PHYS 6/7180

References: 1. P.R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences,* McGraw-Hill, New York, (1969)

On curve fits, errors, and goodness of the fit—
Original text by A. Compaan, with minor edits by R. Ellingson

There will be many places in this laboratory where you can do fits to your data. In many cases doing a very sophisticated fit does not make much sense, and often a straight line fit suffices. In other cases a polynomial or exponential fit will be required. However, please keep in mind some important rules about curve fitting and, most importantly, when you have done a fit, you *must* judge for yourself whether the fit is meaningful! It is very tempting to let a computer program (spreadsheet or other numerical program) give some sort of line through the data. Often, however, the fit turns out to be meaningless!

Never report results with 5 or 8 significant digits unless that many digits are meaningful!! In most cases, some of the most important analysis consists of your explanation for the relevance, significance, and believability of your numbers. In some cases, the results may be good to only 1 or 2 significant figures. Furthermore, if you have a calculation of the expected result (say an electron concentration, mobility, or exciton temperature), your obligation as an experimentalist is to explain any discrepancy between your measurement and the calculated expected value which lies outside of your estimated experimental error. *The development of the ability to give a critical evaluation of the results of your experiment is among the most important goals of this course.*

If you have done a fit, you should be able to evaluate a "goodness of fit" parameter such as the chi-squared value. See attached pages from Bevington's book.

If σ_i is the estimated error in a measured data point y_i which occurs at x_i, then the chi-squared value for a set of data points which are fit to a functional form $y = f(x_i)$ is given by

$$\chi^2 = \Sigma\{[f(x_i)-y_i]/\sigma_i\}^2, \qquad \text{Eq. 1}$$

where the sum is over the N data points. Now χ^2 divided by the number of degrees of freedom is called the reduced χ^2 or $\chi^2_v = \chi^2/v$. $v = N-n-1$ is the number of degrees of freedom left after fitting N data points to n+1 parameters. If χ^2_v is about unity, the fit is probably OK, but if the value of χ^2_v is much larger than unity then the functional form f(x) is probably NOT a good fit. If the value of χ^2_v is much smaller than unity, then you have done something wrong (such as a function with too many free parameters) or you have been very fortuitous! For a small number of points you can do such an analysis on your calculator in a few minutes. I suggest, in your reports, you provide the value of χ^2_v for any fits you do. If a nonlinear least squares fit is done (as some spreadsheets do almost automatically, often with a third or fourth or higher-order polynomial), then you should provide some confidence values for each of the coefficients in

front of the various polynomial terms. If you cannot prove that the coefficient in front of the fourth-order term, for example, is significantly different from zero then do not use it. You may then have to force the numerical fitting routine to use a lower order polynomial. In many cases you may have to do a visual fit to make the judgment of whether adding a higher order term to the fit makes a meaningful improvement to the fit, although the χ^2 value may also help. Please note that when you *add* terms to your fitting function, you *reduce* the degrees of freedom and you will divide χ^2 by a *smaller* number to get the reduced χ^2_v which you are going to use to compare with *one* to judge the goodness of fit.

Note the appearance, in Eq. 1 above, of σ_i which is the error associated with each individual point. Often a judgment or measurement of this error is the most difficult part of an experiment. Sometimes you can evaluate σ_i by doing several, repeated measurements of the value and then computing the r.m.s. error. Other times this will not be possible so that you will need to do some critical evaluation of the propagation of errors within the experimental apparatus.

Many spreadsheets can do a linear least squares fitting to a set of data and some can do a non-linear least squares fit. If you use these, make sure you understand the fits and provide some estimate of the goodness of fit. If the program has a different measure of the goodness of fit, make sure you understand it and explain it in your report.

A Primer on Error Propagation:

1. Additive Variables:

$y = ax_1 + bx_2 \rightarrow \delta_y = a\delta x_1 + b\delta x_2$

but, if errors are assumed uncorrelated,
i.e.,; if when $\delta x_1 > 0$, δx_2 may be > 0 or <0 with equal probability,
then we must add errors in quadrature:

$$\delta y = \sqrt{(a\delta x_1)^2 + (b\delta x_2)^2}$$

2. Multiplicative Variables

$$y = ax_1 x_2, \text{ or } y = \frac{ax_1}{x_2} \rightarrow \delta y = \frac{a\delta x_1}{x_2} + \frac{ax_1(-\delta x_2)}{(x_2)^2}$$
$$= \frac{a\delta x_1}{x_2} - \frac{ax_1\delta x_2}{x_2^2}.$$

Here it is convenient to form the fractional error,

$$\frac{\delta y}{y} = \frac{x_2}{ax_1}\left[\frac{a\delta x_1}{x_2} - \frac{ax_1\delta x_2}{x_2^2}\right]$$
$$+ \frac{\delta x_1}{x_1} - \frac{\delta x_2}{x_2}.$$

Again, in quadrature (but now with fractional errors):

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

3. More Complex Relations:

e.g., rotational Raman: $I_j \sim (2j+1)\ e^{-E_j/kT}$.

We want the temp, T: (from ratio of $I_j/I_{j'}$)

$$\frac{I}{I'} \equiv \frac{I_j}{I_j'} = \frac{(2j+1)}{(2j'+1)}\frac{e^{-E_j/kT}}{e^{-E_j'/kT}} = \frac{2j+1}{2j'+1}e^{(E_j' - E_j)/kT}.$$

Solve for T:

$$T = \frac{B}{k}[\ j'(\ j' + 1) - j(\ j + 1)]\ \frac{1}{\ell n\ \dfrac{(2j' + 1)\, I}{(2j + 1)\ I'}};$$

$$B = \frac{h}{8\pi^2 c I_o}$$

$$I_o = \mu R^2 = \frac{1}{2}\ Md^2\ \ (\textit{for diatomic molecules})$$

What are the variables with significant errors?
…the intensities I, I′ and the internuclear separation d

Now the differential calculus:

δT(I,I′,d) = ...(tedious!).

You can show, if you really want to, that

$$\frac{\delta T}{T} = -\frac{\delta R}{R} - \frac{(\dfrac{\delta I}{I} - \dfrac{\delta I'}{I'})}{\ell n \dfrac{(2j' + 2)I}{2j + 1)\, I'}}.$$

Now add these fractional errors in quadrature again:

$$\frac{\delta T}{T} = \left\{ \left(\frac{\delta R}{R}\right)^2 + \left[\frac{\dfrac{\delta I}{I}}{\ell n \dfrac{(2j' + 1)I}{2j + 1)I'}}\right]^2 + \left[\frac{\dfrac{\delta I'}{I}}{\ell n \dfrac{2j' +)I}{(2j + 1)\, I'}}\right]^2 \right\}^{1/2}$$

That's it!!!

Remember that your intensities were obtained by counting and should have (at least) errors given by Poisson statistics.

Thus I ~ N and $\dfrac{\delta I}{I} = \dfrac{\delta N}{N} = \dfrac{\sqrt{N}}{N} = \dfrac{1}{\sqrt{N}}$.