File: /General/MLAB-Text/Papers/dimer/scitech.tex

Chemical Kinetics Modeling

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Two of the most ubiquitous computational methodologies in use are solving ordinary differential equation systems and estimating parameters via curve-fitting. An area where these two methodologies converge is the domain of chemical kinetics.

Below we show an interesting example of such modeling for dimer kinetics. Suppose we have two substances, A and B which bind to form a complex C, and the substance C, in turn, binds with itself to form a dimer D. We thus have:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C, \qquad C + C \underset{k_4}{\overset{k_3}{\rightleftharpoons}} D.$$

Suppose further we mix 2 mmoles of A and 3 mmoles of B and measure the concentration in mmoles of both C and D at ten equally-spaced times between 0 and 70 seconds. From this data we wish to estimate the association and dissociation constants k_1, k_2, k_3, and k_4.

The MLAB advanced mathematical and statistical modeling system is a convenient tool for mathematical modeling; in particular, it is designed to handle the curve-fitting of differential equation models to data. We may proceed in MLAB as follows.

First we read in the data consisting of values of $c(t)$ and $d(t)$ given at the common times $0 : 70!10$. Although common times are used here, this is *not* required.

```
* data = (0:70!10) &' read(ddata,10,2)
* type data

     time     c       d
  1: 0        0        0
  2: 7.778    .6702    .0426
  3: 15.56    1.039    .1481
```

```
  4: 23.33   .9753   .4371
  5: 31.11   1.085   .6433
  6: 38.89   .9116   .8941
  7: 46.67   .9403   1.139
  8: 54.44   .7923   1.095
  9: 62.22   .9357   1.374
 10: 70      .9040   1.621

* cdata = data col 1:2
* ddata = data col (1,3)
```

Now we define our kinetic model so that $c(t)$ is the concentration of c in mmoles at time t and $d(t)$ is the concentration of d in mmoles at time t.

```
* fct c't(t)=k1*(a0-c-2*d)*(b0-c-2*d)-k2*c-2*d't(t)
* fct d't(t)=k3*c*c-k4*d
* initial c(0)=0
* initial d(0)=0
* a0=2;b0=3
```

Now we guess the values of k_1, k_2, k_3, and k_4. We may use the results of equilibrium studies, analyzed by MLAB, to know values for the ratios k_1/k_2 and k_3/k_4.

```
* k1=.02;k2=.002; k3=.02;k4=.002
* constraints q={k1>0,k2>0,k3>0,k4>0}
```

Now we may curve-fit the two ode-system-defined functions, c and d, to estimate k_1, k_2, k_3, and k_4.

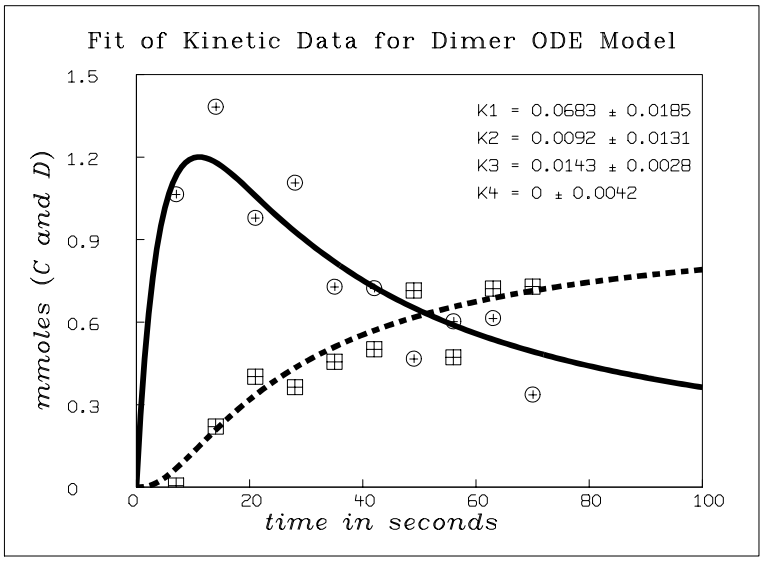
```
* fit(k1,k2,k3,k4), c to cdata, d to ddata, constraints q
final parameter values
  value               error                 dependency   parameter
  0.06916895493       0.02023902877         0.5830898606   K1
  0.01003638127       0.01500173275         0.5933235047   K2
  0.01427015399       0.002713671566        0.7642104538   K3
 3.458442141e-20      0.003966026698        0.7396366489   K4
4 iterations
CONVERGED
best weighted sum of squares = 2.184931e-01
weighted root mean square error = 1.168581e-01
```

```
weighted deviation fraction = 1.207618e-01
lagrange multiplier[4] = -3.832523108
```

Now we may draw the results of the curve-fit.

```
* m=integrate(c't,d't,0:100!140)
* draw m col (1,2) color red
* draw m col (1,4) color green lt dashed
* draw cdata pt circle lt none color red
* draw ddata pt circle lt none color green
* bottom title "time in seconds"
* left title "mmoles (C and D)"
*
* oformat = nformat; nformat ="%4.4lf"
* v=strval(stdest[1]); s=strval(k1)+" '25TF'R "+substr(v,7:strlen(v))
* title s at (.6,.8) ffract size .015
* v=strval(stdest[2]); s=strval(k2)+" '25TF'R "+substr(v,7:strlen(v))
* title s at (.6,.75) ffract size .015
* v=strval(stdest[3]); s=strval(k3)+" '25TF'R "+substr(v,7:strlen(v))
* title s at (.6,.7) ffract size .015
* v=strval(stdest[4]); s=strval(k4)+" '25TF'R "+substr(v,7:strlen(v))
* title s at (.6,.65) ffract size .015
* nformat=oformat

* view
```



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