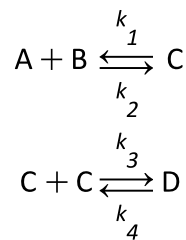


Parameter Estimation for a Chemical Reaction

Introduction

This application estimates the rate parameters for a reversible reaction with dimerization of an intermediate.



It does this by

- parameterizing (with respect to k_1 , k_2 , k_3 and k_4) the numerical solution of the different equations that describe the reaction kinetics
- calculating the sum of the square of the errors between the model predictions and experimental data
- minimizing the sum of the square of the errors to find the best fit values of k_1 , k_2 , k_3 and k_4 .

> restart : with(plots) : with(Optimization) :

Parameters and Experimental Data

> $A_0 := 2.1$:

$B_0 := 3.1$:

Concentrations of C and D over time

> times := [0 7 14 21 28 35 42 49 56 63 70] :

> C_exp := [0 1.065 1.383 0.9793 1.107 0.7289 0.7236 0.4674 0.6031 0.6149 0.3369] :

> D_exp := [0 0.0058 0.2203 0.4019 0.3638 0.456 0.5014 0.715 0.4723 0.7219 0.7294] :

Reaction Kinetics

> de1 := $\frac{d}{dt} C_C(t) = k_1 \cdot (A_0 - C_C(t) - 2 \cdot C_D(t)) \cdot (B_0 - C_C(t) - 2 \cdot C_D(t)) - k_2 \cdot C_C(t) - 2 \cdot k_3 \cdot C_C(t)^2 + 2 \cdot k_4 \cdot C_D(t)$:

$$\text{> de2} := \frac{d}{dt} C_D(t) = k_3 \cdot C_C(t)^2 - k_4 \cdot C_D(t) :$$

$$\text{> ic} := C_C(0) = 0, C_D(0) = 0 :$$

Sum of Square of Errors

$$\text{> res} := \text{dsolve}(\{ \text{de1}, \text{de2}, \text{ic} \}, \text{parameters} = [k_1, k_2, k_3, k_4], \text{numeric})$$

`res := proc(x_rkf45) ... end proc`

(4.1)

$$\text{> sse} := \text{proc}(k_1, k_2, k_3, k_4)$$

`res(parameters = [k1, k2, k3, k4]) :`

`add((C_exp[i]-rhs(select(has, res(times[i]), C_C)[]))2 + (D_exp[i]-rhs(select(has, res(times[i]), C_D)[]))2,`

`i = 1 .. numelems(times))`

`end proc:`

$$\text{> sse}(0.01, 0.002, 0.02, 0.002)$$

2.00578059621453

(4.2)

Minimize the Sum of the Square of the Errors

$$\text{> optPars} := \text{Minimize}('sse'(k_1, k_2, k_3, k_4), \text{initialpoint} = \{k_1 = 0.011, k_2 = 0.002, k_3 = 0.02, k_4 = 0.002\}, \text{assume} = \text{nonnegative}, \text{optimalitytolerance} = 0.00001)$$

$$\text{optPars} := [0.231411169620961532, [k_1 = 0.0632294154111440, k_2 = 0.0186953983808340, k_3 = 0.0144413290425876, k_4 = 0.]]$$

(5.1)

Compare Experimental Results to Model

$$\text{> res} := \text{dsolve}(\{ \text{de1}, \text{de2}, \text{ic} \}, \text{parameters} = [k_1, k_2, k_3, k_4], \text{numeric}) :$$

$$\text{> res}(\text{parameters} = [\text{optPars}[2][]]) :$$

$$\text{> p_C} := \text{odeplot}\left(\text{res}, [t, C_C(t)], t = 0 .. 70, \text{color} = \text{ColorTools:-Color}\left(\left[\frac{149}{255}, \frac{165}{255}, \frac{166}{255}\right]\right), \text{legend} = "C", \text{filled} = \text{true}\right) :$$

$$\text{> p_C_exp} := \text{plot}\left(\text{times}, C_exp, \text{style} = \text{point}, \text{symbol} = \text{solidcircle}, \text{symbolsize} = 20, \text{color} = \text{ColorTools:-Color}\left(\left[\frac{149}{255}, \frac{165}{255}, \frac{166}{255}\right]\right)\right) :$$

$$\text{> p_D} := \text{odeplot}\left(\text{res}, [t, C_D(t)], t = 0 .. 70, \text{color} = \text{ColorTools:-Color}\left(\left[\frac{58}{255}, \frac{83}{255}, \frac{155}{255}\right]\right), \text{legend}$$

= "D") :

- > p_D_exp := plot(times, D_exp, style = point, symbol = solidcircle, symbolsize = 20, color = ColorTools:-Color([[$\frac{58}{255}$, $\frac{83}{255}$, $\frac{155}{255}$]])) :
- > display(p_C, p_C_exp, p_D, p_D_exp, symbol = solidcircle, size = [800, 400], axesfont = [Calibri], legendstyle = [font = [Calibri]], labels = ["Time", "Concentration"], labelfont = [Calibri], labeldirections = [horizontal, vertical], gridlines)

