

Nonlinear regression: Kinetics of sucrose inversion, 2nd edition

**Theresa Julia Zielinski
Monmouth University
Department of Chemistry, Medical Technology, and Physics
400 Cedar Avenue
West Long Branch, NJ 07764**

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Introduction: Often in chemistry laboratory students study first order kinetics. In this document data from the traditional inversion of sucrose experiment is used to illustrate nonlinear curve fit. The advantages of this approach include not requiring students to do an infinite time reading of rotation angle a week after the main parts of the experiment are completed and introducing students to a valuable mathematical tool, nonlinear curve fitting.

Goal: to provide students with experiences through which they learn the fundamental concepts of nonlinear curve fitting using data that they generate in their laboratory courses.

Objectives : After completing the exercises in this template you will be able to

1. determine the rate constant for a first order chemical reaction without using linearizing techniques
2. use nonlinear curve fitting as a general tool for extracting information from available data.
3. compute the standard deviation of the fitted line and
4. prepare a residuals plot to assess the goodness of the fitted line.

Step 1. Enter the data you collected. Sample data for an inversion of sucrose experiment is given here for you to practice the concepts in this template.

Time is stored in the tx array and optical rotation is stored in the alpha array. The data you have been typed in or read into this document using Mathcad's READ("file") feature.

$i := 0 .. 10$

The index i labels the cells of the array for the 11 data points.

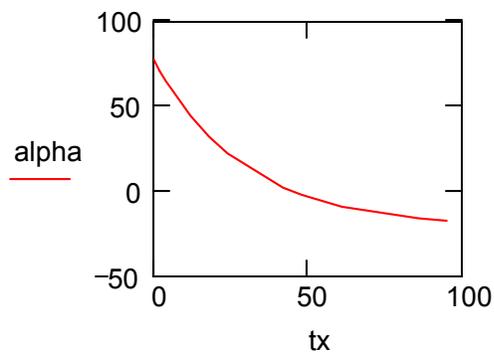
$$\text{tx} := \begin{pmatrix} 0 \\ 2 \\ 4 \\ 12 \\ 18 \\ 24 \\ 42 \\ 48 \\ 61 \\ 86 \\ 95 \end{pmatrix} \quad \text{alpha} := \begin{pmatrix} 78 \\ 71 \\ 65.1 \\ 44.6 \\ 32.4 \\ 22.45 \\ 2.3 \\ -1.96 \\ -9 \\ -15.8 \\ -17.25 \end{pmatrix}$$

Step 2 Write the function for 1st order kinetics. You should note the exponential form of this function. Note also that this function contains three fitting parameters, α_0 , α_{inf} and k , the rate constant. Review first order kinetics in your text book to refresh your mind about this.

$$f(t, \alpha_0, \alpha_{\text{inf}}, k) := \alpha_{\text{inf}} + (\alpha_0 - \alpha_{\text{inf}}) \cdot e^{-k \cdot t}$$

Exercise 1: Why is α_{inf} required as a fitting function for this experiment?

Step 3: plot the experimental data to visually inspect for estimates to the fitting parameters.



By examining the plot we can see that α_0 is approximately 75 and α_{inf} is about -20.

Estimating the rate constant is a bit less direct. One cannot just take the slope of the curve at an time because we have an exponential curve and this would give a varying rate constant, not ver constant indeed. For an estimate of k one must at least use a two point calculation and the linearized first order rate law. By doing this one obtains 0.04 as an approximate value for the rate constant.

Exercise 2. Use the data provided to verify that 0.04 is a reasonable estimate of the rate constant for this example of the inversion of sucrose.

Here we set the initial estimates for the fitting parameters

$$\alpha_0 := 78 \quad k := .04 \quad \alpha_{\text{inf}} := -20$$

Step 4. In this step we write the function we want to fit to the data and a criterion for the goodn the fit. Our criterion is the sum of the squares of the deviations (SSD) between the data and the of the function at each t.

$$f(t, \alpha_0, \alpha_{\text{inf}}, k) := \alpha_{\text{inf}} + (\alpha_0 - \alpha_{\text{inf}}) \cdot e^{-k \cdot t}$$

$$\text{SSD}(\alpha_0, \alpha_{\text{inf}}, k) := \sum_i (\text{alpha}_i - f(\text{tx}_i, \alpha_0, \alpha_{\text{inf}}, k))^2$$

Exercise 3. Examine the equation for the SSD. Identify each part of the equation and that this is indeed the sum of the squares of the deviations of the data from the value of the function at the same time.

Exercise 4. Determine the value for SSD.

Exercise 5. Plot $f(\text{tx}, \alpha_0, \alpha_{\text{inf}}, k)$ and the data in array alpha as a function of tx. How well does the line with our estimated parameters fit the data?

Step 6. Use a Mathcad Solve Block to minimize the SSD and return back optimum fitting parameters.

Given

$$k > 0 \quad \alpha_0 > 0 \quad \alpha_{\text{inf}} < 0$$

To find the minimum in SSD, at least two other conditions on permissible values of parameters are required. Thus we tell Mathcad that k is greater than zero, α_0 is greater than zero, and α_{inf} is less than zero.

$$\text{SSD}(\alpha_0, \alpha_{\text{inf}}, k) = 0$$

This part tells Mathcad to find the values of the fitting parameters that make SSD as small as possible.

$$\begin{pmatrix} \alpha_0 \\ \alpha_{\text{inf}} \\ k \end{pmatrix} := \text{Minerr}(\alpha_0, \alpha_{\text{inf}}, k)$$

$$\begin{pmatrix} \alpha_0 \\ \alpha_{\text{inf}} \\ 100 \cdot k \end{pmatrix} = \begin{pmatrix} 77.807 \\ -21.115 \\ 3.422 \end{pmatrix}$$

The fitting parameters in an array.

Exercise 6. Prepare a plot of the data and the fitted function. Compare the quality of the fit to what you had when you used your estimated fitting parameters. Was there an improvement? Explain.

Exercise 7. Compute the SSD using the optimized fitting parameters. How does this compare to what you computed above using the estimated fitting parameters? Explain the significance of this result.

Step 6. Examining the Residuals

Other than the value of SSD, Mathcad gives no indication of quality of fit. However, you may have found that the graph is reassuring. Next we will prepare a plot of residuals and examine the behavior.

Create a new function called fit(t) as shown here.

$$\text{fit}(t) := f(t, \alpha_0, \alpha_{\text{inf}}, k)$$

The residual is the difference between the experimental point and the value of the fit function at the same t. A residual is the same as a deviation. From the residuals (deviations) we can compute the standard deviation σ . DF is the number of degrees of freedom for this exercise. Since we had 11 points and three parameters DF=8.

$$\text{DF} := 8 \quad (11 \text{ data minus } 3 \text{ parameters})$$

$$\text{resid}_i := \alpha_i - \text{fit}(t_i)$$

Exercise 8. Display the residual array in space to the right. Examine the residuals. Can you easily see if these are satisfactory results. What criterion would you use to determine if the results were satisfactory.

$$\sigma := \sqrt{\frac{\sum_i (\text{resid}_i)^2}{\text{DF}}} \quad \sigma = 0.147$$

Exercise 9. Prepare a plot of the residuals as a function of tx. In Format plot use show markers to create place holders for the value of 2σ and -2σ . Describe the residuals plot and indicate the level of confidence you have in the experimental results based on the residuals plot.

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