Case Study III: Modeling a Rate Quenching Process

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Data from a rate quenching process was modeled with three different approaches in order to determine the activation energy of the process. These include fitting the exponential data with a linear model, with a nonlinear model assuming % errors in y, and a nonlinear model assuming constant errors in x. The energy values extracted by all three approaches were very close, approximately 20 meV, but the x-errors approach gave the smallest standard error in the fitting parameters.

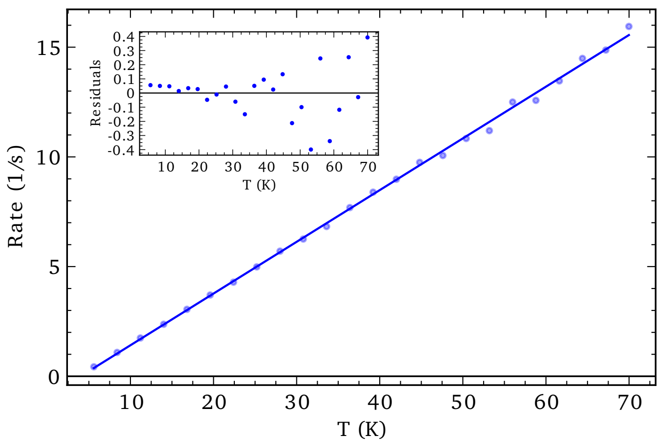

FIG. 1. Linear fit with residuals (inset).

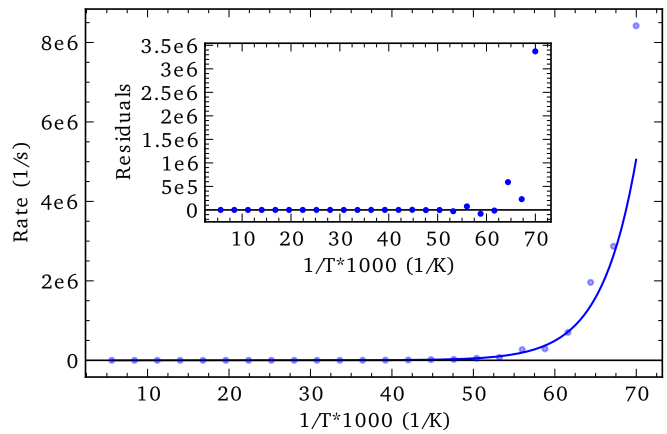

FIG. 2. Nonlinear fit with residuals (inset) for % errors in r.

The raw data for this case study describes some temperature dependent rate r with an Arrhenius dependence. That is, the data can be fit by an equation of the form:

$$r = r_o \exp\left(\frac{E_o}{k_B T}\right) \tag{1}$$

Where r_o is the high-temperature rate limit, E_o is the activation energy of the process described by the rate, k_B is Boltzmann's constant, and T is temperature. This can be rearranged to a linear form:

$$\ln r = \frac{E_o}{1000 k_B} x + \ln r_o \tag{2}$$

Where x is 1000/T. The natural log of the data can then be plotted against 1000/T to give a linear trend with slope $\frac{E_o}{1000k_B}$ and intercept $\ln r_o$. This can then be fit with a simple linear model of the form $y = mx+b$, as shown in Fig. 1. This fit yields an activation energy $E_o = 20.3\pm0.2$ meV and a preexponential of $0.389 \pm 0.031 s^{-1}$, with a χ^2 of 0.693 (residuals of $\ln r$ rather than r).

If Eq. 1 is used directly in a nonlinear fit, very different parameter values with larger errors will be obtained ($E_o = 27.4 \pm 1.2$ meV and $r_o = 0.00183 \pm 0.00179 s^{-1}$). This is because the larger values at low temperature have correspondinly large errors. By fitting nonlinearly, the effect of these errors on the fit is amplified. A nonlinear fit with Eq. 1 can be used if the errors are accounted for, however. If errors are assumed to be a % of the value of r, they can be implemented in a Levenberg-Marquardt fit as a simple scaling factor proportional to the r value when each residual is minimized. In this case χ^2 would be defined by:

$$\chi^2(E_o, r_o) = \sum_{i=1}^{n} \left[\frac{r_i - f(x_i, E_o, r_o)}{\sigma_i}\right]^2 \tag{3}$$

With $\sigma_i = r_i$ as the weighting factor (the exact percent will not matter because it will vary all weights by the same factor). Fitting with this weighted version yields parameters much closer to the linear fit, with $E_o = 20.1\pm 0.2$ meV and $r_o = 0.407 \pm 0.033 s^{-1}$. The result of this fit is shown in Fig. 2.

A third approach is to assume errors in the temperature measurement. This may be a more reasonable expectation, although the measurement details are unknown. A 1 degree error in temperature is suggested in the problem statement, but scaling each point by the same scalar error ends up giving each point equal weight, effectively equivalent to not scaling at all. Even so, to fit assuming errors in x rather than y requires inverting

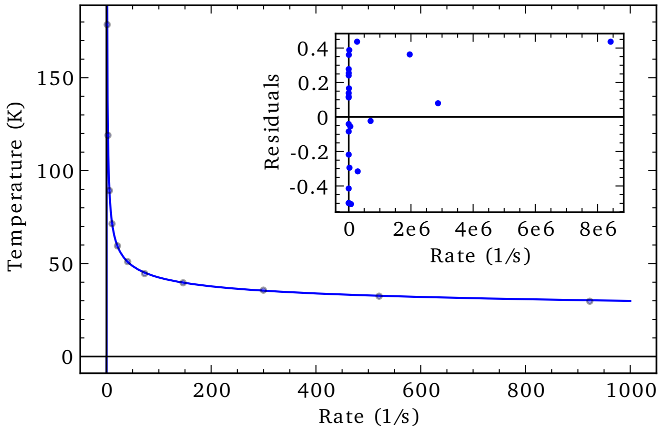

FIG. 3. Inverted nonlinear fit with residuals (inset) for T(r).

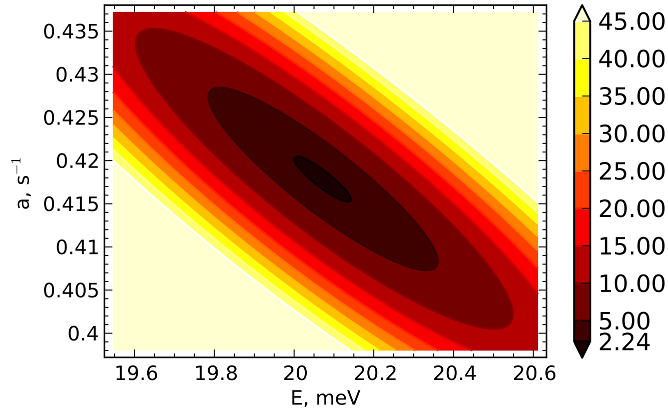

FIG. 4. Contour plot of χ^2 landscape for fit assuming constant errors in T.

TABLE I. Parameters of the three fits.

	$E_o(meV)$	$r_o(s^{-1})$
Linear	20.3 ± 0.2	0.389 ± 0.031
% Error in r	20.1 ± 0.2	0.407 ± 0.033
Constant error in T	20.1 ± 0.1	0.418 ± 0.002

the model expression and plotting the temperature as a function of the rate. This gives the fit in Fig. 3, with $E_o = 20.1 \pm 0.1$ meV and $r_o = 0.418 \pm 0.002 s^{-1}$. The parameter values obtained from the three fits are compared in Table I.

The χ^2 Landscape

Since this data follows a model with only two parameters, the χ^2 landscape can be fully visualized in a single contour plot. That is, if errors in the x coordinate are assumed to be negligible, the sum of the squares of the residuals depends only on the two model parameters E_o and r_o. The value of χ^2 can thus be plot as a 3D surface or contour plot with respect to E_o and r_o.

From the previous fits, assuming errors in T (by reversing the dependent and independent variables) seems to be the best strategy. The χ^2 landscape of this fit is shown as a contour plot in Fig. 4. Such a plot can be useful in several ways. It can be used as a diagnostic; if multiple minima are found within a reasonable range of parameter values, the solution found by the fitting algorithm may not be optimum or unique. It also provides complementary information to the parameter correlations. In this case only a single minimum is seen, but its slope is very shallow along one axis. This suggests that varying the two parameters simultaneously along this axis yields nearly the same fit, meaning they should have a strong correlation along this axis. The fit yields a covariance matrix from which a correlation coefficient of -0.901 is calculated.

Although only one data set is available, we can interpolate the data by adding some random error to the model fit to the original data, and then fitting this new artificial data (e.g. assuming a temperature error of $\sigma = 1\,^{\circ}$C). By doing this 500 times and plotting the best-fit values of the two parameters on top of the contour plot, Fig. 5 is obtained. The strong linear correlation is seen in the distribution of points, and the slope is aligned with the shallow χ^2 axis. Thus with only two parameters, the contour plot and the parameter correlation are aligned. This will not necessarily be the case for models including more than two parameters because of the interconnected way all the parameter correlations interact; such two-parameter chi^2 plots implicitly assume all the other parameters are held constant. Interestingly, the cluster is offset somewhat from the chi^2 minimum of the original data. The centroid of this distribution, representing an average set of parameter values for the 500 fits, could perhaps represent a 'best fit' which better represents the true parameter values with less influence from experimental errors.

Conclusion

The activation energy values obtained from the three fits are all within the same narrow margin of error at approximately 20 meV. The pre-exponentials vary a bit more, with the third fit giving a much smaller standard deviation compared to the other two. Because of this small error, and since temperature measurement is probably the most likely source of error in the data, the third approach is probably the best. Considering the inverse temperature dependence of the rate and an activation energy on the order of meV, the measurement may represent something like a photoluminescence thermal quench-

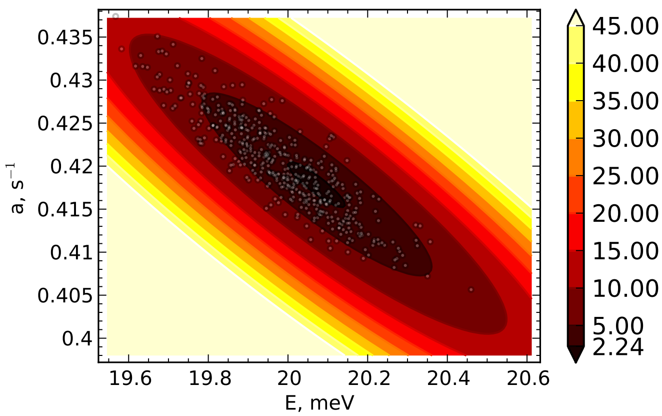

FIG. 5. Contour plot of χ^2 landscape for fit assuming constant errors in T, with interpolated best-fit parameter values.

ing process.