SIMULATING SERIES REACTIONS WITH MAPLE

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Abstract:

In this short note, simultaneous series reactions are analyzed. A symbolic solution for the concentration of species as a function of the rate constants and time is obtained. The symbolic solution obtained is found to be useful in determining the range of parameters for which a maximum may or not occur for the intermediate species.

Key words: Series Reactions, Exponential Matrix.

Series Reactions

The time dependent concentration of species in a series reaction (Constantinides and Mostoufi, 1999, p.276) ($A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \underset{k_4}{\overset{k_3}{\rightleftharpoons}} C$) can be written by the set of linear equations

$$\frac{dC_A}{dt} = -k_1 C_A + k_2 C_B$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B - k_3 C_B + k_4 C_C \qquad [1]$$

$$\frac{dC_C}{dt} = k_3 C_B - k_4 C_C$$

An interesting question to ask is what are the values of parameters ($k_1 \ldots k_4$) for which there could be a maximum for the species B? Deriving an analytical solution by classical techniques could be time consuming and messy. Alternatively, these equations can be written in matrix form as (Constantinides and Mostoufi, 1999),

$$\frac{d\mathbf{Y}}{dt} = \mathbf{AY} \qquad [2]$$

where,

$$\mathbf{Y} = \begin{bmatrix} C_A & C_B & C_C \end{bmatrix}^T \qquad [3]$$

and the coefficient matrix is,

$$\mathbf{A} = \begin{bmatrix} -k_1 & k_2 & 0 \\ k_1 & -k_2 - k_3 & k_4 \\ 0 & k_3 & -k_4 \end{bmatrix} \qquad [4]$$

The solution for the vector differential equation 2 is well known and given by the exponential matrix (Amundson, 1966; Constantinides and Mostoufi, 1999; Varma and Morbidelli, 1997; Subramanian and White, 2000a; Subramanian and White, 2000b; Taylor and Krishna, 1993)

$$\mathbf{Y} = \exp(\mathbf{A}t)\mathbf{Y_0} \qquad [5]$$

where $\mathbf{Y_0}$ is the initial condition vector. Constantinides and Mostoufi solved this problem for a given set of numerical values for the parameters (k_1 = 1 min^{-1}, k_2 = 0 min^{-1}, k_3 = 2 min^{-1}, k_4 = 0 min^{-1}). One can find the eigenvalues and the exponential matrix by diagonalising the coefficient matrix **A**. However, with this method, special care should be taken if eigenvalues are repeated or approach zero. We illustrate in the Appendix how Maple can be used to find the exponential matrix and solve this problem symbolically and efficiently. Also, we demonstrate how the symbolic solution can be used to analyze the effect of parameters in the maximum concentration of the intermediate species, B. It should be noted that, similar symbolic solutions could be obtained using MATLAB also.

Conclusion

From the appendix, one can conclude that Maple can be used to solve linear series reactions analytically (symbolically) and efficiently. The utility of the solution obtained is illustrated by studying the effect of the parameters on the maximum concentration of the intermediate species B. In addition, we showed how Maple could be used to handle the special case when the eigenvalues are zero or repeated. The time taken for this program to run is less than a minute in a 833 MHz, 512MB RAM dual Pentium Processor.

References:

Amundson, N. R., (1966). *Mathematical Methods in Chemical Engineering – Matrices and Their Application*. New Jersey: Prentice Hall.

Constantinides, A., & Mostoufi, N. (1999). *Numerical Methods for Chemical Engineers with MATLAB Applications*. New Jersey: Prentice Hall.

Varma, A., & Morbidelli, M. (1997). *Mathematical Methods in Chemical Engineering*. New York: Oxford University Press.

Subramanian, V.R., & White, R. E. (2000). Solving Differential Equations with Maple. *Chemical Engineering Education*, ***34***, 328.

Subramanian, V.R. and White, R. E. (2000). A Semianalytical Method for Predicting Primary and Secondary Current Density Distributions: Linear and Nonlinear Boundary Conditions. *Journal of the Electrochemical Society*, ***147***, 1636.

Taylor. R and Krishna. R, (1993). *Multi component Mass Transfer*. New York: John Wiley & Sons Inc.

APPENDIX: SIMULATING SERIES REACTIONS WITH MAPLE

```
> restart:with(linalg):
```

The governing equations in a series reaction can be written as (equation 1).

```
> eq[1]:=diff(Ca(t),t)=-
k[1]*Ca(t)+k[2]*Cb(t);eq[2]:=diff(Cb(t),t)=k[1]*Ca(t)-
k[2]*Cb(t)-
k[3]*Cb(t)+k[4]*Cc(t);eq[3]:=diff(Cc(t),t)=k[3]*Cb(t)-
k[4]*Cc(t);
```

$$eq_1 := \frac{\partial}{\partial t}\mathrm{Ca}(t) = -k_1\,\mathrm{Ca}(t) + k_2\,\mathrm{Cb}(t)$$

$$eq_2 := \frac{\partial}{\partial t}\mathrm{Cb}(t) = k_1\,\mathrm{Ca}(t) - k_2\,\mathrm{Cb}(t) - k_3\,\mathrm{Cb}(t) + k_4\,\mathrm{Cc}(t)$$

$$eq_3 := \frac{\partial}{\partial t}\mathrm{Cc}(t) = k_3\,\mathrm{Cb}(t) - k_4\,\mathrm{Cc}(t)$$

These three equations are written in the matrix form (Maple is used to generate the matrix).

```
> vars:=[Ca(t),Cb(t),Cc(t)];
```

$$vars := [\mathrm{Ca}(t), \mathrm{Cb}(t), \mathrm{Cc}(t)]$$

```
> eqs:=[seq(rhs(eq[i]),i=1..3)];
```

$$eqs := [-k_1\,\mathrm{Ca}(t) + k_2\,\mathrm{Cb}(t),\ k_1\,\mathrm{Ca}(t) - k_2\,\mathrm{Cb}(t) - k_3\,\mathrm{Cb}(t) + k_4\,\mathrm{Cc}(t),\ k_3\,\mathrm{Cb}(t) - k_4\,\mathrm{Cc}(t)]$$

```
> A:=genmatrix(eqs,vars,A);
```

$$A := \begin{bmatrix} -k_1 & k_2 & 0 \\ k_1 & -k_2 - k_3 & k_4 \\ 0 & k_3 & -k_4 \end{bmatrix}$$

with the initial conditions

```
> Ca(0):=1.0;Cb(0):=0;Cc(0):=0;Y0:=matrix(3,1,[1.,0.,0.]);
```

$$\mathrm{Ca}(0) := 1.0$$

$$\mathrm{Cb}(0) := 0$$

$$\mathrm{Cc}(0) := 0$$

$$Y0 := \begin{bmatrix} 1. \\ 0. \\ 0. \end{bmatrix}$$

The solution for the vector differential equation can be expressed as (equation 5)

```
> mat:=exponential(A,t):
> sol:=evalm(mat&*Y0):
```

Note that the solution is obtained as a function of k_1, k_2, k_3 and k_4 and t. If semicolon is used instead of colon in the previous statement, the full solution can be viewed. For brevity, the result is not printed here. Now the solution is obtained for a particular set of values for the parameters.

```
> pars:=[1.,0.,2.,3.];
```

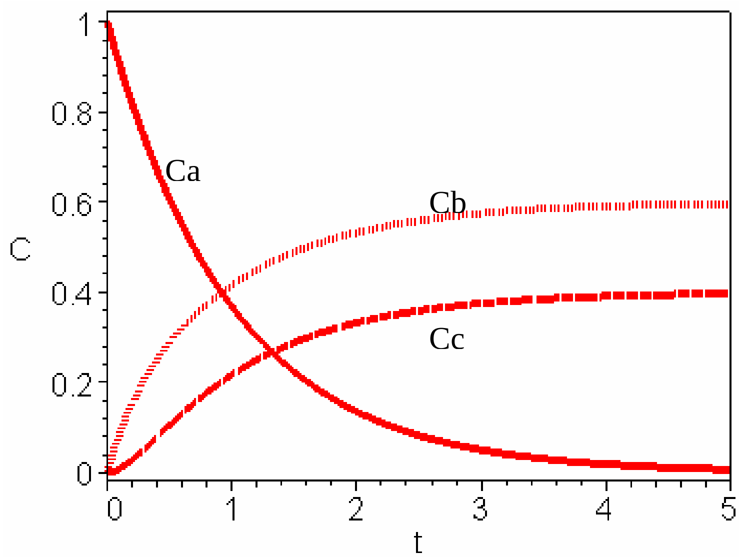
$$pars := [1., 0., 2., 3.]$$

```
>sol1:=evalm(subs(k[1]=pars[1],k[2]=pars[2],k[3]=pars[3],k[4]=par
s[4],evalm(sol)));
```

$$sol1 := \begin{bmatrix} 1.000000000\,\mathbf{e}^{(-1.000000000\,t)} \\ -.5000000000\,\mathbf{e}^{(-1.000000000\,t)} + .6000000000 - .1000000000\,\mathbf{e}^{(-5.000000000\,t)} \\ -.5000000000\,\mathbf{e}^{(-1.000000000\,t)} + .4000000000 + .1000000000\,\mathbf{e}^{(-5.000000000\,t)} \end{bmatrix}$$

Note that analytical solutions are obtained as a function of time for all the species. User has to specify with(plots) for plotting.

```
> with(plots):
> p[1]:=plot(sol1[1,1],t=0..5,thickness=4,linestyle=1):
> p[2]:=plot(sol1[2,1],t=0..5,thickness=4,linestyle=2):
> p[3]:=plot(sol1[3,1],t=0..5,thickness=4,linestyle=3):
> display({seq(p[i],i=1..3)},axes=boxed,labels=[t,C]);
```



This figure matches exactly with figure E5.2 , p 282 of Constantinides and Mostoufi,1999. For a different value of parameters, the solution is obtained by just substituting the numerical values.

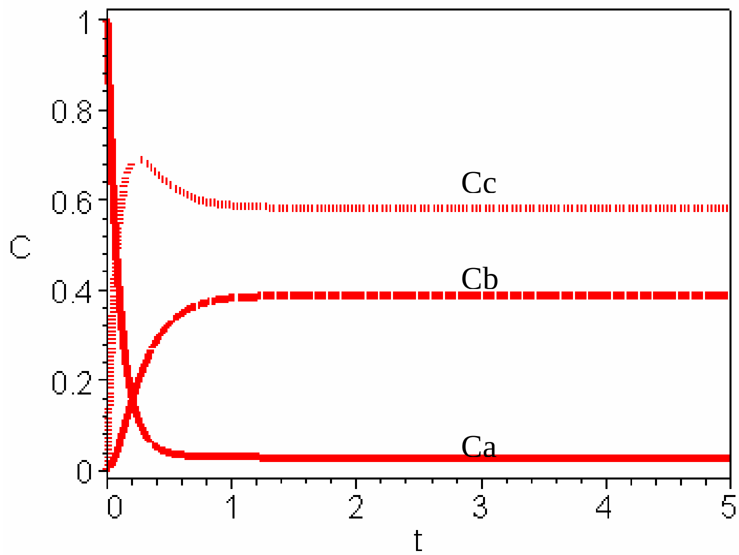
```
> pars:=[10,.5,2.,3.];
```

$$pars := [10, .5, 2., 3.]$$

```
> sol1:=evalm(subs(k[1]=pars[1],k[2]=pars[2],k[3]=pars[3],k[4]=pars[4],evalm(sol)));
```

$$sol1 := \begin{bmatrix} .06240543149\, \mathbf{e}^{(-4.823825022\, t)} + .02912621372 + .9084683541\, \mathbf{e}^{(-10.67617498\, t)} \\ .6460428672\, \mathbf{e}^{(-4.823825022\, t)} + .5825242716 - 1.228567139\, \mathbf{e}^{(-10.67617498\, t)} \\ -.7084482988\, \mathbf{e}^{(-4.823825022\, t)} + .3883495144 + .3200987842\, \mathbf{e}^{(-10.67617498\, t)} \end{bmatrix}$$

```
> p[1]:=plot(sol1[1,1],t=0..5,thickness=4,linestyle=1):
> p[2]:=plot(sol1[2,1],t=0..5,thickness=4,linestyle=2):
> p[3]:=plot(sol1[3,1],t=0..5,thickness=4,linestyle=3):
> display({seq(p[i],i=1..3)},axes=boxed,labels=[t,C]);
```



We observe that there is a maximum for B. We can find the time at which the maximum occurs.

The second row of the sol vector corresponds to the species B.

```
> eq:=simplify(diff(sol[2,1],t)):
> tmax:=solve(eq,t);
```

$$tmax := -1.\ln((k_3+k_1+k_2-1.\sqrt{k_1^2+2.k_1k_2-2.k_1k_3-2.k_1k_4+k_2^2+2.k_2k_3-2.k_2k_4+k_3^2+2.k_3k_4+k_4^2}-1.k_4)\Big/(k_3+k_1+\sqrt{k_1^2+2.k_1k_2-2.k_1k_3-2.k_1k_4+k_2^2+2.k_2k_3-2.k_2k_4+k_3^2+2.k_3k_4+k_4^2}+k_2-1.k_4))\Big/\sqrt{k_1^2+2.k_1k_2-2.k_1k_3-2.k_1k_4+k_2^2+2.k_2k_3-2.k_2k_4+k_3^2+2.k_3k_4+k_4^2}$$

One can verify that the second derivative is < 0.

```
> CBmax:=subs(t=tmax,sol[2,1]):
```

CBmax is not printed to conserve space. We can find if a maximum exists or not by substituting the numerical values for the rate constants. For Cb to have maximum, tmax should be real and positive.

```
> simplify(subs(k[1]=1.,k[2]=0.,k[3]=2.,k[4]=3.0,tmax));
```

$$-.7853981635\,I$$

```
> simplify(subs(k[1]=2.,k[2]=0.,k[3]=2.,k[4]=3.0,tmax));
```

$$.2310490602-1.047197551\,I$$

```
> simplify(subs(k[1]=10.,k[2]=1.,k[3]=1.,k[4]=1.0,tmax));
```

$$.2635466905$$

```
> simplify(subs(k[1]=10.,k[2]=5.,k[3]=1.,k[4]=1.0,tmax));
```

$$.2279357491$$

```
> simplify(subs(k[1]=10.,k[2]=1.,k[3]=1.,k[4]=5.,tmax));
```

$$.3783108854$$

```
> simplify(subs(k[1]=10.,k[2]=1.,k[3]=1.,k[4]=9.,tmax));
```

$$.8608178821$$

```
> simplify(subs(k[1]=10.,k[2]=1.,k[3]=1.,k[4]=9.9,tmax));
```

$$1.867408724$$

```
> simplify(subs(k[1]=10.,k[2]=1.,k[3]=1.,k[4]=9.99,tmax));
```

$$2.998197919$$

```
> simplify(subs(k[1]=10.,k[2]=1.,k[3]=1.,k[4]=9.9999,tmax));
```

$$5.298339860$$

as we keep increasing k_4 , the maximum occurs later.

```
> simplify(subs(k[1]=10.,k[2]=1.,k[3]=1.0,k[4]=1.,tmax));
```

$$.2635466905$$

```
> simplify(subs(k[1]=10.,k[2]=1.,k[3]=.1,k[4]=1.,tmax));
```

$$.4750465356$$

```
> simplify(subs(k[1]=10.,k[2]=1.,k[3]=.01,k[4]=1.,tmax));
```

$$.7018929819$$

```
> simplify(subs(k[1]=10.,k[2]=1.,k[3]=1.,k[4]=1.0,tmax));
```

$$.2635466905$$

as we keep decreasing k_3 , the maximum occurs later. However, we see that increasing k_4 is more effective for delaying the occurrence of maximum.

```
> simplify(subs(k[1]=10.,k[2]=1.,k[3]=1.,k[4]=1.0,tmax));
```

$$.2635466905$$

```
> simplify(subs(k[1]=10.,k[2]=.5,k[3]=1.,k[4]=1.0,tmax));
```

$$.2689639883$$

```
> simplify(subs(k[1]=10.,k[2]=0.01,k[3]=1.,k[4]=1.0,tmax));
```

$$.2745364855$$

As we keep decreasing k_2 , the maximum occurs later. However, we see that increasing k_4 or decreasing k_3 is more effective. For a particular value of k_1 and k_2 , we can plot CBmax for a given range of k_3 and k_4 .

```
> t1max:=evalm(subs(k[1]=10.,k[2]=1.,tmax));
```

$$t1max := -1.\frac{\ln\left(\frac{k_3+11.-1.\sqrt{121.-18.\,k_3-22.\,k_4+k_3^2+2.\,k_3\,k_4+k_4^2}-1.\,k_4}{k_3+11.+\sqrt{121.-18.\,k_3-22.\,k_4+k_3^2+2.\,k_3\,k_4+k_4^2}-1.\,k_4}\right)}{\sqrt{121.-18.\,k_3-22.\,k_4+k_3^2+2.\,k_3\,k_4+k_4^2}}$$

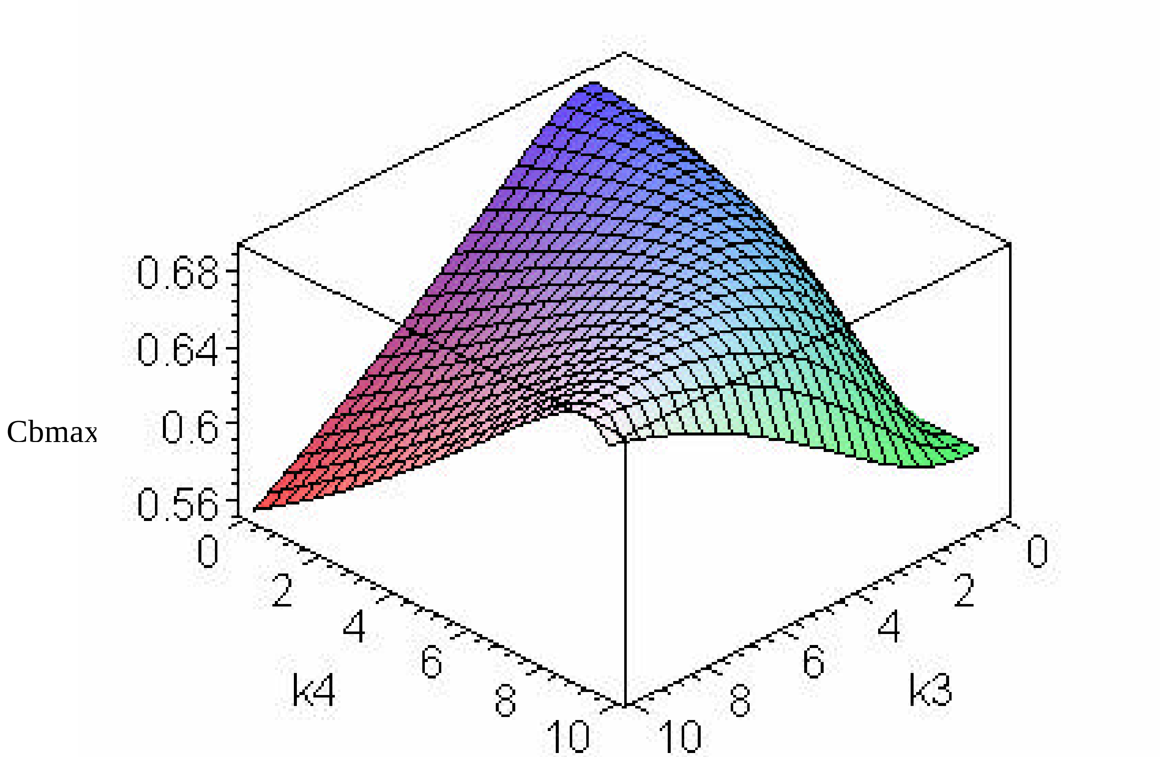
```
> Cbmax:=simplify(subs(t=t1max,sol1[2,1]));
```

$$Cbmax := .6460428672\left(\frac{k_3+11.-1.\sqrt{121.-18.\,k_3-22.\,k_4+k_3^2+2.\,k_3\,k_4+k_4^2}-1.\,k_4}{k_3+11.+\sqrt{121.-18.\,k_3-22.\,k_4+k_3^2+2.\,k_3\,k_4+k_4^2}-1.\,k_4}\right)^{\left(4.823825022\frac{1}{\sqrt{121.-18.\,k_3-22.\,k_4+k_3^2+2.\,k_3\,k_4+k_4^2}}\right)}$$

$$+ .5825242716 - 1.228567139$$

$$\left(\frac{k_3 + 11. - 1.\sqrt{121. - 18.\,k_3 - 22.\,k_4 + k_3^{\,2} + 2.\,k_3\,k_4 + k_4^{\,2}} - 1.\,k_4}{k_3 + 11. + \sqrt{121. - 18.\,k_3 - 22.\,k_4 + k_3^{\,2} + 2.\,k_3\,k_4 + k_4^{\,2}} - 1.\,k_4}\right)^{\left(10.67617498\,\frac{1}{\sqrt{121. - 18.\,k_3 - 22.\,k_4 + k_3^{\,2} + 2.\,k_3\,k_4 + k_4^{\,2}}}\right)}$$

```
> plot3d(Cbmax,k[3]=0..10,k[4]=10..0,axes=boxed,labels
=[k3,k4,"Cbmax"]);
```



An interesting case is when $k_1 = k_3$ and $k_2 = k_4$

```
> pars:=[2,1/2,2,1/2];
```

$$pars := \left[2, \frac{1}{2}, 2, \frac{1}{2}\right]$$

```
>A1:=evalm(subs(k[1]=pars[1],k[2]=pars[2],k[3]=pars[3],k[4]=pars[
4],evalm(A)));
```

$$A1 := \begin{bmatrix} -2 & \frac{1}{2} & 0 \\ 2 & \frac{-5}{2} & \frac{1}{2} \\ 0 & 2 & \frac{-1}{2} \end{bmatrix}$$

```
> eigenvalues(A1);
```

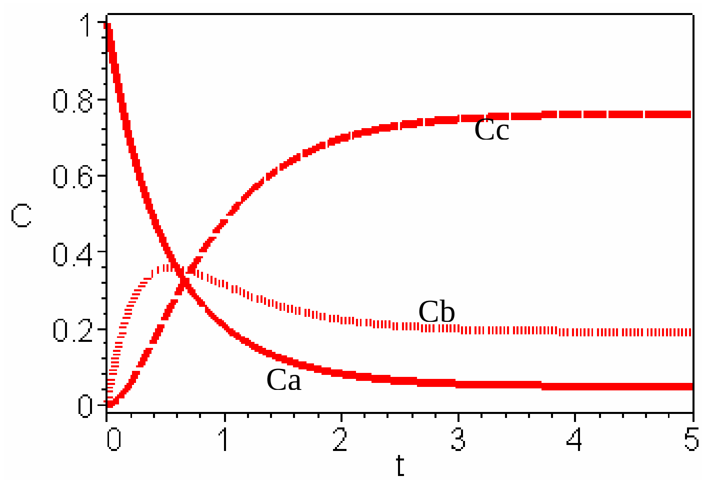
$$0, \frac{-3}{2}, \frac{-7}{2}$$

One of the eigenvalues is zero in this case.

```
>sol1:=evalm(subs(k[2]=pars[2],k[3]=pars[3],k[4]=pars[4],evalm(so
l))):
> sol1:=map(limit,sol1,k[1]=pars[1]);
```

$$sol1 := \left[\begin{array}{c} .04761904762 \frac{\sqrt{e^{(2.t)}} + 6.\ e^{(-2.500000000t)} + 14.\ e^{(-.5000000000t)}}{\sqrt{e^{(2.t)}}} \\ .09523809524 \frac{7.\ e^{(-.5000000000t)} + 2.\sqrt{e^{(2.t)}} - 9.\ e^{(-2.500000000t)}}{\sqrt{e^{(2.t)}}} \\ -.1904761905 \frac{7.\ e^{(-.5000000000t)} - 3.\ e^{(-2.500000000t)} - 4.\sqrt{e^{(2.t)}}}{\sqrt{e^{(2.t)}}} \end{array}\right]$$

```
> p[1]:=plot(sol1[1,1],t=0..5,thickness=4,linestyle=1):
> p[2]:=plot(sol1[2,1],t=0..5,thickness=4,linestyle=2):
> p[3]:=plot(sol1[3,1],t=0..5,thickness=4,linestyle=3):
> display({seq(p[i],i=1..3)},axes=boxed,labels=[t,C]);
```



Another interesting case is when $k_1 = k_3$ and $k_2 = k_4 = 0$.

```
> pars:=[1,0,1,0];
```

$$pars := [1, 0, 1, 0]$$

```
>A1:=evalm(subs(k[1]=pars[1],k[2]=pars[2],k[3]=pars[3],k[4]=pars[
4],evalm(A)));
```

$$A1 := \begin{bmatrix} -1 & 0 & 0 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \end{bmatrix}$$

```
> eigenvalues(A1);
```

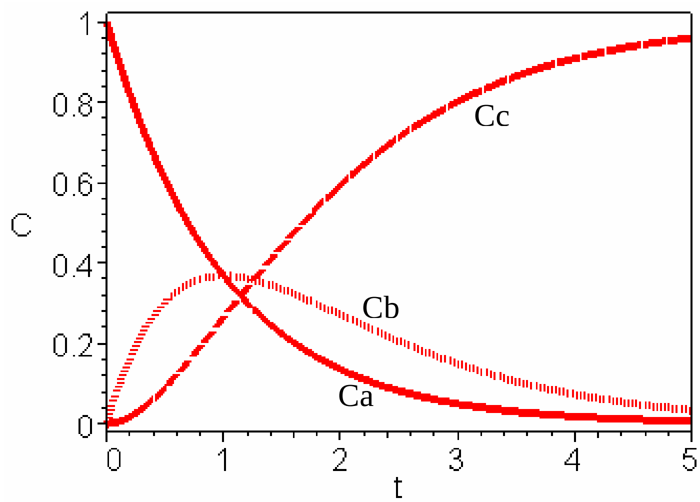
$$-1, -1, 0$$

One of the eigenvalues is zero and the other two eigenvalues are repeated in this case.

```
>sol1:=evalm(subs(k[2]=pars[2],k[3]=pars[3],k[4]=pars[4],evalm(so
l))):
> sol1:=map(limit,sol1,k[1]=pars[1]);
```

$$sol1 := \begin{bmatrix} \mathbf{e}^{(-1.\,t)} \\ t\,\mathbf{e}^{(-1.\,t)} \\ (-1. - 1.\,t + \mathbf{e}^{t})\,\mathbf{e}^{(-1.\,t)} \end{bmatrix}$$

```
> p[1]:=plot(sol1[1,1],t=0..5,thickness=4,linestyle=1):
> p[2]:=plot(sol1[2,1],t=0..5,thickness=4,linestyle=2):
> p[3]:=plot(sol1[3,1],t=0..5,thickness=4,linestyle=3):
> display({seq(p[i],i=1..3)},axes=boxed,labels=[t,C]);
```



We hope that this appendix illustrates how Maple can be used to obtain symbolic and efficient solutions for simultaneous series reactions.