Parameter Estimation for a Chemical Reaction

Introduction

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

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C$$

$$C + C \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{D}$$

It does this by

- parameterizing the numerical solution of the different equations that describe the reaction kinetics (with respect to the rate constants k_1, k_2, k_3 and k_4),
- defining a procedure that calculates the sum of the square of the errors between the model predictions and experimental data,
- and 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) : with(ColorTools) :
```

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

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

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

> $ic := C_C(0) = 0, C_D(0) = 0$:

Sum of Square of Errors

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

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

$res(parameters = [k_1, k_2, k_3, k_4])$:

$add((C\_exp[i] - rhs(select(has, res(times[i]), C_C)[\,])\,)^2 + (D\_exp[i] - rhs(select(has, res(times[i]), C_D)[\,])\,)^2,$
$i = 1 .. numelems(times))$
end proc:

> $sse(0.01, 0.002, 0.02, 0.002)$

$$2.00578059621453 \qquad \textbf{(4.1)}$$

Minimize the Sum of the Square of the Errors

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

$$optPars := [0.231411156610435181, [k_1 = 0.0632123940906571, k_2 = 0.0186831393034251, k_3 = 0.0144423045550203, k_4 = 0.]] \qquad \textbf{(5.1)}$$

Compare Experimental Results to Model

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

> $res(parameters = [optPars[2][\,]])$:

```
> p_C := odeplot(res, [t, C_C(t)], t = 0..70, color = Color([149/255, 165/255, 166/255]), legend = "C", filled
      = true):
> p_C_exp := plot(times, C_exp, style = point, symbol = solidcircle, symbolsize = 10, color
      = Color([149/255, 165/255, 166/255])):
> p_D := odeplot(res, [t, C_D(t)], t = 0..70, color = Color([58/255, 83/255, 155/255]), legend = "D"):
> p_D_exp := plot(times, D_exp, style = point, symbol = solidcircle, symbolsize = 10, color
      = Color([58/255, 83/255, 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)
```