

3 Errors: classification and propagation

There are errors and uncertainties. The latter are unavoidable; eventually it is the omnipresent thermal noise that causes the results of measurements to be imprecise. After trying to identify and correct avoidable errors, this chapter will concentrate on the propagation and combination of uncertainties in composite functional relations.

3.1 Classification of errors

There are several types of error in experimental outcomes:

- (i) (accidental, stupid or intended) mistakes
- (ii) systematic deviations
- (iii) random errors or *uncertainties*

The first type we shall ignore. Accidental mistakes can be avoided by careful checking and double checking. Stupid mistakes are accidental errors that have been overlooked. Intended mistakes (e.g. selecting data that suit your purpose) purposely mislead the reader and belong to the category of *scientific crimes*.

Systematic errors

Systematic errors have a non-random character and distort the result of a measurement. They result from erroneous calibration or just from a lack of proper calibration of a measuring instrument, from careless measurements (uncorrected parallax, uncorrected zero-point deviations, time measurements uncorrected for reaction time, etc.), from impurities in materials, or from causes the experimenter is not aware of. The latter are certainly the most dangerous type of error; such errors are likely to show up when results are compared to those of other experimentalists at other laboratories. Therefore independent corroboration of experimental results is required before a critical experiment (e.g. one that overthrows an accepted theory) can be trusted.

Random errors or uncertainties

Random errors are unpredictable by their very nature. They can be caused by the limited precision of instrumental readings, but are ultimately due to *physical noise*, i.e. by natural fluctuations due to thermal motions or to the random timing of single events. Since such errors are unavoidable and unpredictable, the word “error” does not convey the proper meaning and we prefer to use the term *uncertainty* for the possible random deviation of a measured result from its true value.

If a measurement is repeated many times, the results will show a certain *spread* around an average value, from which the estimated inaccuracy in the average can be determined. The probability distribution, from which the measured values are *random samples*, is supposed to obey certain statistical relations, from which rules to process the uncertainties can be derived. In the case of a single measurement one should estimate the uncertainty, based on knowledge of the measuring instrument. For example, a length read on a ruler will be accurate to ± 0.2 mm; a length read on a vernier caliper will be accurate to ± 0.05 mm. Chemists reading a liquid level on a buret or graduated cylinder can estimate volumes with a precision of ± 0.3 scale divisions. Be aware of the precision of *digital* instruments: they usually display more digits than warranted by their precision. The precision of reliable commercial instruments is generally indicated by the manufacturer, sometimes as an individual calibration report. Often the *maximum* error is given, which can have a (partly) systematic character and which exceeds the standard deviation.

Know where the errors are

As experimentalist you should develop a realistic feeling for the errors inherent in your experiments. Thus you should be able to focus attention on the most critical parts and balance the accuracy of the various contributing factors. Suppose you are a chemist who performs a titration by adding fluid from a syringe and weighs the syringe before and after the titration. How accurate should your (digital) weight measurement be? If the end of a titration is marked by one drop of fluid (say, 10 mg), it suffices to use a 3-decimal balance (measuring to ± 1 mg). Using a better balance wastes time and money! If you are a physicist measuring time-dependent fluorescence following a 1 ns light pulse, it suffices to analyze the emission in 100 ps intervals. Using higher resolution wastes time and money!

3.2 Error propagation

Propagation through functions

In general the required end result of a series of measurements is a *function* of one or more measured quantities. For example, if you measure the

length l and width w of a rectangular plane object, both the circumference $C = 2(l + w)$ and the area $A = lw$ are (simple) functions of l and w . Assume the deviations in l and w are independent of each other with standard uncertainties Δl and Δw , respectively, what then is the standard uncertainty in C or in A ? A somewhat more complicated relation is the determination of the change in standard Gibbs function ΔG^0 for an equilibrium reaction with measured equilibrium constant K :

$$\Delta G^0 = -RT \ln K, \quad (3.1)$$

where R is the gas constant and T the absolute temperature. What is the standard uncertainty in ΔG^0 given the standard uncertainty in K ? And if the equilibrium constant K of a dimerization reaction $2A \rightleftharpoons A_2$ is determined by measuring concentrations $[A]$ and $[A_2]$:

$$K = \frac{[A_2]}{[A]^2}, \quad (3.2)$$

how can we determine the standard uncertainty in K given those in $[A]$ and $[A_2]$, assuming the deviations of $[A]$ and $[A_2]$ to be independent? How will the latter be modified if the deviations are *not* independent, e.g. if we measure both the total concentration $[A] + 2[A_2]$ and $[A_2]$ independently?

What we need to establish is the *propagation* of uncertainties. The clue is *differentiation*:

If the standard uncertainty in x equals σ_x , then the standard uncertainty σ_f in $f(x)$ equals

$$\sigma_f = \left| \frac{df}{dx} \right| \sigma_x. \quad (3.3)$$

Example

Consider the example of Equation (3.1) above. You have measured $K = 305 \pm 5$ at $T = 300$ K, which yields $\Delta G^0 = 14.268$ kJ/mol. The standard uncertainty $\sigma_{\Delta G}$ in ΔG now becomes $(RT/K)\sigma_K = 41$ J/mol. The result you write as $\Delta G^0 = 14.27 \pm 0.04$ kJ/mol.

Combination of independent terms

If the uncertainty in a result (e.g. the sum of two variables) is composed of uncertainties in two or more independent measured quantities, these uncertainties must be combined in an appropriate way. Simple addition of standard uncertainties cannot be correct: the deviations due to different independent

Table 3.1 *Propagation of standard uncertainties in combined quantities or functions.*

$f = x + y$ or $f = x - y$	$\sigma_f^2 = \sigma_x^2 + \sigma_y^2$
$f = xy$ or $f = x/y$	$(\sigma_f/f)^2 = (\sigma_x/x)^2 + (\sigma_y/y)^2$
$f = xy^n$ or $f = x/y^n$	$(\sigma_f/f)^2 = (\sigma_x/x)^2 + n^2(\sigma_y/y)^2$
$f = \ln x$	$\sigma_f = \sigma_x/x$
$f = e^x$	$\sigma_f = f\sigma_x$

sources can be either + or – and will often partly compensate each other. The correct way to “add up” uncertainties is to take the square root of the sum of the squares of the individual uncertainties. More specifically, this applies to standard deviations σ :

$$\text{If } f = x + y, \quad \text{then } \sigma_f^2 = \sigma_x^2 + \sigma_y^2, \quad (3.4)$$

i.e., *independent uncertainties add up quadratically*. Why this is so is explained in Appendix A1 on page 135. In general, when f is a function of x, y, z, \dots :

$$\sigma_f^2 = \left(\frac{\partial f}{\partial x}\right)^2 \sigma_x^2 + \left(\frac{\partial f}{\partial y}\right)^2 \sigma_y^2 + \dots \quad (3.5)$$

From (3.5) it follows immediately that for additions and subtractions the *absolute* uncertainties add up quadratically, while for multiplications and divisions the *relative* uncertainties add up quadratically. Examples of (3.5) are given in Table 3.1, valid for independent contributions.

Example 1

Consider the example of (3.2). What is the s.d. in $K = [A_2]/[A]^2$ when the deviations in $[A]$ and $[A_2]$ are independent? From the x/y^n rule in Table 3.1 it follows that

$$\left(\frac{\sigma_K}{K}\right)^2 = \left(\frac{\sigma_{[A_2]}}{[A_2]}\right)^2 + 4\left(\frac{\sigma_{[A]}}{[A]}\right)^2.$$

Suppose you have measured $[A_2] = 0.010 \pm 0.001$ mol/L and $[A] = 0.100 \pm 0.004$ mol/L. Then the *relative* s.d. of K becomes $\sqrt{0.1^2 + 4 \cdot 0.04^2} = 0.13$, resulting in $K = 1.0 \pm 0.1$ L/mol.

Example 2

Consider again the example of (3.2). What is the s.d. in K if the deviations in the total concentration $[A] + 2[A_2]$ and in $[A_2]$ are independent? Rename the independent variables:

$$x = [A] + 2[A_2]; \quad y = [A_2],$$

so that

$$K = \frac{y}{(x - 2y)^2}.$$

Apply the general rule (3.5), which yields

$$\sigma_K^2 = (x - 2y)^{-6} (4y^2 \sigma_x^2 + (x + 2y)^2 \sigma_y^2).$$

Suppose you have measured the dimer concentration $y = 0.010 \pm 0.001$ mol/L and the total concentration of A $x = 0.120 \pm 0.005$ mol/L. Then the variance of K becomes

$$\sigma_K^2 = 400\sigma_x^2 + 19600\sigma_y^2 = 0.030.$$

So the s.d. becomes $\sqrt{0.030} = 0.17$, resulting in $K = 1.0 \pm 0.2$ L/mol.

Combination of dependent terms: covariances

When uncertainties are not independent of each other, the *covariances* between x and y play a role (see Appendix A1 for details):

$$\sigma_f^2 = \left(\frac{\partial f}{\partial x}\right)^2 \sigma_x^2 + \left(\frac{\partial f}{\partial y}\right)^2 \sigma_y^2 + 2 \frac{\partial f}{\partial x} \frac{\partial f}{\partial y} \text{cov}(x, y) + \dots \quad (3.6)$$

See Appendix A1 on page 135 for the definition of the covariance between x and y : $\text{cov}(x, y)$.

Systematic errors due to random deviations

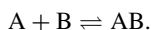
When the function $f(x)$ has an appreciable curvature (second derivative) in the region of x over which the uncertainty of x spreads, a *systematic* deviation in f will occur: the expected value $E[f(x)]$ does not equal $f(E[x])$. This effect is generally in practice not very important. Appendix A2 on page 138 gives details.

Monte Carlo methods

There are cases where you can't express an explicit functional relation between a result and the factors that contribute to the result. For example, given a large number of observations of temperature, pressure, composition, etc., you predict tomorrow's weather using a forecasting model. Knowing the uncertainties of the input data, how uncertain will be the prediction? In a deterministic model (as opposed to a stochastic model) there is a functional relationship between input data and result, but it is complicated and implicit, with lots of correlations and interdependencies. The propagation of uncertainties is related to the *sensitivity* of the result for variations in each of the input data.

Here the computer comes to the rescue. When the number of input parameters is relatively small, numerical values for the derivatives, as required in (3.6), can be obtained by making a small step (preferably in both directions) for each input parameter. For a large number of input data this may not work. You may then find the uncertainty in the result by choosing many input combinations, randomly chosen from the (known) uncertainty distributions of the inputs. The computed output values will be samples of the uncertainty distribution you are looking for. Methods that use random numbers to generate results are in general called *Monte Carlo methods*.¹

A simple example will make this clear. You are a chemist who wishes to determine the equilibrium constant of the association reaction in solution



For this purpose you dissolve 5.0 ± 0.2 mmol of substance A in 100 ± 1 mL solvent and 10.0 ± 0.2 mmol B in 100 ± 1 mL solvent; then you mix the two solutions. You determine the concentration x of AB spectroscopically (AB has an absorption band in a spectral region where neither A nor B absorbs) and find $x = 5.00 \pm 0.35$ mmol/L. The uncertainties given are all standard deviations of supposedly normal distributions. What is the value of the equilibrium constant K and what is its standard uncertainty?

The equilibrium constant is given by

$$K = \frac{[AB]}{[A][B]}, \quad (3.7)$$

¹ Monte Carlo methods can be applied in many fields, notably in statistics, in statistical mechanics and in mathematics to compute multidimensional definite integrals. They are used to generate samples from a given multidimensional distribution. Often a random step is followed by an acceptance criterion, allowing an efficient biased random search that concentrates on the "important" regions of the explored multidimensional space. See Hammersley and Handscomb (1964); for applications in molecular simulation see Frenkel and Smit (2002).

where $[A]$ is the concentration of A, etc. Hence

$$K = \frac{x}{(a/(V_1 + V_2) - x)(b/(V_1 + V_2) - x)}, \quad (3.8)$$

where a is the amount of A originally dissolved in volume V_1 , b the amount of B dissolved in V_2 and x the measured concentration of AB. Of course it is quite feasible to determine K with its uncertainty from the data using the standard method based on (3.5), but it is easier to use a Monte Carlo approach. This is done by generating a large number n (e.g. $n = 1000$) of normally distributed values for each of the input variables a, b, V_1, V_2, x , using the given values for mean and standard deviation (each input variable is now an array of length n) and applying (3.8) to the arrays. The output K is an array of samples representing the probability distribution of K . Doing this we find

$$K = (5.6 \pm 0.6) \text{ L/mol}. \quad (3.9)$$

The cumulative distribution of K is given on a probability scale in Fig. 3.1 (on a probability scale a normal distribution shows as a straight line; see page 39

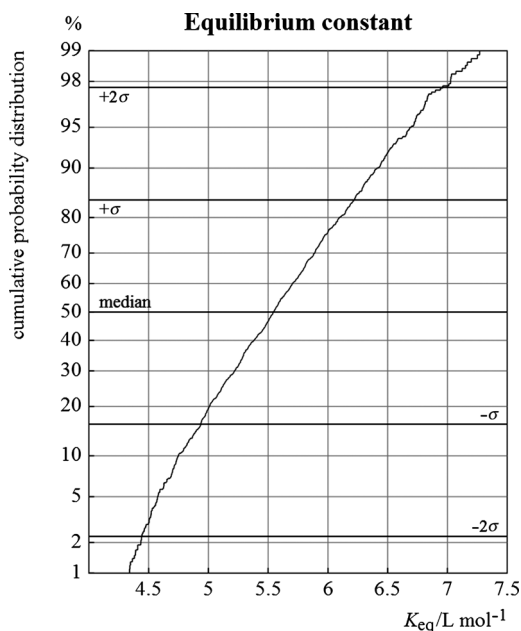


Figure 3.1 The cumulative probability distribution function of the Monte Carlo-generated result of (3.8), using 1000 samples.

for further explanation). You see that the distribution is fairly normal between $\mu \pm \sigma$, but deviates from normal beyond $\mu \pm 2\sigma$. This is due to the nonlinear relation between K and the input variables. Thus the Monte Carlo method has advantages: distortions of the resulting distribution due to nonlinearity are immediately apparent and so are systematic errors due to nonlinearity. The latter are visible as a difference between the mean of the distribution and the value computed directly from the input values without added noise.



See **Python code 3.1** on page 173 for the generation of Monte Carlo samples and figures for this example.

Summary *This chapter distinguished between systematic and random errors, the latter leading to uncertainties in the results. Random errors add up quadratically in sums or differences (i.e., the uncertainty in the result is the square root of the sum of squares of the contributing terms). Relative random errors add up quadratically in products or quotients. Table 3.1 gives more functional relations. In general, an error in x propagates in a function $f(x)$ through multiplication by the derivative $\partial f/\partial x$, see (3.3) and (3.5). When input errors are correlated, their covariances also play a role. When the functional relation is strongly nonlinear, random errors may cause systematic deviations. To investigate error propagation in complex cases it is advantageous to use Monte Carlo methods: generate a large number of samples of the results by randomly selecting the input parameters from appropriate probability distributions.*

Exercises

- 3.1 Perform the following operations and give the result with standard deviation. The standard deviations of quantities are indicated by \pm ; they are independent of each other.
- (a) $15.000/(5.0 \pm 0.1)$
 - (b) $(30.0 \pm 0.9)/(5.0 \pm 0.2)$
 - (c) $\log_{10}(1000 \pm 2)$
 - (d) $(20.0 \pm 0.3) \exp[-(2.00 \pm 0.01)]$
- 3.2 The half-life time $\tau_{1/2}$ of a first-order chemical reaction is determined at four different temperatures. The temperatures are accurate; the standard uncertainties in $\tau_{1/2}$ are indicated:

Temperature (°C)	half-life $\tau_{1/2}$ (s)
510	2000 ± 100
540	600 ± 40
570	240 ± 20
600	90 ± 10

Determine the rate constant k (what unit?) and its standard uncertainty, as well as $\ln k$ and its standard uncertainty, at every temperature. Now plot $\ln k$ with error bars versus the reciprocal absolute temperature. Also, plot k with appropriate error bars on a logarithmic scale versus the reciprocal absolute temperature. Compare the two plots.

- 3.3 Suppose you determine the acceleration of gravity g by measuring the oscillation period T of a pendulum with length l . The value of g follows from

$$g = 4\pi^2 l / T^2.$$

You measure $T = 2.007 \pm 0.002$ s and $l = 1.000 \pm 0.002$ m. Determine g and its standard uncertainty.

- 3.4 The Gibbs activation function for a chemical reaction ΔG^\ddagger follows from the rate constant k according to *Eyring's equation*

$$k = (k_B T / h) \exp(-\Delta G^\ddagger / RT).$$

Here k_B is Boltzmann's constant, h is Planck's constant and R the gas constant (see the data sheet PHYSICAL CONSTANTS on page 209, or use the Python module *physcon.py*).

- If the rate constant k has an uncertainty of 10%, what is the resulting uncertainty in ΔG^\ddagger ?
 - Discuss how an uncertainty in the temperature propagates into ΔG^\ddagger .
 - If $\Delta G^\ddagger = 30$ kJ/mol and $T = 300$ K, how large is the uncertainty in ΔG^\ddagger as a result of an uncertainty of 5°C in the temperature?
- 3.5 (this exercise relates to Appendix A2 on page 138)
Generate an array with 1000 samples of the volume of spheres, of which the radii are samples of a normal distribution with mean 1.0 mm and standard deviation 0.1 mm. Compare the mean of the distribution with the volume of a sphere with radius 1.0 mm and discuss whether the latter is a biased result. Discuss the significance of the bias. Plot the cumulative volume distribution on a probability scale.