

UNCERTAINTIES IN CHEMICAL CALCULATIONS

Gary L. Bertrand, Professor of Chemistry
University of Missouri-Rolla

Background

In making quantitative scientific observations, there is always a limit to our ability to assign a number to the observation, so there is always an **uncertainty** associated with any measured quantity. There is then the question of how the **quantity** and its **uncertainty** are best represented. We will see that even the most straightforward observations have an uncertainty, and two people observing the same quantity may report different values.

The simplest case to be considered is when there is only one observation of the quantity (or the measuring device is not precise enough to observe any variation in the observed value), and one must estimate the **minimum uncertainty**. This is really no more than a guess by the observer as to how reliably the measurement is made. When reading a digital clock or timer which can be read to a second (say 38 seconds), the actual time is somewhere between 38 and 39 seconds IF the timer is perfectly calibrated, and IF the reading was made (or the timer was stopped) at the exact time of the event. Under the very best of conditions, this quantity could be represented as 38.5 seconds with an uncertainty of 0.5 seconds. If one recognizes that the mechanism might not have worked perfectly, a greater uncertainty would be assigned. In practice, most experimentalists would report this time as 38 ± 1 seconds. If the time interval was measured repeatedly as 38 seconds, the experimentalist might report this as 38.0 ± 0.5 seconds. A different observer might report the value as 38.5 ± 0.5 seconds. This observation could be reported in three different ways, and it is clear that there is considerable uncertainty in the assignment of uncertainty.

This type of estimate is usually based on how accurately the number may be read. When reading a graduated scale, it is easy to see that a reading may fall between two of the smallest divisions. Pierre Vernier (1580-1637) developed the **Vernier Scale** which can interpolate between divisions to 1/5, 1/10, or even 1/20 of the smallest division on a scale. Without a device of this type, the reading can at best be interpolated to 1/10 of a division, and the uncertainty is more likely to be 1/5 of the smallest division of the scale, or more.

When the measuring device is sufficiently sensitive, the readings are seen to vary randomly over a range of values, and sometimes the variation may appear to be systematic as if the reading is oscillating in time, when a constant value is expected. It is generally desirable to represent these fluctuating values as a single value with some measure of its uncertainty.

Consider a group of observations: 106,111,108,105,109,115,110,112,114,101

There are a few cases in which one might pick the maximum (115) and minimum (101) observed values to represent the range of observations, take the average of these two extremes (108) to represent the "best" value to report, and report the uncertainty as one-half of the range of values (7). The set of 10 observations could be

represented as 108 ± 7 . However, one can not rule out the possibility that the next value to be observed might be greater than 115 or less than 101.

Probability theory is based on the assumption that if there is a “**true value**” which we are attempting to observe, it is more likely that any given observation will lie closer to this value, rather than farther away. This could also be stated as “the probability of an observed deviation from the **true value** decreases with the absolute magnitude of the deviation.” If the “true value” of an observation were 108, we would expect a greater number of observations to lie in the range 106 - 110 than in the range 101 - 105 or 111 - 115. This is not quite the case in the set of observations above. The theory predicts that the “best” approximation of the “true value” is the quantity that minimizes the sum of the squares of deviations of the observed values from it. While this is a complex concept, the value of this “**best**” approximation is calculated simply as the **arithmetic mean** (average) of the observations.

The average of the ten values above is 109.1. When 109.1 is subtracted from each of the ten values, and the differences are squared, the sum of the squared deviations is 164.9. If we change the target value to 109.0 or 109.2, and repeat the process, the sum of the squared deviations is 165.0. Changing the target value to 108.9 or 109.3 produces 165.3 for the sum of the squares of the deviations. On this basis, 109 is a better representation of the observations than is the mid-range value of 108.

The Statistical Method

The method can be applied to very complex situations in which observations of two or more variables are to be described with a correlating equation, but this discussion will only address the simplest application of assigning uncertainty to a mean.

The statistical approach recognizes that it is impossible to precisely state how accurate an observation may be, or even how accurate an observed average or mean might be. The method focuses instead on a statistical quantity, which is called the **standard deviation** (σ). This quantity is used to calculate the probability that any single observation will fall within a specified deviation from the observed mean, and on the probability that another determination of the mean will fall within a specified deviation of the mean. The equations for calculating these quantities are based on the assumption of a very large number of observations, then they are adapted for application to smaller numbers of observations (as is the normal experimental situation). Some texts use different names for the standard deviation (“**variance**”, “**estimated standard deviation**”) if there are a limited number of observations. Another quantity that is used in these calculations is the “**degrees of freedom**” of the calculated quantity (**df**), which (in the case of a mean) is simply the **number of observations (N)** minus 1 (**df = N - 1**).

The square of the standard deviation (σ^2) is defined as the sum of the squares of the deviations from the average divided by the degrees of freedom. The square of the “standard deviation of the mean” (σ_m^2) is defined as the square of the standard deviation divided by the number of observations. This is more easily understood by performing calculations on the set of data above:

=====
Calculating the standard deviation (s) and the standard deviation of the mean (s_m):

observations	dev of obs. from mean	(dev of obs. from mean) ²
106	106 - 109.1 = - 3.1	9.61
111	111 - 109.1 = 1.9	3.61
108	108 - 109.1 = - 1.1	1.21
105	105 - 109.1 = - 4.1	16.81
109	109 - 109.1 = - 0.1	0.01
115	115 - 109.1 = 5.9	34.81
110	110 - 109.1 = 0.9	0.81
112	112 - 109.1 = 2.9	8.41
114	114 - 109.1 = 4.9	24.01
101	101 - 109.1 = - 8.1	65.61
sum:	<u>1091</u>	<u>164.90</u>

number of obs. N = 10 ; df = N - 1 = 9

Mean = sum/N = 1091/10 = 109.1

$$s^2 = (\text{sum of squares})/df = 164.90/9 = 18.3$$

$$s = 4.3$$

$$s_m^2 = s^2/N = 18.3/10 = 1.83$$

$$s_m = 1.4$$

=====
 The statistical theory calculates that for a large number of observations, 50% of the observations will fall within 0.675 of the mean and 68.3% will be within of the mean. Some other probabilities are given below. Applying these probabilities to the set above (recognizing that this set does not qualify as a large number of observations), 50% of the observations are expected to fall in the interval 109.1 ± (0.674)(4.3) = 106 to 112; 68% in the interval 109.1 ± 4.3 = 105 to 113; and 90% in the interval 109.1 ± (1.65)(4.3) = 102 to 116. These statistics are seen to apply to this set of observations.

interval	probability that an observation will fall within the interval
mean ± 0.674	50%
mean ± 1.00	68.3%
mean ± 1.65	90%
mean ± 1.96	95%
mean ± 2.58	99%
mean ± 3.30	99.9%

=====

Similar estimates are made regarding the probability that another determination of the mean will fall within a certain interval, with this based on the standard deviation of the mean. This means that if many more sets of ten observations were made and averaged, 50% of the means would be expected to fall within $\pm(0.675)(1.4) = \pm 0.9$ of the overall mean of all of the determinations; 68% within ± 1.4 of the overall mean; and 90% within $\pm (1.65)(1.4) = \pm 2.3$.

The reader has probably noticed that there is considerable ambiguity in the number of significant figures that are being used for these uncertainties. In practice, there is little justification in stating an uncertainty to more than one significant figure.

These statistical calculations assume that a large number of observations are used to calculate the mean and the standard deviation. When smaller numbers of observations are used, there is less confidence that the calculated values are really representative of the statistical probabilities. An additional factor is introduced, which is based on the degrees of freedom, giving a combined factor which is called the **Student t-factor** (W. S. Gosset developed this factor under the pseudonym "Student"). The standard deviation of the mean is multiplied by the t-factor, which is based on the degrees of freedom and the desired confidence level, to obtain the **Confidence Interval** () at the specified percentage (the **level of confidence**). For the set of data above (df = 9), various confidence intervals may be calculated:

$$50\% = (.703)(1.4) = 1.0 \quad ; \quad 90\% = (1.83)(1.4) = 2.6 \quad ; \quad 95\% = (2.26)(1.4) = 3.1$$

These quantities are stated as "the uncertainty is ± 1 at the 50% level of confidence", or "the mean value is 109 ± 3 at the 95% level of confidence".

=====

t-factors for Various Levels of Confidence:

df	t _{50%}	t _{90%}	t _{95%}	t _{99%}
1	1.00	6.31	12.70	63.7
2	0.816	2.92	4.30	9.92
3	0.765	2.35	3.18	5.84
4	0.741	2.13	2.78	4.60
5	0.727	2.01	2.57	4.03
6	0.718	1.94	2.45	3.71
7	0.711	1.89	2.36	3.50
8	0.706	1.86	2.31	3.36
9	0.703	1.83	2.26	3.25
10	0.700	1.81	2.23	3.17
15	0.691	1.75	2.13	2.95
20	0.687	1.72	2.09	2.85
30	0.683	1.70	2.04	2.75
	0.674	1.64	1.96	2.58

=====

When an author states that a mean value is 109 ± 1 , what confidence level should you assign to that value? Unless more detailed information is given, the stated uncertainty is probably the standard deviation of the mean, and the mean is based on a limited number observations. If there were only two observations, the confidence level would be 50%, and if there were hundreds of observations, the confidence level would be 68%. In most cases, 50% is the more likely level.

Combining Uncertainties in Calculations - Propagation of Uncertainty

Various measurements that are made in science are usually combined in order to calculate other quantities or properties that may be used in subsequent calculations. Each of the quantities will have an uncertainty, and the calculated value must be assigned an uncertainty. This is described as a **propagation of uncertainty** through the calculation. The method comes from **differential equations**, treating the uncertainties as differential quantities (). The value of some quantity (Z - the dependent variable) will be calculated from an equation using observed values (W, X, and Y - the independent variables), which have known or estimated uncertainties (w , x , y).

***** potentially bewildering stuff ahead *****

The equation gives Z as a function of W, X, and Y,

$$Z = Z(W, X, Y) .$$

The differential of Z (dZ) is related to the partial derivatives of Z with respect to each of the independent variables and the differentials of these variables.

$$dZ = (\partial Z / \partial W)_{X, Y} dW + (\partial Z / \partial X)_{W, Y} dX + (\partial Z / \partial Y)_{X, W} dY .$$

The partial derivatives are evaluated from the equation used to calculate Z, and are represented by functions of the variables. The estimated uncertainty in Z is calculated as

$$z^2 = [(\partial Z / \partial W)_{X, Y}]^2 w^2 + [(\partial Z / \partial X)_{W, Y}]^2 x^2 + [(\partial Z / \partial Y)_{X, W}]^2 y^2$$

***** resume speed *****

This is the fundamental equation for propagating uncertainties. Fortunately, most of the applications that you will encounter may be reduced to two simple relationships.

For Multiplication and Division: $Z = WX/Y$

$$(\partial Z / Z)^2 = (\partial W / W)^2 + (\partial X / X)^2 + (\partial Y / Y)^2$$

For Addition and Subtraction: $Z = W - X + Y$

$$z^2 = w^2 + x^2 + y^2 .$$

If there are powers involved in the equation using multiplication and division,

$$Z = W^2 X^3 / Y^{1/2} , (\partial Z / Z)^2 = 4 (\partial W / W)^2 + 9 (\partial X / X)^2 + (1/4) (\partial Y / Y)^2$$

and if there is multiplication by scalars in the equation using addition and subtraction,

$$Z = 2W - 3X + Y/2 , z^2 = 4 w^2 + 9 x^2 + (1/4) y^2 .$$

In applying these relationships, it is important to have the uncertainties of all the independent variables at the same level of confidence. If the uncertainties of W, X, and Y are at the 50% level, the calculated uncertainty in Z will be at the 50% level.

Examples:

1. Measuring a volume as the difference between two buret readings:

$$R_1 = 5.42 \quad , \quad R_2 = 42.76 \quad ; \quad V = R_2 - R_1 = 37.34 \text{ ml} \quad , \quad v = ?$$

The last digit on the buret reading is an interpolation within the smallest division, 0.1 ml. A reasonable estimate of the uncertainty in each reading is ± 0.02 at the 50% level of confidence. Applying the rule for addition and subtraction:

$$v^2 = R_1^2 + R_2^2 = (0.02)^2 + (0.02)^2 = 0.0008 \quad , \quad v = 0.028$$

$$V = 37.34 \pm 0.03 \text{ ml at the 50% confidence level}$$

2. Calculating concentration from a titration:

A sample of an acid of unknown concentration is pipetted into a flask with a 25 ml pipet, and titrated with standard base solution ($0.0988 \pm 0.0001 \text{ M}$), requiring $37.34 \pm 0.03 \text{ ml}$. The pipet may be assumed to have an uncertainty of $\pm 0.03 \text{ ml}$. The equation is

$$[\text{acid}] V_{\text{acid}} = [\text{base}] V_{\text{base}}$$

$$[\text{acid}] = [\text{base}] V_{\text{base}} / V_{\text{acid}} = (0.0988 \pm 0.0001)(37.34 \pm 0.03) / (25.00 \pm 0.03) \text{ M}$$

$$[\text{acid}] = 0.1476 \pm ? \text{ M}$$

$$([\text{acid}] / [\text{acid}])^2 = ([\text{base}] / [\text{base}])^2 + (v_{\text{base}} / V_{\text{base}})^2 + (v_{\text{acid}} / V_{\text{acid}})^2$$

$$([\text{acid}] / 0.1476)^2 = (0.0001 / 0.0988)^2 + (0.03 / 37.34)^2 + (0.03 / 25.00)^2$$

$$= 1.0 \times 10^{-6} + 0.65 \times 10^{-6} + 1.44 \times 10^{-6} = 3.09 \times 10^{-6}$$

$$[\text{acid}] = (0.1476)(1.76 \times 10^{-3}) = 2.6 \times 10^{-4}$$

$$[\text{acid}] = 0.1476 \pm 0.0003 \text{ M}$$

3. Calculations on Glass Beads:

	mass of 5 beads (g)		volume of 8 beads (ml)	
	1.790		1.06	
	1.916		1.11	
	1.870		1.06	
	1.728		1.10	
	1.726		<u>1.12</u>	
	1.836	mean	1.09	= 0.028
	1.814			m = 0.013
	<u>1.864</u>			df = 4 , $t_{50\%} = 0.741$
mean	1.818	= 0.068		50% = 0.010
		m = 0.026		
		df = 7 , $t_{50\%} = 0.711$		
		50% = 0.018		

Mean for 5 beads = $1.818 \pm 0.018 \text{ g}$ Mean for 8 beads = $1.09 \pm 0.01 \text{ ml}$
 mean for 1 bead = $0.364 \pm 0.004 \text{ g}$ mean for 1 bead = $0.136 \pm 0.0012 \text{ ml}$
 Density = mass/volume = $(0.364 \pm 0.004) / (0.136 \pm 0.0012) = 2.68 \pm 0.04 \text{ g/ml}$
 $(D/D)^2 = (0.004/0.364)^2 + (0.0012/0.136)^2 = 0.0002$; $D = (2.68)(0.014)$

Applications to Curve Fitting:

The link "Data Processing with Microsoft Excel" covers curve-fitting data by the method of Linear Least Squares Regression. This describes fitting data to an equation of the sort

$$Y = A + BX + CX^2 + \dots, \quad \text{or more generally,} \quad Y = A + BX + CW + \dots,$$

By a procedure which gives values of the parameters (A, B, C) and the standard deviations for these values (dA, dB, dC in that manuscript refer to A , B , C). The standard deviations of these parameters are to be considered in the same sense as the standard deviation of the mean in the discussion above. The sum of the squares of deviations in this case refers to the deviations of the input Y-values from the values calculated from the "best fit" parameters (A, B, C) at the input values of X or X, W. The **degrees of freedom** (df) now refers to the number of observations minus the number of parameters in the equation.

Example: The data set:

X	Y
4.003	51.6608
28.103	53.6134
39.948	54.6060
44.01	54.9698

is regressed to the equation: $Y = A + BX$, giving

$$A = 51.32055, \quad dA = 0.02572$$

$$B = 0.08244, \quad dB = 0.00078$$

$$R^2 = 0.99982, \quad dY = 0.024, \quad df = 2.$$

The uncertainty in A (A) is $(0.816 \times 0.02572) = 0.02$ at the 50% confidence level,
 $(2.92 \times 0.02572) = 0.08$ at the 90% confidence level,
 $(4.30 \times 0.02573) = 0.1$ at the 95% confidence level.

The uncertainty in B (B) is $(0.816 \times 0.00078) = 0.0006$ at the 50% confidence level,
 $(2.92 \times 0.00078) = 0.002$ at the 90% confidence level,
 $(4.30 \times 0.00078) = 0.003$ at the 95% confidence level.