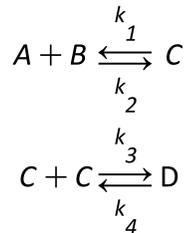


Parameter Estimation for a Chemical Reaction

▼ Introduction

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



It does this by

- parameterizing 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

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

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

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

$add((C_exp[i] - rhs(select(has, res(times[i]), C_C)[]))^2 + (D_exp[i] - rhs(select(has,$
 $res(times[i]), C_D)[]))^2,$
 $i = 1 .. numelems(times))$

endproc:

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

2.00578059621453

(4.1)

▼ Minimize the Sum of the Square of the Errors

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

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

▼ Compare Experimental Results to Model

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

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

- > $p_C := \text{odeplot}\left(\text{res}, [t, C_c(t)], t = 0..70, \text{color} = \text{Color}\left(\left[\frac{149}{255}, \frac{165}{255}, \frac{166}{255}\right]\right), \text{legend} = "C", \text{filled} = \text{true}\right):$
- > $p_C_exp := \text{plot}\left(\text{times}, C_exp, \text{style} = \text{point}, \text{symbol} = \text{solidcircle}, \text{symbolsize} = 10, \text{color} = \text{Color}\left(\left[\frac{149}{255}, \frac{165}{255}, \frac{166}{255}\right]\right)\right):$
- > $p_D := \text{odeplot}\left(\text{res}, [t, C_D(t)], t = 0..70, \text{color} = \text{Color}\left(\left[\frac{58}{255}, \frac{83}{255}, \frac{155}{255}\right]\right), \text{legend} = "D"\right):$
- > $p_D_exp := \text{plot}\left(\text{times}, D_exp, \text{style} = \text{point}, \text{symbol} = \text{solidcircle}, \text{symbolsize} = 10, \text{color} = \text{Color}\left(\left[\frac{58}{255}, \frac{83}{255}, \frac{155}{255}\right]\right)\right):$
- > $\text{display}(p_C, p_C_exp, p_D, p_D_exp, \text{symbol} = \text{solidcircle}, \text{size} = [800, 400], \text{axesfont} = [\text{Calibri}], \text{legendstyle} = [\text{font} = [\text{Calibri}]], \text{labels} = ["Time", "Concentration"], \text{labelfont} = [\text{Calibri}], \text{labeldirections} = [\text{horizontal}, \text{vertical}], \text{gridlines})$

