively closely, a large percentage of the measurements; when the width of this function is large compared to the average value, it does not represent the overall set as well. Thus, some measure of the distribution's width will specify the precision of the measurement. I say more about this particular function below.

The statements in the previous paragraph apply, in principle, to a very large set of measurements (theoretically infinitely large). Generally, experimenters do not generate such large sets, so one has to develop a formalism applicable to sets of finite size. For a set that is less than infinite, one can calculate the average by a straightforward procedure. One may also calculate the average sum of squares of the deviation from the average. In so doing, it is important to remember that there are now $N - 1$ degrees of freedom (since one degree of freedom was used up in defining the average)

$$\langle \delta w^2 \rangle = \frac{1}{N-1} \sum_i (w_i - \langle w \rangle)^2.$$

This number, the **variance** of the set, gives a measure of the spread of the data around the average. For the example set, one calculates

$$\langle \delta w^2 \rangle = 7.5000 \times 10^{-8} \text{ gram}^2.$$

The square root of the variance is the **standard deviation**, σ . For the data above, the standard deviation is²

$$\sigma = 0.00003 \text{ gram}$$

Using the standard deviation to represent the precision, one might choose to report the example measurement in the following way:

$$w = 2.0000 \pm 0.0003 \text{ grams}$$

This is less than either the half range or the average absolute deviation.

One may also express precision as the relative uncertainty (in this case, the standard deviation of the set divided by the average of the set):

² Note that the variance has units of the square of the quantity, whereas the standard deviation has units that are the same as the measured quantity.

$$\text{relative uncertainty} = \frac{0.0003}{2.0000} = 0.015\%$$

Giving the standard deviation specifies the error at a specific level of confidence, which may be lower than scientists would generally accept.

Gaussian (Normal Probability) Distribution for an Infinitely Large Set

The standard deviation, the variance and the average arise from the theory of probability. For a very large set of repeated determinations of a value subject only to random error, the distribution of measurements is symmetrically distributed about the average value. This situation is described by a **gaussian** (or **normal probability**) function:

$$P(\varepsilon, \sigma) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right)$$

where ε is the deviation from the average (which can be either negative or positive) and σ is the standard deviation of the gaussian distribution. σ is related to the full width at half height of the function.³ The smaller it is, the narrower will be the spread of values about the average; the larger it is, the larger the spread. A mathematical calculation shows that σ is the root-mean-square deviation of the set from the average:

$$\sigma = \sqrt{\langle \varepsilon^2 \rangle} = \left[\frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{+\infty} \varepsilon^2 \exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right) d\varepsilon \right]^{1/2}$$

The standard deviation defined in this way for a large (effectively infinite) continuous set of data is equivalent to the standard deviation calculated by the operation described above on a finite set of measurements.

Since the integral of the gaussian function is 1, it represents a probability. Thus, the integral of this function from one value to a second value represents the fraction of data points that fall within that range. So, the gaussian function allows one to specify the probability that, any number from the set will fall in a given range. Usually, this range is specified in terms of standard deviation. The table gives the fraction of determinations that fall in the indicated ranges. A range that extends by $\pm 2 \sigma$ about the average encompasses over 95% of all measured data for an infinitely large set. Scientists often quote uncertainties to encompass 95% of the values. One is said to quote the uncertainty "at the 95% confidence level".

Fractional Probability Inside a Range, $\langle w \rangle - n\sigma < w < \langle w \rangle + n\sigma$			
n	P(n)	n	P(n)
0.5	0.38292	2.0	0.95450

³ The full width at half height (FWHH) of the normal probability distribution is $\sqrt{2 \ln 2} \sigma$.

1.0	0.68269	2.5	0.98758
1.5	0.86639	3.0	0.99730

Practical Uncertainty Estimates in Single Measurements

When only a single determination of a parameter's value is made or when it is not possible to repeat an experiment enough times for a reasonable

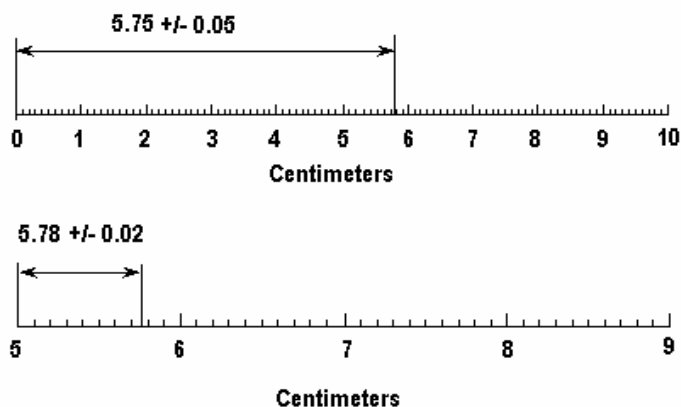


Figure 1 Measurements of length with a scale.

When measuring against a scale, one has to estimate how precisely one can infer the value of a parameter. In many cases, the uncertainty in a single measurement is given as $\frac{1}{2}$ the smallest scale graduation. For example, consider the measurement of an object's length using a ruler, as shown in Figure 1. The measurement gives a value between 5.7 and 5.8 cm, which one would assign as 5.75 cm. As for uncertainty, the value lies between the two graduations, so one assigns an uncertainty of ± 0.05 . So, the reported result of the measurement is 5.75 ± 0.05 cm.

In some cases, it is possible to estimate the value more closely, depending on the scale and the ability to view it. In the bottom part of Figure 1 an expanded view is shown. In this case, one might be able to estimate length to the nearest 0.02 cm. So, one would report the result as 5.78 ± 0.02 cm.

In reading a scale, whether it be a ruler or a meter, one specifies the uncertainty from a judgment about the ability to discern the parameter's value. A good rule of thumb is to report the largest possible uncertainty with which you feel comfortable.

To avoid systematic errors in reading a scale, care must be taken in making the judgment. For example, because the meter movement and the scale are not in the same plane, where the pointer appears on the scale depends on the position of the eye relative to the pointer and scale. Readings taken from different positions can give different apparent results. To avoid this source of systematic error, some instruments provide a mirror whose plane is very near the

statistical treatment of the data, uncertainty must be approximated. This often occurs when one is, for example, reading a scale or a meter. Ultimately, every datum in a set can be said to have an associated uncertainty. These uncertainties are not based on a statistical analysis, but rather on the judgment of the experimenter, and it is important to be consistent in judging the uncertainty at this level.

plane of the scale. By lining up the image of the pointer with its image in the mirror, one is assured that the line of sight is the same in each measurement.

Uncertainties in Graphing

When graphical techniques are used to determine a quantity, one must analyze the uncertainty in the measurement of the quantity, as one would do in

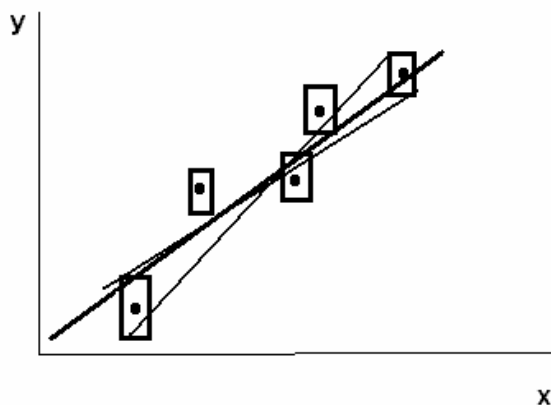


Figure 2 Determining the uncertainty in slopes and intercepts by the method of limiting slopes.

determining the uncertainty in a set of repeated measurements of a quantity. In all cases, one should ensure that the range of data points used for determination of a quantity spans the range of the data over which one wishes to express the relationship. Generally one is seeking to determine parameters that express the trend of one variable with respect to another; this is the reason for a graph. That is, one may be seeking,

for example, a linear relation between two parameters:

$$y = mx + b$$

and the object is to determine the "best" values of m and b , given a set of pairs $\{(x_i, y_i)\}$. Generally one might wish to treat sets with a small number of data points (say, less than 10) differently from those with a large number of data points (greater than 25).

Method of Limiting Slopes

It is easy to estimate error in the slope, m , and intercept, b , of a linear graph by the "method of limiting slopes". (This works best with a limited number of points, as the plotting can become tedious with very large numbers of points.) The technique consists of drawing rectangles to represent uncertainties in the quantities at each point. The "best" values of b and m are determined from the "best" line through all the points, which is usually obvious from the data, as is indicated in Figure 2. Two other lines, which approximate the maximum or minimum acceptable slopes, are also drawn so that they pass through the rectangles, thereby giving a minimum and maximum acceptable deviation from this best line. The difference between the slopes of these two lines can be taken as twice the uncertainty in the slope of the line, and the difference between the intercepts of these limiting lines can be taken as twice the uncertainty in the intercept. Remember that this process is a judgment on the part of the experimenter.

Regression Analysis

When one has a relatively large number of data, for which the relationship between x and y is predicted to be of a certain form, a satisfactory way to analyze the data is a procedure known as **regression analysis**. Many hand-held calculators give a form of least-squares linear regression. Computer programs such as Excel and Mathcad do a similar analysis. The problem is often transforming the information given by the program into meaningful estimates of uncertainty.

Simple regression analysis begins with the assumption that each datum consists of the real value plus some random noise. It is frequently assumed that one of the variables, usually x , has little or no error and that the dominant source of error is random noise in y . The criterion for “best line” is then the minimization of all the deviations of the actual data from this theoretical best line over the whole set of data. There are several ways to define the deviation, but the common way considers the deviations that are perpendicular to the x axis:

$$\Delta_i = y_i - (m x_i + b)$$

If these are truly random and the set is large enough, then the sum of these deviations will tend towards zero:

$$\sum_i \Delta_i = 0$$

However, the sum of the squares of these quantities, called the **residual**, will not be zero in general. In fact, it will be a function of the values of m and b .

$$R(m,b) = \sum_i \Delta_i^2 = \sum_i y_i^2 - 2m \sum_i y_i x_i - 2b \sum_i y_i + 2mb \sum_i x_i + m^2 \sum_i x_i^2 + N b^2$$

where N is the number of pairs of values. The minimum of this sum of squares is found by setting the derivatives of R with respect to m and b equal to zero. These relationships give equations for the “best” m and b . These equations can be found in various reference books.⁴

Obviously, these best values of m and b are not without uncertainty. The question is how to express the uncertainty. A quantity often reported with linear least squares regression is the **correlation factor**, r , or its square. For a perfect fit (one in which every point falls exactly on the theoretical line), $r^2 = 1$; for total lack of correlation (that is, no fit), $r^2 = 0$. One may use this quantity together with calculable functions of the set of data to give expressions for the standard deviation of the slope, σ_m , and the standard deviation of the intercept, σ_b . These are given by the equations below:

$$\left| \frac{\Delta m}{m} \right| = \sqrt{\frac{1}{N-2} \frac{1-r^2}{r^2}}$$

$$\left| \frac{\Delta b}{m \sum_i x_i^2} \right| = \sqrt{\frac{1}{N(N-2)} \frac{1-r^2}{r^2}}$$

⁴ For example, see Appendix I of J. H. Noggle, *Physical Chemistry, 3rd Edition*, Addison-Wesley-Longmans, San Francisco, 1997.

Hence, one may use the correlation coefficient to estimate the relative standard deviation of the slope and, with a calculation of a single sum, the standard deviation of the intercept of the line that best expresses the linear relationship. Knowing the standard deviation of these parameters and the number of degrees of freedom, $N-2$, one has a prescription for stating the uncertainty.

One should always remember that tools like linear least squares regression work well if applied to situations in which there is a reason for believing a linear relationship exists. The use of any tool in situations to which it does not apply yields only nonsensical results.

There are many other regression analyses that may be applied, more or less easily, to determine some characteristic relation between two measured quantities. For example, one may generalize the regression to include polynomial expressions. For complex functions, one may use an algorithm such as Simplex to determine a set of parameters of the function that select the “best” curve to describe the data. Almost all of these procedures rely in some way on finding the minimum in some residual over the set of data. Still, a human being must always make the judgment about whether the data appropriately are modeled by the functional form.

Propagation of Uncertainty

When the quantity one wishes to specify is not directly measured, but is calculated from two or more directly measured quantities, the uncertainty in the derived quantity must be determined from the (presumably known) uncertainties in the measured quantities from which it is calculated. This is the concept of the **propagation of uncertainty**.

Differential Analysis

To propagate uncertainty, one must have a connection between the quantity calculated, x , and several other measured parameters, $\{a, b, c, \dots\}$. Mathematically, these measured quantities are independent variables and x is a dependent variable. The relation is expressed functionally by the general equation:

$$x = f(a, b, c, \dots)$$

Suppose that we have a series of points at which a, b, c, \dots have been determined and that these vary from determination to determination. Then, for each determination, use of the functional form above will give a slightly different value of x . We may, however, determine the average of these, which we might designate

$$\langle x \rangle = \frac{1}{N} \sum_i f(a_i, b_i, c_i, \dots)$$

Since the measured variables a, b, c, \dots are not identical from measurement to measurement, they have associated uncertainties which can be calculated, as shown above. The question to answer is “How do these uncertainties get translated into uncertainties in x ?”

We begin with a fundamental rule of calculus: a differential change in a function is caused by a differential change in the independent variables:

$$dx = df = \left(\frac{\partial f}{\partial a}\right)da + \left(\frac{\partial f}{\partial b}\right)db + \left(\frac{\partial f}{\partial c}\right)dc + \dots$$

This equation tells how the functional form transforms changes in the independent variables into changes of the dependent variable. The deviations from the average values are caused by deviations of the independent variables about their average values, e.g. $\Delta a_i = a_i - \langle a \rangle$. Of course, the sum of these deviations due to random error in each of the measured quantities, the average deviation of the calculated quantity, is zero.

$$\langle \Delta x \rangle = \frac{1}{N} \sum_i (x_i - \langle x \rangle) = \langle x \rangle - \langle x \rangle = 0$$

Thus, this quantity does not give information about uncertainty. Consider the average of the square of this deviation, using the differential form above for the deviations and considering only three variables (Extension to more variables should be obvious.).

$$\langle \Delta x^2 \rangle = \frac{1}{N} \sum_i \left(\left(\frac{\partial f}{\partial a}\right) \Delta a_i + \left(\frac{\partial f}{\partial b}\right) \Delta b_i + \left(\frac{\partial f}{\partial c}\right) \Delta c_i \right)^2$$

Expansion of the right-hand side, along with the definition of the average of a quantity gives:

$$\langle \Delta x^2 \rangle = \left(\frac{\partial f}{\partial a}\right)^2 \langle \Delta a^2 \rangle + \left(\frac{\partial f}{\partial b}\right)^2 \langle \Delta b^2 \rangle + \left(\frac{\partial f}{\partial c}\right)^2 \langle \Delta c^2 \rangle +$$

$$2\left(\frac{\partial f}{\partial a}\right)\left(\frac{\partial f}{\partial b}\right)\langle \Delta a \Delta b \rangle + 2\left(\frac{\partial f}{\partial a}\right)\left(\frac{\partial f}{\partial c}\right)\langle \Delta a \Delta c \rangle + 2\left(\frac{\partial f}{\partial b}\right)\left(\frac{\partial f}{\partial c}\right)\langle \Delta b \Delta c \rangle$$

If the quantities a, b, and c are truly independent variables, then deviations in one measurement of a and b should be uncorrelated from those in another, and the average $\langle \Delta a \Delta b \rangle$ should be zero. Similarly, the other two cross terms are zero. We make the assumption that these are independent in that sense, and the last three terms in this equation do not contribute. Now, one defines the uncertainties in each of the quantities as the root-mean-square deviation over the set to find the relation:

$$\Delta x = \sqrt{\langle \Delta x^2 \rangle} = \sqrt{\left[\left(\frac{\partial f}{\partial a}\right)^2 (\Delta a)^2 + \left(\frac{\partial f}{\partial b}\right)^2 (\Delta b)^2 + \left(\frac{\partial f}{\partial c}\right)^2 (\Delta c)^2 + \dots\right]}$$

This gives a simple equation for estimating the uncertainty in a calculated quantity from the uncertainty in measured quantities from which it is calculated. This is what is meant by propagation of error.

Here are simple examples. See if you can determine the resulting equation for the uncertainty from the derivatives of the function in each case.

Functional Form	Uncertainty
$x = a + b$	$\Delta x = \sqrt{(\Delta a)^2 + (\Delta b)^2}$
$x = a - b$	$\Delta x = \sqrt{(\Delta a)^2 + (\Delta b)^2}$
$x = a b$	$\Delta x = \sqrt{b^2 (\Delta a)^2 + a^2 (\Delta b)^2}$
$x = \frac{a}{b}$	$\Delta x = \sqrt{\frac{1}{b^2} (\Delta a)^2 + \frac{a^2}{b^4} (\Delta b)^2}$
$x = a^m b^n$	$\Delta x = \sqrt{m^2 a^{2(m-1)} b^{2n} (\Delta a)^2 + n^2 a^m b^{2(n-1)} (\Delta b)^2}$
$x = \ln a$	$\Delta x = \sqrt{\frac{(\Delta a)^2}{a^2}}$

In the equations of the table, a and b refer average values of the measured quantities and x is the function whose uncertainty is to be determined. The third and fourth equations are correct, but a clearer view of how uncertainty propagates can be obtained by rewriting these slightly.

The "Worst- Case" or Range Method

A quick method for estimating uncertainty uses the maximum uncertainties to estimate the range of values of a calculated quantity. It can best be illustrated by example. Consider the calculation of x through the formula:

$$x = a + b$$

Suppose that a and b have been measured and are known to have the following values:

$$a = a_0 \pm \Delta a$$

$$b = b_0 \pm \Delta b$$

Obviously, the most likely value for x is $a_0 + b_0$. However, one needs to specify the uncertainty in this value, given the known uncertainties in a and b. To do so, one must find the range of possible values given the ranges of a and b. One may do this, for addition, by noting that adding the maximum of the range of values of a with maximum of the range of values of b gives the maximum of the range of x. Adding the minima of these ranges gives the minimum of the range of x. The maximum value of x is therefore, $a_0 + b_0 + \Delta a + \Delta b$ and the minimum of this range is $a_0 + b_0 - \Delta a - \Delta b$. Thus, the range of values of x is:

$$\begin{aligned} \text{Range}(x) &= a_0 + b_0 + \Delta a + \Delta b - (a_0 + b_0 - \Delta a - \Delta b) \\ &= 2(\Delta a + \Delta b) \end{aligned}$$

One may then determine an uncertainty as one-half of this range. So, the reported determination of x would be as shown in the table.

Function	Value of x	Uncertainty in x
$x = a + b$	$a_0 + b_0$	$\Delta a + \Delta b$
$x = a - b$	$a_0 - b_0$	$\Delta a + \Delta b$
$x = a b$	$a_0 b_0$	$a_0 \Delta b + b_0 \Delta a$
$x = \frac{a}{b}$	$\frac{a_0}{b_0}$	$\frac{a_0 \Delta b + b_0 \Delta a}{b_0^2 + (\Delta b)^2}$

In general, these values of the uncertainty will be somewhat larger than the root-mean-square uncertainties for the same functions determined by the calculus of variations shown above. Nevertheless, these are reasonable estimates of the uncertainty.

Once again one may show that, for the product (line 3), the relative uncertainty in x is the sum of the relative uncertainties in a and b. However, for the quotient in line 4, one finds the following for the relative uncertainty:

$$\left| \frac{\Delta x}{x} \right| = \left(\frac{1}{1 + \left(\frac{\Delta b}{b_0} \right)^2} \right) \left(\left| \frac{\Delta b}{b_0} \right| + \left| \frac{\Delta a}{a_0} \right| \right)$$

If the uncertainty in b is small compared to the average value, then the relative uncertainties in a and b add to give the relative uncertainty in the quotient, just as for the product.

Significant Figures

One thing that shows a grader a student's lack of knowledge of uncertainty is the number of significant figures reported by the student. Reporting the proper number of figures to describe the uncertainty of a calculation shows an understanding of the process of propagation of uncertainty. One often sees students' data reported with large numbers of digits that substantially overstate the precision of the experimental determination of a quantity by orders of magnitude. The National Institute of Standards and Technology expends a great deal of effort to measure and report data as precisely as possible. For example, the speed of light in a vacuum is reported to be

$$c = 299\,792\,458 \text{ m s}^{-1}.$$

However, for most of us, achieving that precision is exceedingly difficult, if not impossible.

The concept of significant figures applies only to calculations involving imprecisely known numbers.⁵ Suppose one is calculating the density of an object from measurements of its weight and volume. Each of these measured

⁵ Nobody is concerned about significant figures when doing arithmetic in a mathematics class since all the numbers are assumed to be absolutely precise.

numbers is defined to a certain precision, and the density is found by division, e.g. as

$$49.853\text{g}/50.002\text{mL}$$

In principle, one can use a calculator to specify this number. On the calculator screen one might then see the number

$$0.997020119 \text{ g/mL.}$$

Of course, this number is certainly not known to that precision. Propagating uncertainty, as discussed above, can inform a scientist of the true nature of uncertainty. For the example above, a calculation based on percentage error, assuming an uncertainty of ± 1 in the last digit of each factor, shows that the density calculated has a precision of $\pm 0.00003 \text{ g/mL}$. So, including this precision, the value of the density – showing reasonable significant digits – should be reported as

$$49.853\text{g}/50.002\text{mL} = 0.9970 \text{ g/mL}$$

to indicate (in fact, it slightly overestimates the uncertainty) the uncertainty propagated. This is a shorthand statement of the uncertainty. Stating the result this way means the true value lies between 0.9969 g/mL and 0.9971 g/mL . Of course, the actual uncertainty would allow one to report this as:

$$49.853\text{g}/50.002\text{mL} = 0.99702 (\pm 0.00003) \text{ g/mL}$$

A rule of thumb in assessing the number of significant figures to report is that the number of significant figures in a calculated result can never be greater than the number of significant figures in the factor with the least number of significant figures.⁶ By this rule, one might have supposed that the number of significant figures in the density calculated above would have been 5 since each of the two factors has 5 significant figures. With this rule, one would have reported a result as

$$49.853\text{g}/50.002\text{mL} = 0.99702 \text{ g/mL}$$

This reporting of significant figures is FAR, FAR better than reporting all of the figures a calculator gives.

Significant Figures in Factors

Before using numbers in calculations, one must identify the significant figures they contain. This is often obvious. However, when zeros are present, there is some confusion. Here are the conventions used:

- (a) Zeros to the left of the first nonzero digit are not significant; they are placeholders. One can see this by expressing the number in scientific notation. For example, the number 0.00123 has three significant figures. This can easily be seen by rewriting this number as 1.23×10^{-3} .
- (b) Zeros to the right of a nonzero digit may or may not be significant. The significance lies in whether the person who wrote the number is trying to say by incorporating the zeros that the value is precise to that many figures. Sometimes it is simply not possible to tell whether all of the digits in a reported number are significant. Using scientific notation usually

⁶ This is a commonsense rule. It states that the percentage error in the calculated result can never be less than the percentage error in any factor. Such a statement, of course, has exceptions. For example, taking roots of an imprecise number may result in an increase in the number of significant digits.

makes the ambiguity of significance of zeros a moot point. For example, the number 20,000 may have 1, 2, 3, 4, or 5 significant figures. By writing this as 2.000×10^4 , it is clear that it is indicated to be precise to 4 significant figures. Written in this manner, this statement implies that the number is somewhere between 19,999 and 20,001. However, use discretion.

Carrying Significant Figures in Calculations

As said above, the values determined experimentally have associated uncertainty which can be expressed directly. When multiple determinations of some value are made, a standard deviation of the set gives the precision. The problem is often how to express this precision in terms of significant figures.

The most common calculation that most chemists do is the calculation of concentration. Suppose the concentration of HCl is determined in triplicate, as shown in the table.

Calculation 1	0.18492 moles/L
Calculation 2	0.18517 moles/L
Calculation 3	0.18534 moles/L

The “best” estimate of the concentration, given these three calculations, is the average:

$$c_{ave} = \frac{1}{3} (0.18492 + 0.18517 + 0.18534) \frac{\text{moles}}{\text{L}} = 0.18514 \frac{\text{moles}}{\text{L}}$$

The standard deviation of this result is $\sigma = 0.00021$ moles/L. Thus, one should properly express this to four significant figures:

$$c_{ave} = 0.1851 \frac{\text{moles}}{\text{L}}$$

If a result is to be used in calculations, one may want to retain an additional figure or two past the first uncertain one.⁷ Looking at the three lines in the table, the first three figures are identical, 0.185, by rounding. This means one has to keep at least the next figure in each to introduce uncertainty into the calculation. Even the fourth digits span only a small range: 49-53, a range of 4 in that place. As a rule of thumb, if the range of the uncertain figure is less than 6, keep this figure after the first uncertain one for purposes of calculating of the average and standard deviation. Doing this to the above calculation gives an average of 0.18513 moles/L, essentially the same as the result when keeping all five digits. Rounding off individual values or dropping digits too early in a calculation can result in a much lower precision than one may be entitled to report. When in doubt, it is better to keep an extra figure until the standard deviation is determined, on the basis of which one can make a decision on the number of significant figures.

⁷ Often calculators that retain many digits are used. It is fine to retain these in calculations, but at the end one must specify the result only to the number of digits valid, given the limited certainty of the numbers put into the calculation.