Parameter Estimation for a Chemical Reaction

Introduction

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

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

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

It does this by doing the following:

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

> 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)

res := **proc**(x_rkf45) ... **end proc** **(4.1)**

> sse := **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 **(4.2)**

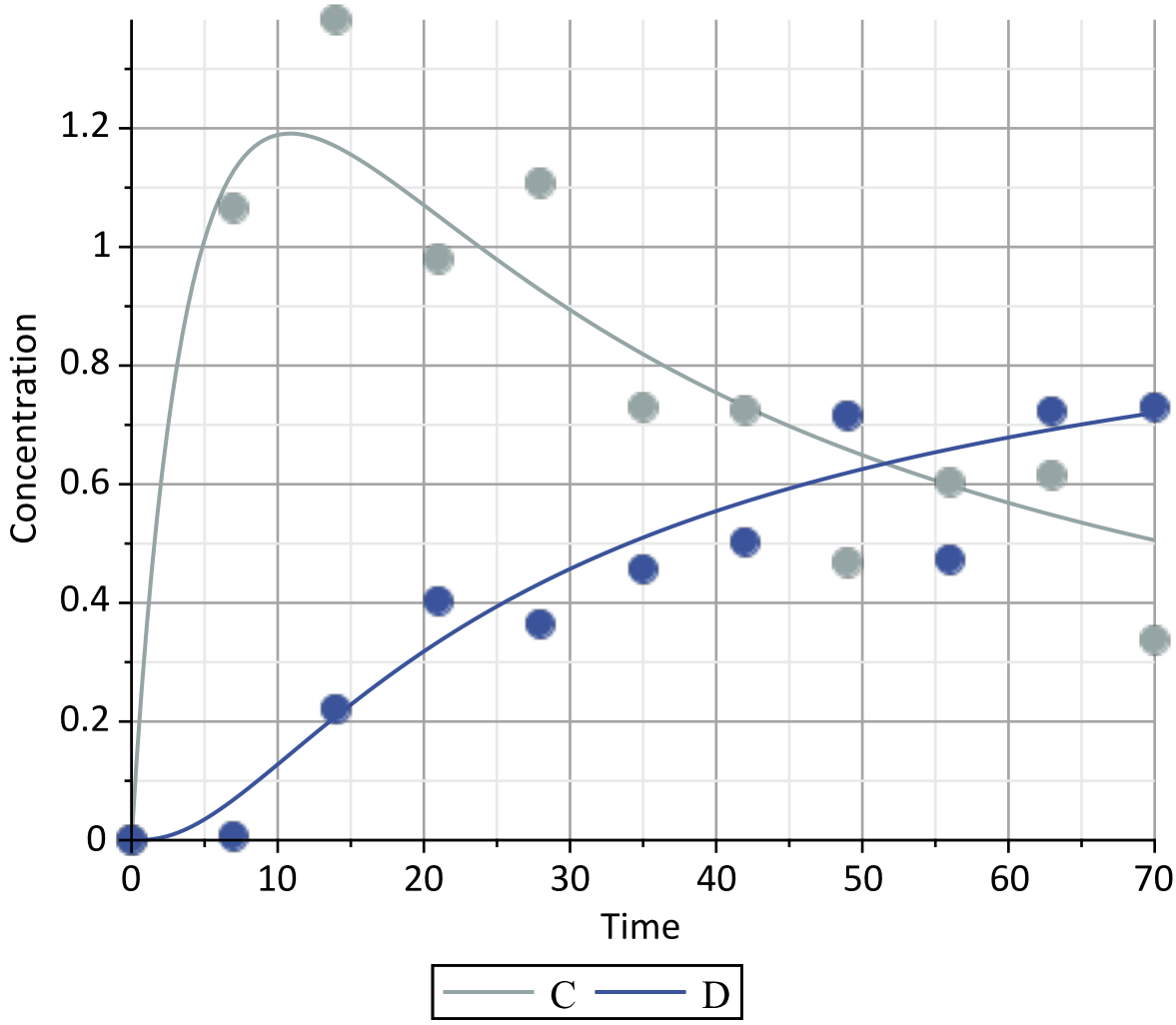
Minimize the Sum of the Square of the Errors

> 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 := [0.231411169620961532, [$k_1 = 0.0632294154111440$, $k_2 = 0.0186953983808340$, $k_3 = 0.0144413290425876$, $k_4 = 0.$]] **(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 = ColorTools:-Color( [149/255, 165/255, 166/255] ),
      legend = "C", filled = true) :
> p_C_exp := plot( times, C_exp, style = point, symbol = solidcircle, symbolsize = 20, color
      = ColorTools:-Color( [149/255, 165/255, 166/255] )) :
> p_D := odeplot( res, [t, C[D](t)], t = 0..70, color = ColorTools:-Color( [58/255, 83/255, 155/255] ),
      legend = "D") :
> p_D_exp := plot( times, D_exp, style = point, symbol = solidcircle, symbolsize = 20, color
      = ColorTools:-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)
```


Concentration
1.2
1
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
60
70
Time
C
D

>

>

>