TU Clausthal

Clausthal University of Technology

Institute of Chemical and Electrochemical Process Engineering

5. Exercise Optimization in Engineering Summer Term 2025

Nonlinear Regression
Fitting of kinetic parameters

The kinetic approach to describe the crystal growth rate G (in µm/s)

$$G = k_0 \exp\left(-\frac{E_A}{RT}\right)\sigma^n$$

as a function of temperature T (in K) and supersaturation σ (in 1), is to be parameterized. For this purpose, growth rates at different combinations of temperature and supersaturation were determined experimentally. The measured data are listed in the following table:

	σ = 0.025	σ = 0.050	σ = 0.075	σ = 0.100
T = 40 °C	0.0245 µm/s	0.0508 µm/s	0.1051 µm/s	0.1345 µm/s
T = 60 °C	0.0441 µm/s	0.1172 µm/s	0.2163 µm/s	0.3215 µm/s
T = 80 °C	0.0842 µm/s	0.2386 µm/s	0.4202 µm/s	0.6332 µm/s

Task 1:

Fit the parameter vector $x = [k_0\ E_A\ n]^T$ to the measured values. Use the MATLAB function lsqnonlin(), with the algorithm of Marquardt-Levenberg ('Algorithm',{'levenberg-marquardt',0.005}). In Python you can use the function least_squares() from scipy.optimize.

Bonus Task

Transform the problem of Task 1 into a linear optimization problem by linearizing the growth rate G. Formulate the error function and the corresponding Jacobian matrix! Apply the discussed Gauss-Newton method for sum of squares. What advantages does this approach offer compared to the approach of Task 1? How can you explain the deviations compared to the results of Task 1?

Task 2:

The reaction rate constant k and the reaction order n of a volume constant reaction A → B are to be determined in a batch experiment. The following ODE can be used to describe the concentration course of component A:

$$\frac{dc_A}{dt} = -k * {c_A}^n$$

In the experiment, the following concentrations of component A were measured at a temperature of T = 320 K:

t_{exp} / [s]	2	72	322	372	422	472	522	672	822
c_A / [mol/l]	10	8	5	4	3	2.5	2	1	0.5

a) Set up a model to calculate the time-dependent concentration of component A and solve it using an ODE solver. Let the ODE solver calculate the concentrations at the time points t_{exp}. Assume values for k and n! Plot the concentration course of component A.

b) Fit the parameter vector $x = [k\ n]^T$, analogous to Task 1, to the measured values. Use the Matlab function lsqnonlin(), with the algorithm of Marquardt-Levenberg ('Algorithm',{'levenberg-marquardt', 0.005}). In Python you can use the function least_squares() from scipy.optimize. Additionally, provide a graphical representation of the fit alongside the experimental data (in one figure).

c) Although, in this task, only two unknown parameters need to be determined, the computation time required to solve this task is significantly greater than that of Task 1. How can this be explained?

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