

Data and Error analysis

Wednesday, January 15, 2014 3:07 PM

References:

1. [EMP] Experiments in modern physics, Ch. 10
2. [Lyons] Practical guide to data analysis for physical science students, by Louis Lyons (Cambridge University Press).
3. [Berendsen] A student's guide to data and error analysis, by Herman Berendsen (Cambridge University Press).
4. [Taylor] An introduction to error analysis, by John Taylor (University Science Book)

Lecture Outline

- Experimental errors and uncertainties [Lyons & Berendsen Ch. 1-3]
 - o Why estimate errors?
 - o Classification of errors
- The presentation of physical quantities with their inaccuracies [Berendsen Ch. 2]
 - o How to report a series of measurements
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 - Determining the parameters
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(Lecture #1)

Our goal is to present experimental (or simulation) data including a consistent treatment of

experimental errors and inaccuracies.

Experimental errors and uncertainties

- Why estimate errors?
- Classification of errors
 - (accidental, stupid or intended) mistakes
 - Systematic errors or deviations
 - Random errors or uncertainties

There are errors and uncertainties. The latter are unavoidable; eventually it is omnipresent thermal noise and quantum noise that causes the results of measurements to be imprecise.

First, let's try to identify and correct avoidable errors.

There are several types of error in experimental outcomes:

- (accidental, stupid or intended) mistakes
- Systematic errors or deviations
- Random errors or uncertainties

The first type can be avoided. Accidental mistakes can be avoided by careful checking and double and triple checking. Stupid mistakes are accidental errors that have been overlooked. Intended mistakes (e.g. selecting data that suit your purpose) purposely mislead the reader is a scientific misconduct, if not a 'crime'.

Next, why do we care about error analysis?

(Why?)

It is impossible to measure physical quantities without errors. In most cases errors result from deviations and inaccuracies caused by the measuring apparatus or from the inaccurate reading of the displaying device, but also with optimal instruments and digital displays there are always fluctuations in the measurement data. Ultimately there is random thermal noise affecting all quantities that are determined at a finite temperature or quantum noise limiting a specific measuring method.

Any experimentally determined quantity therefore has a certain inaccuracy. If the experiment were to be repeated, the result would be (slightly) different. One could say that the result of a particular experiment is no more than a random sample from a probability distribution.

When reporting the result of an experiment, it is important to also report the extent of the uncertainty, e.g. in terms of the best estimate of some measure of the width of the probability distribution. When experimental data are processed and conclusion are drawn from them, knowledge of the experimental uncertainties is essential to assess the reliability of the conclusion.

(Systematic errors) [Berendsen p. 18]

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 measurement (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) [Berndsen p. 19]

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. Because such errors are unavoidable and unpredictable, the work "error" does not convey the proper meaning and we prefer to use the term uncertainty for the possible random deviation of a measured results 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 graduated cylinder can estimate volumes with a precision of ± 0.3 scaled 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) [Berendsen]

As experimentalist (or theorist who has to deal with statistics of simulation data) 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 contribution factors.

Suppose you are a chemist who perform a titration (volumetric analysis) 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 waster 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!

Titration is a common laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of an identified analyte.

(Lecture #2)

How to present physical quantities with their inaccuracies [Berendsen Ch. 2]

- How to report a series of measurements
 - List all data, a histogram or percentiles
 - List properties of the data set
- How to represent numbers

- *Decimal separators: comma or period?*
Scientists are strongly advised NOT to use periods or commas to divide long numbers into groups of three digits, like 300,00 (English) or 300.000 (eg. French). Instead, use a space (or even better, if your text editor allows it, a thin space) to separate groups of three digits: 300 000.
- **Significant figures**
The end result of a measurement must be presented with as many digits as are compatible with the accuracy of the result. Also when a number ends with zeros! These are the significant figures of the result. However, intermediate results in a calculation should be expressed with a higher precision in order to prevent accumulation of rounding errors. Always indicate the accuracy of the end result! **If the accuracy is not explicitly given, it is assumed that the error in the last digit is ± 0.5 .**

Examples, for the English language

- (i) 1.65 ± 0.05
- (ii) 2.500 ± 0.003
- (iii) $35\,600 \pm 200$: better as $(3.56 \pm 0.02) \times 10^4$
- (iv) 5.627 ± 0.036 is allowed, but makes sense only when the inaccuracy itself is known with sufficient accuracy. If not, this value should be written as 5.63 ± 0.04 .
- (v) Avogadro's number is known as $(6.022\,141\,79 \pm 0.000\,000\,30) \times 10^{23} \text{ mol}^{-1}$ (CODATA 2006). The notation $6.022\,141\,79(30) \times 10^{23} \text{ mol}^{-1}$ is a commonly accepted abbreviation.
- (vi) 2.5 means 2.50 ± 0.05
- (vii) 2.50 means 2.500 ± 0.005
- (viii) In older literature one sometimes finds a subscript $_5$, indicating an inaccuracy of about one quarter in the last decimal: $2.3_5 = 2.35 \pm 0.03$, but this is not recommended.

When inaccuracies must be rounded, then do this in a conservative manner: when in doubt, round up rather than down. For example, if a statistical calculation yields an inaccuracy of 0.2476, then round this to 0.3 rather than 0.2, unless the statistics of your measurement warrants the expression in two decimals (0.25). See Section 5.5 on page 60. **Be aware of the fact that calculators know nothing about statistics and generally suggest a totally unrealistic precision.**

- **How to express inaccuracies**
There are many ways to express the (in)accuracy of a result. When you report an inaccuracy it must be absolutely clear which kind of inaccuracy you mean. In general, when no further indication is given, it is assumed that the quoted number represents the standard deviation or root-mean-square error of the estimated probability distribution.
 - **Absolute and relative errors**
You can indicate inaccuracies as absolute, with the same dimension as the reported quantity, or as a dimensionless relative value. Absolute inaccuracies are often given as numbers in parentheses, relating to the last decimal(s) of the quantity itself.
 - **Using probability distributions**
If the degree of knowledge you have about the reported quantity θ can be

expressed as a probability distribution of that quantity, you can report one or more confidence intervals. This is usually the case if a Bayesian analysis has been made

○ Reporting units

○ **SI units**

Physical quantities not only have a numerical value with inaccuracy, but also a unit. **Always include the proper unit in the correct notation when you report a physical quantity.** There are international agreements on units and notation. The agreed system of units is the “Système International d’Unités” (SI).⁴ The SI units are derived from the SI base units m, kg, s, A, K, mol, cd (see data sheet UNITS on page 215). You should make it a habit to adhere strictly to these units, even if you are often confronted with non-SI units in the literature (dominantly originating from the USA). So, kJ/mol and not kcal/mol, nm (or pm) and not Å, N and not kgf, Pa and not psi.

○ **Non-SI units**

Some non-SI units are allowed, such as the minute (min), hour (h), day (d), degree (°), minute angle (′), second angle (″), liter (L = dm³), metric ton (t = 1000 kg) and astronomical unit (ua = 1.495 978 70×10¹¹ m).

○ **Typographical conventions**

There are also agreed typographical conventions, which should be adhered to not only in scientific manuscripts, but even in informal reports. With modern text editors there is no excuse not to use roman, italic or bold type when required.

The rules are simple:

- italic type for scalar quantities and variables,
- roman type for units and prefixes (mind capitalization),
- italic boldface for a vector or matrix quantity,
- sans-serif bold italic for tensors,
- roman type for chemical elements and other descriptive terms, including mathematical constants, functions and operators.

Examples

- (i) The input voltage $V_{\text{in}} = 25.2 \text{ mV}$,
- (ii) The molar volume $V_{\text{m}} = 22.4 \text{ L/mol}$,
- (iii) The force on the i -th particle $F_i = 15.5 \text{ pN}$,
- (iv) The symbol for nitrogen is N, the nitrogen molecule is N₂,
- (v) A nitrogen oxide mixture NO _{x} with $x = 1.8$,
- (vi) $e = 2.718 \dots$; $\pi = 3.14 \dots$,
- (vii) $F = ma = -\text{grad } V$,
- (viii) The surviving fraction of the k -th species, $f_k^{\text{surv}}(t) = \exp(-t/\tau_k)$.

○ **Graphical representation of experimental data**

Experimental results are often presented in graphical form. The expectation or mean is given as the position (x, y) of (the center of) a symbol in a plot. The usual representation of inaccuracies in x and/or y is an error bar with a total length of twice the standard error. While both x and y values may be subject to experimental errors, very often one of the values (usually x)

is so accurate that it makes no sense to plot an error bar. Figures 2.6 and 2.7 give examples of such a graphical representation, using the data given in Table 2.2. The reason to use a logarithmic scale for the concentration is that an expected exponential decay with time would show up as a straight line. The linear plot can hardly show the small standard deviations of the last three points; on the logarithmic plot the s.d. on the small values show as much larger and asymmetric error bars. Note that the error bars on the last two points extend below the lower limit (1 mmol/L) of the logarithmic scale and therefore appear too short on the graph. Negative ordinate values (which may occur as a result of random errors) cannot be shown at all on a logarithmic scale.

Table 2.2 *Concentration of a reactant as a function of time. The inaccuracy is given as the estimated standard error.*

time t/s	conc. $c/\text{mmol L}^{-1} \pm \text{s.d.}$
20	75 ± 4
40	43 ± 3
60	26 ± 3
80	16 ± 3
100	10 ± 2
120	5 ± 2
140	3.5 ± 1.0
160	1.8 ± 1.0
180	1.6 ± 1.0

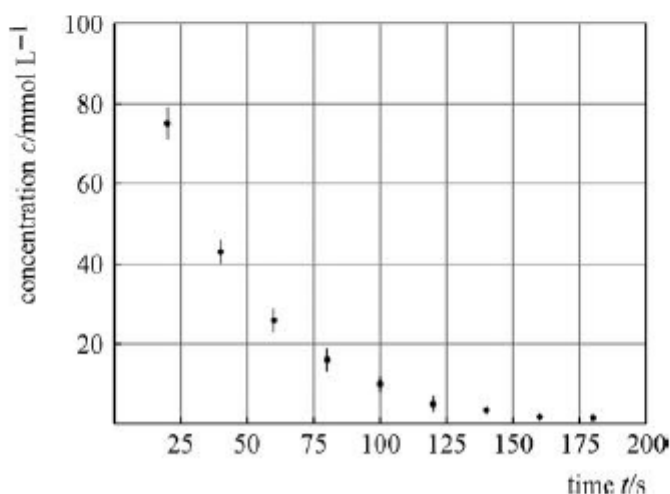


Figure 2.6 A linear plot of concentration of a reactant versus time, with error bars representing \pm the standard error. The data are given in Table 2.2.

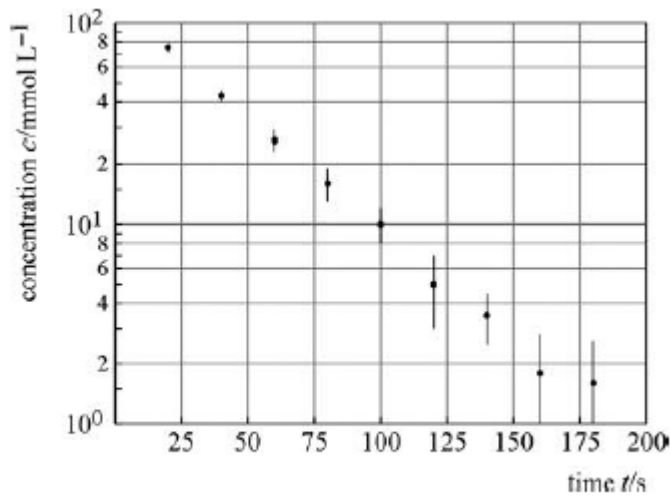


Figure 2.7 A logarithmic plot of the same data.

Error propagation [Lyons & Berendsen Ch. 3]

- **Propagation through functions**

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

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

- **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 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.

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

- **Combination of dependent terms: covariances**

When uncertainties are not independent of each other, the covariances between x and y play a role

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

Why do squared uncertainties add up in sums? [Berendsen Appendix A1]

Processing of experimental data

Let's consider the processing of data in its simplest form: given a number of similar observations $x_i = \mu + e_i$ of an unknown quantity μ , yielding values that only differ in their random fluctuations e_i ,
 how can you make the best estimate μ^* of the true μ ?
 And how can you best estimate the accuracy of μ^* , i.e., how large do you expect the deviation of μ^* from the true μ to be?

Each observation is a sample from an underlying distribution;
 how can you characterize that distribution?

If you have reasons to assume that the underlying distribution is normal, how do you estimate its mean and variance and how do you assess the relative accuracy of those parameters?
 And how do you proceed if you don't wish to make any assumptions about the underlying distribution?

You will have to look at the distribution function of the data and then indicate how the properties of the data lead to estimation of the properties of the distribution function.

Distributions (Frequency functions of one variable) [EMP Ch. 10 & Lyons & Berendsen Ch. 4]

- Mean and variance
- Theoretical frequency functions
- The Bernoulli or binomial frequency function
- The Poisson frequency function
- Gaussian distribution or normal frequency function
- The meaning of σ (standard deviation)

(i) The *average* $\langle x \rangle$ of a series of equivalent (i.e., equally probable) independent samples $x_i, i = 1, \dots, n$ is given by

$$\langle x \rangle = \frac{1}{n} \sum_{i=1}^n x_i. \quad (5.3)$$

(ii) The *mean squared deviation* (msd) from the average is defined as

$$\langle(\Delta x)^2\rangle = \frac{1}{n} \sum_{i=1}^n (\Delta x_i)^2, \quad (5.4)$$

where Δx_i is the deviation of the average:

$$\Delta x_i = x_i - \langle x \rangle. \quad (5.5)$$

The root of the msd, which is naturally called the *root-mean-squared deviation* (rms deviation or rmsd), is a measure for the spread of the data around the average.

In order to determine the msd, you must pass through the data twice: first to determine $\langle x \rangle$ and subsequently to determine $\langle(\Delta x)^2\rangle$. This can be avoided by using the following identity (see Exercise 5.2):

$$\langle(\Delta x)^2\rangle = \langle x^2 \rangle - \langle x \rangle^2, \quad (5.6)$$

where

$$\langle x^2 \rangle = \frac{1}{n} \sum_{i=1}^n x_i^2. \quad (5.7)$$

Graphical handling of data with errors [Berendsen Ch. 6]

- Introduction
- Linearization of functions
- Graphical estimates of the accuracy of parameters
- Using calibration

Often you perform a series of experiments in which you vary an independent variable, such as temperature. What you are really interested in is the relation between the measured values and the independent variables, but the issue is that your experimental values contain statistical deviations.

You may already have a theory about the form of this relation and use the experiment to derive the still unknown parameters. It can also happen that the experiment is used to validate the theory or to decide on a modification. It is also possible that you discover a new phenomenon beyond the prediction of existing theories.

It is sometimes advantageous to take a global view to qualitatively evaluated fundamental relations using simple graphical presentations of the experimental data. The trick of transforming functional relations to a linear form allows quick graphical interpretations. Even the inaccuracies of the parameters can be graphically estimated. To obtain more accurate results, you will need to fit functions to data.

A series of equivalent measurements that should have produced equal results if there had been no random deviations in the measured data. Very commonly, however, a quantity y_i is measured as a function $f(x_i)$ of an independent variable x_i such as time, temperature, distance, concentration or bin number.

The measured quantity may also be a function of several such variables. Usually the independent variables – which are under the control of the experimenter – are known with high accuracy and the dependent variables – the measured values – are subject to random errors.

$$y_i = f(x_i) + \varepsilon_i, \quad (6.1)$$

where x_i is the independent variable (or the set of independent variables) and ε_i is a random sample from a probability distribution.

Generally, you already have a theory about the function f , although that theory may contain unknown parameters $\theta_k (k = 1, \dots, m)$:

$$y = f(x, \theta_1, \dots, \theta_m). \quad (6.2)$$

An example is the linear relation

$$y = ax + b, \quad (6.3)$$

but the relation can be more complex like

$$y = c \exp(-kx). \quad (6.4)$$

It is often possible to *linearize* the relation by a simple transformation. For the latter case:

$$\ln y = \ln c - kx \quad (6.5)$$

yields a linear relation between $\ln y$ and x . It is usually recommended to make such a linearization, as a simple graphic plot will show a straight line, permitting a quick judgment of the suitability of your presumed functional relations.

We will work out a few examples later.

Let us return to the linear relation $y = ax + b$. Suppose you measured n data points (x_i, y_i) , $i = 1, \dots, n$, and expect the measured values y_i to satisfy *as closely as possible* the relation

$$y_i \approx f(x_i), \quad (6.6)$$

where $f(x) = ax + b$ is the expected relation. Your task is to determine the parameters a and b such that the measured values y_i deviate as little as possible from the function values. But what does that mean? The deviations ε_i of the measured values with respect to the function:

$$\varepsilon_i = y_i - f(x_i) \quad (6.7)$$

should be the sole consequence of random errors and we expect in general that the deviations ε_i are random samples from a probability distribution with zero mean. In practice this distribution is often normal. The correct method for this kind of parameter estimation is the *least-squares fit*, which is treated in [Chapter 7](#). A computer program is needed to perform a least-squares fit.

It is not always necessary to perform a precise least-squares fit. It is always meaningful to plot the data in such a way that you expect a linear relation.

A straight line can be adequately judged by visual inspection. A straight line drawn “by eye” to fit the points often gives sufficiently accurate results and even the inaccuracies in the parameters a and b can be estimated by varying the line within the cloud of measured data points. There is nothing wrong with making a quick sketch on old-fashioned graph paper!

Computer programs are useful when there are many data points, when different points have different weights or when high accuracy is required, but they are never a substitute for bad measurements and almost never give you more insight into the functional relations. Be careful with computer programs that are not well-documented or do something you don’t quite understand!

Linearization of functions

In this section a few examples of the linearization of functions are given.

- (i) $y = ae^{-kx}$: $\ln y = \ln a - kx$ (examples: concentration as function of time for a first-order reaction, number of counts per minute for a radioactive decay process). Plot $\ln y$ on a linear scale versus x , or plot y on a logarithmic scale versus x . If you do this by hand, use semi-log paper (one coordinate linear, the other logarithmic with e.g. two decades). Or use a simple Python plot. Figure 2.7 on page 16 is an example. The slope ($-k$ in this example) is read from the graph by selecting a segment (take a large segment for better accuracy) and read the coordinates of the end points (x_1, y_1) and (x_2, y_2) ; the slope equals $\ln(y_2/y_1)/(x_2 - x_1)$. If you take a full decade for the end points (e.g. passing through $y = 1$ and $y = 10$), then the slope is simply $\ln 10/(x_2 - x_1)$.
- (ii) $y = a + be^{-kx}$: $\ln(y - a) = \ln b - kx$. First estimate a from the values of y for large x and then plot $y - a$ versus x on a logarithmic scale. If the plot doesn’t yield a linear relation, adjust a somewhat (within reasonable bounds).
- (iii) $y = a_1e^{-k_1x} + a_2e^{-k_2x}$. This is difficult to handle graphically, unless k_1 and k_2 are very different. A computer program also has difficulties with this kind of analysis! First estimate the “slow” component (with smallest k), subtract that component from y and plot the difference on a logarithmic scale. Figure 6.1 gives the result for the data given in Table 6.1; the standard error in each y is ± 1 unit.

The column z in Table 6.1 gives the differences between y and the values given by the line in the left panel of Fig. 6.1. This line has been drawn “by eye” and goes through the points $(0, 25)$ and $(100, 2.5)$, yielding $k_2 = [\ln(25/2.5)]/100 = 0.023$. Hence the equation for this line is

Table 6.1 Measured values y that result from a sum of two exponentials. The column z results from subtraction of the “slowest” exponential. The standard uncertainty in y equals one unit.

x	y	z	x	y	z
0	90.2	65.2	40	11.7	1.7
5	62.2	39.9	50	8.8	0.9
10	42.7	22.9	60	6.9	0.6
15	30.1	12.4	70	4.6	-0.4
20	23.6	7.8	80	5.0	1.1
25	17.9	3.8	90	2.9	-0.3
30	14.0	1.5			

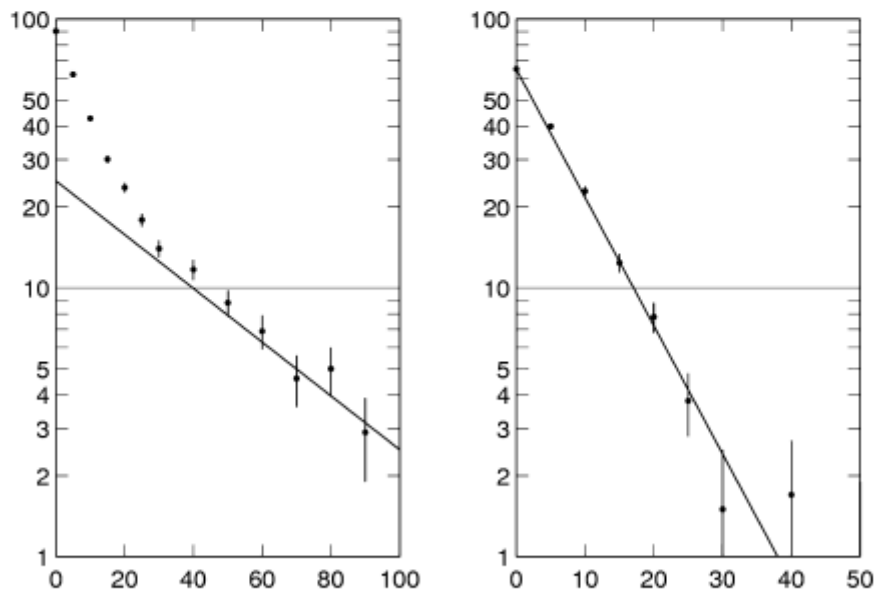


Figure 6.1 Graphical analysis of data which represent the sum of two exponentially decaying quantities. In the left panel the data points y have been plotted on a logarithmic scale versus the independent variable x and the “slowest” component is approximated by a straight line. In the right panel the differences z between the data y and the “slow” component are plotted. Note the different scales for x .

$25 \exp(-0.023x)$. In the right panel of this figure z has been plotted: the points approximately follow a linear relation. The drawn line goes through the points (0,65) and (38, 1), yielding $k_1 = (\ln 65)/38 = 0.11$. Therefore, the function that approximates the behavior of all data points is given by

$$f(x) = 65 e^{-0.11x} + 25 e^{-0.023x}. \quad (6.8)$$

This simple graphical approach does not provide a solid basis to make a reliable guess of the uncertainties in the parameters of this equation. But it provides an excellent basis for the *initial guess* of the parameters in a *nonlinear least squares fit*. The latter is the subject of Chapter 7. Such a fit must be carried out by computer; a suitable program not only provides the best fit, but also gives an estimate of the inaccuracies and correlations of the parameters.

- (iv) $y = (x - a)^p$ (example: the isothermal compressibility χ of a fluid in the neighborhood of the critical temperature behaves as a function of temperature according to $\chi = C(T - T_c)^{-\gamma}$, where γ is the *critical exponent*). Plot $\log y$ versus $\log(x - a)$ (or y versus $(x - a)$ on a double-logarithmic scale); if a is not known beforehand, then vary a somewhat until the relationship becomes a straight line. The slope of the line yields p .
- (v) $y = ax/(b + x)$ (examples: adsorbed quantity n_{ads} of a solute versus concentration c in solution or versus pressure p in the gas phase in the case of Langmuir-type adsorption: $n_{ads} = n_{max}c/(K + c)$; reaction rate v as function of substrate concentration $[S]$ in the case of Michaelis–Menten kinetics¹ $v = v_{max}[S]/(K_m + [S])$). By taking the reciprocal of both sides, this equation becomes a linear relation between $1/y$ and $1/x$:

$$\frac{1}{y} = \frac{1}{a} + \frac{b}{a} \frac{1}{x}. \quad (6.9)$$

In enzyme kinetics a graph of $1/v$ versus $1/[S]$ is called a *Lineweaver–Burk plot*.² There are two other ways to produce a linear relation: plot x/y versus x (the *Hanes method*):

$$\frac{x}{y} = \frac{b}{a} + \frac{x}{a}, \quad (6.10)$$

or plot y/x versus y (the *Eadie–Hofstee method*):

$$\frac{y}{x} = \frac{a}{b} - \frac{y}{b} \quad (6.11)$$

Graphical estimates of the accuracy of parameters

In the previous section you have seen how you can plot your data in such a way that a linear relationship is obtained and how you can estimate the two parameters of a linear function by drawing the “best” line through the data points. In this section you will see how you can make a simple estimate of the uncertainties in those parameters. Sometimes such estimates are sufficient. If they are not, a more accurate least-squares fit is required.

Using Calibration

Suppose you work with an instrument or method that produces a reading y (e.g. a digital number, a needle deflection, a meniscus height) from which a quantity x (e.g. a concentration, an electrical current, a pressure) must be deduced. When the instrument is not properly calibrated, i.e., when the reading does not correspond directly and reliably to the measured

quantity, you should calibrate the instrument yourself. For this purpose you produce a calibration table, and preferably a calibration curve, by measuring the reading for a number of accurately known values of x . These data you either tabulate, or plot and interpolate in a curve, or express the relation between y and x in a mathematical function. Often you will tabulate a correction table or plot a correction curve that contains the differences between the readings and the correct values. Be sure to be explicit what the difference means: usually the correction is to be added to the reading to obtain the true value. In all cases you can deduce the value of x for any measured reading by inversion of the calibration relation.

How do you proceed and how do you determine the uncertainty in x ?

Be explicit!

Make sure in the calibration procedure that you cover the whole range of values for which the method will be used. Extrapolation is generally unreliable, but there is also no need to cover values that in practice will never occur.

Draw the best line through the points; if the line is not straight, hopefully you can build it up from straight segments between calibrated points. If you want to be sophisticated, compute a cubic spline fitting function. Now, for any new measurement of x , given by a reading y , the quantity x can simply be read back from the calibration curve.

Now consider the inaccuracy of a measurement. There are two sources of error: one is the inaccuracy σ_y in the reading y ; the other is the inaccuracy in the calibration curve itself, due to inaccuracies of the calibration measurements. You should also be aware of additional errors that may occur, e.g. resulting from aging of the instrument after the last calibration. Both types of error lead to an uncertainty in x and both sources add up quadratically, because they are independent of each other. The two contributions are depicted in Fig. 6.8, which shows how a concentration in solution is deduced from a measurement of the optical density in a spectrometer. The calibration error is visualized by drawing two parallel sections of the calibration curve at distances representing the standard uncertainty in the calibration itself.

If the calibration has been very carefully performed, the calibration error is likely to be smaller than the direct error in the reading. In that case only the standard uncertainty σ_y of the reading counts. It leads to a standard uncertainty σ_x in the measured quantity by the relation

$$\sigma_x = \frac{\sigma_y}{\left| \left(\frac{dy}{dx} \right)_{\text{cal}} \right|}$$