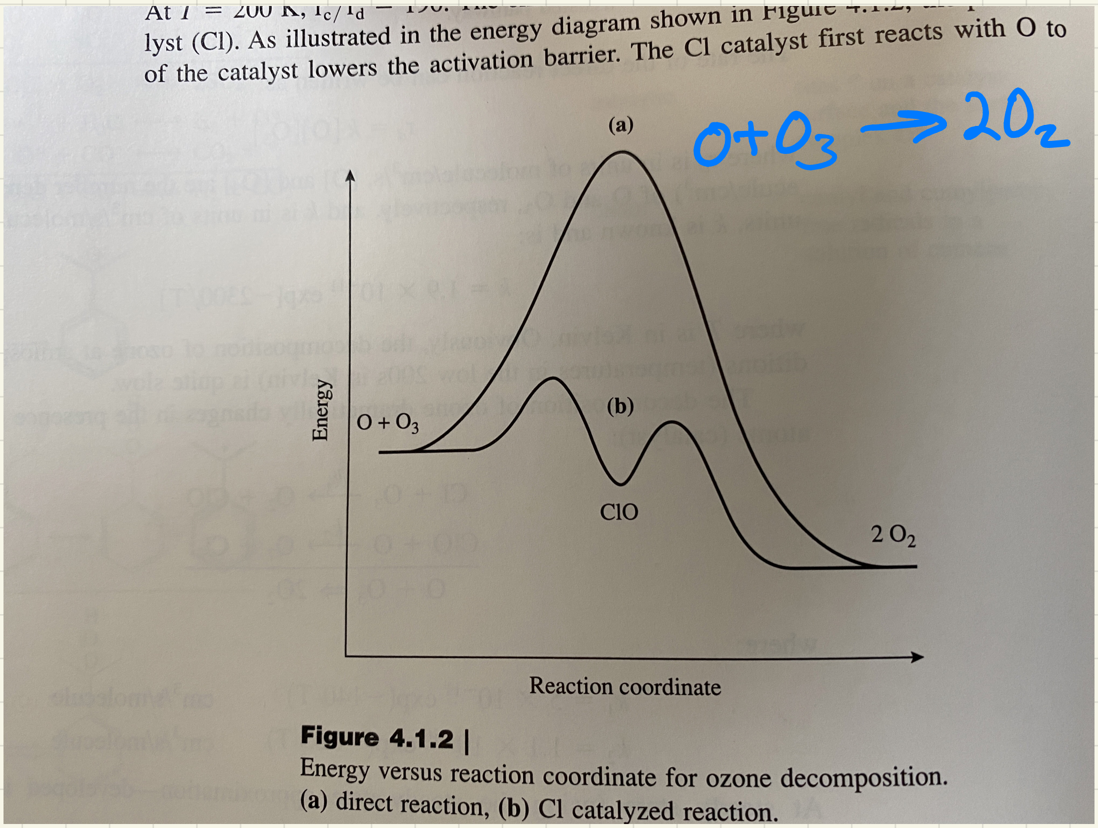
CBE 40445

9/11/20

ANALYSIS OF COMPLEX REACTION SCHEMES . . .

RECALL . . . .

OZONE DECOMPOSITION



At $T = 200$ K, $r_c/r_d = 190$.
lyst (Cl). As illustrated in the energy diagram shown in Figure 4.1.2,
of the catalyst lowers the activation barrier. The Cl catalyst first reacts with O to

Figure 4.1.2 |
Energy versus reaction coordinate for ozone decomposition. (a) direct reaction, (b) Cl catalyzed reaction.

$O + O_3 \rightarrow 2O_2$

DIRECT REACTION

$$r_d = k[O][O_3]$$

$$k = 1.9\times10^{-11}\exp\left(-\frac{2300}{T}\right)$$

"SLOW" !!

IF CHLORINE IS PRESENT...

$$Cl + O_3 \xrightarrow{k_1} O_2 + ClO$$
$$ClO + O \xrightarrow{k_2} O_2 + Cl$$
$$\overline{\quad O + O_3 \rightarrow 2O_2 \quad}$$

$$k_1 = 5\times10^{-11}\exp\left(-\frac{140}{T}\right)$$

$$k_2 = 1.1\times10^{-10}\exp\left(-\frac{220}{T}\right) \quad \frac{cm^3}{s\ \text{MOLECULE}}$$

$$\frac{r_c}{r_d} = \frac{k_2}{k}\times10^{-3} = 6\times10^{-3}\exp\left(\frac{2080}{T}\right)$$

$$@\ T = 200\text{K},\quad \frac{r_c}{r_d} = 200 \leftarrow$$

CATALYZED REACTION IS 200 TIMES FASTER

THE STEADY-STATE APPROXIMATION

CONSIDER

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$C_A(t=0) = C_{A0}$, $C_{B0} = 0$, $C_C^0 = 0$

$$x \equiv \frac{C_A}{C_A^0}$$

$$y = \frac{C_B}{C_A^0}$$

$$w = \frac{C_C}{C_A^0}$$

$$\frac{dx}{dt} = -k_1 x$$

$$\frac{dy}{dt} = k_1 x - k_2 y$$

$$\frac{dw}{dt} = k_2 y$$

FOR THIS SIMPLE SEQUENTIAL REACTION THE COMPLETE SOLUTION IS EASILY OBTAINED.

^0_A denotes the concentration of A
nce equations for this system are:

$$\frac{dx}{dt} = -k_1 x \qquad \frac{dy}{dt} = k_1 x - k_2 y \qquad \frac{dw}{dt} = k_2 y \tag{4.2.1}$$

WON'T ALWAYS BE POSSIBLE

ere $x = C_A/C_A^0$, $y = C_B/C_A^0$, and $w = C_C/C_A^0$. Integration of Equation (4.2.1)
h $x = 1$, $y = 0$, $w = 0$ at $t = 0$ gives:

$$\left.\begin{aligned} x &= \exp(-k_1 t) \\ y &= \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \\ w &= 1 - \underbrace{\frac{k_2}{k_2 - k_1}\exp(-k_1 t)} + \underbrace{\frac{k_1}{k_2 - k_1}\exp(-k_2 t)} \end{aligned}\right\} \tag{4.2.2}$$

TWO TIME SCALES

BEING GOOD CHEMICAL ENGINEERS WE PLOT THE RESULT

CHAPTER 4 The Steady-State Approximation: Catalysis **107**

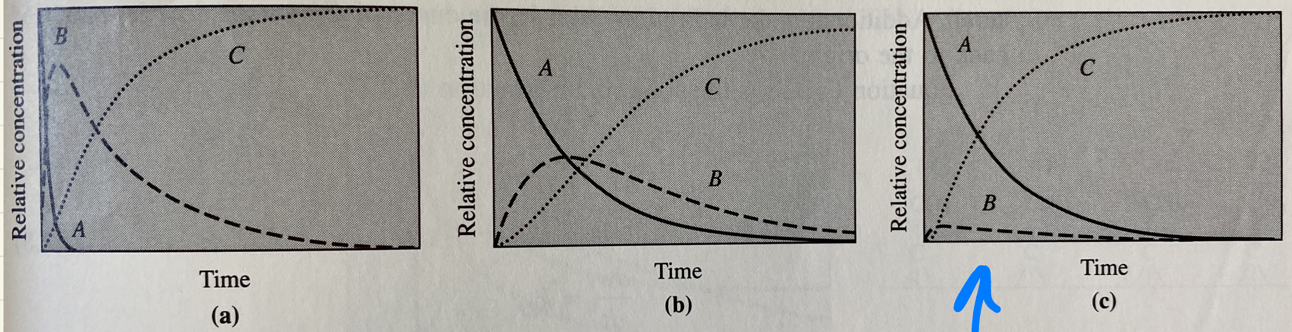


Figure 4.2.1 |
Two first-order reactions in series.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

(a) $k_2 = 0.1\ k_1$, (b) $k_2 = k_1$, (c) $k_2 = 10\ k_1$.

THIS LOOKS INTERESTING

NOT MUCH B, AND DOESN'T CHANGE..

($k_2 >> k_1$)

FOR $k_2 >> k_1$ THE SIMPLIFICATON IS:

$$x = \exp(-k_1 t)$$

$$y = \frac{k_1}{k_2}\exp(-k_1 t)$$

$$w = 1 - \exp(-k_1 t)$$

THIS IS THE SOLUTION TO!

CAN SOLVE WITHOUT y EQ.

$$\frac{dx}{dt} = -k_1 x$$

$$0 = k_1 x - k_2 y$$

$$\frac{dw}{dt} = k_2 y = k_1 x$$

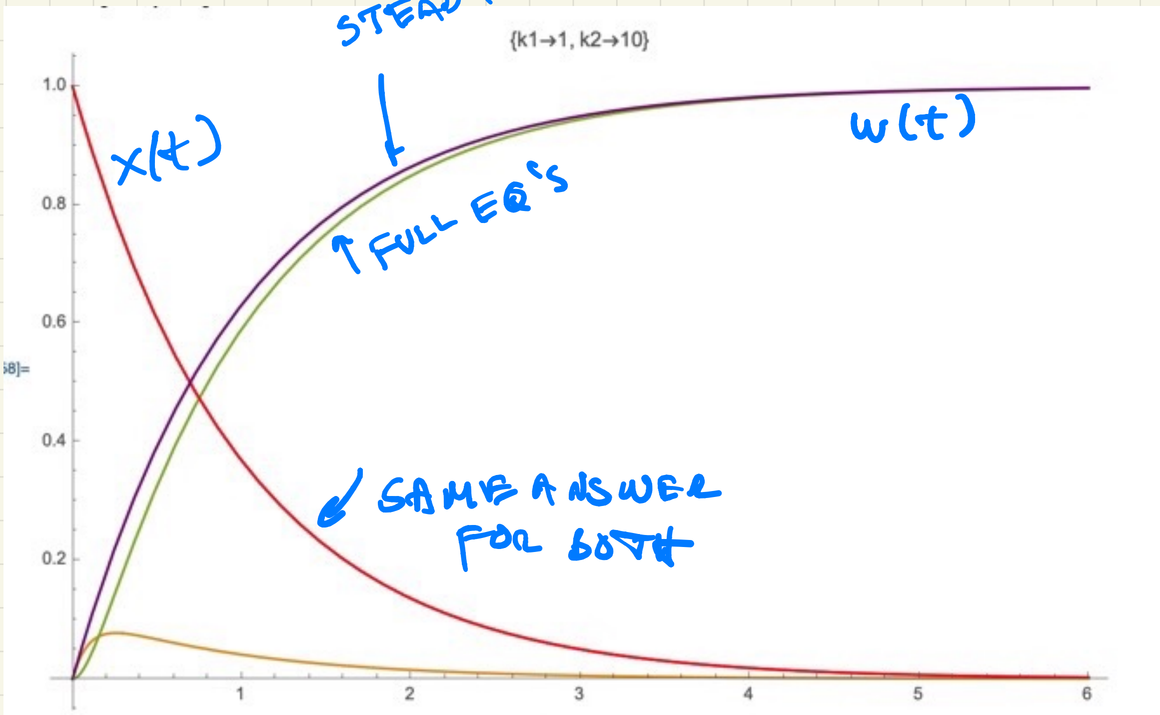
THUS WE PRESUME!

$$\frac{dy}{dt} = 0$$

"STEADY-STATE" ASSUMPTION.

WE WILL USE ("TRYOUT") THIS SIMPLIFICATION FOR REACTION INTERMEDIATES ...

STEADY-STATE APPROXIMATION

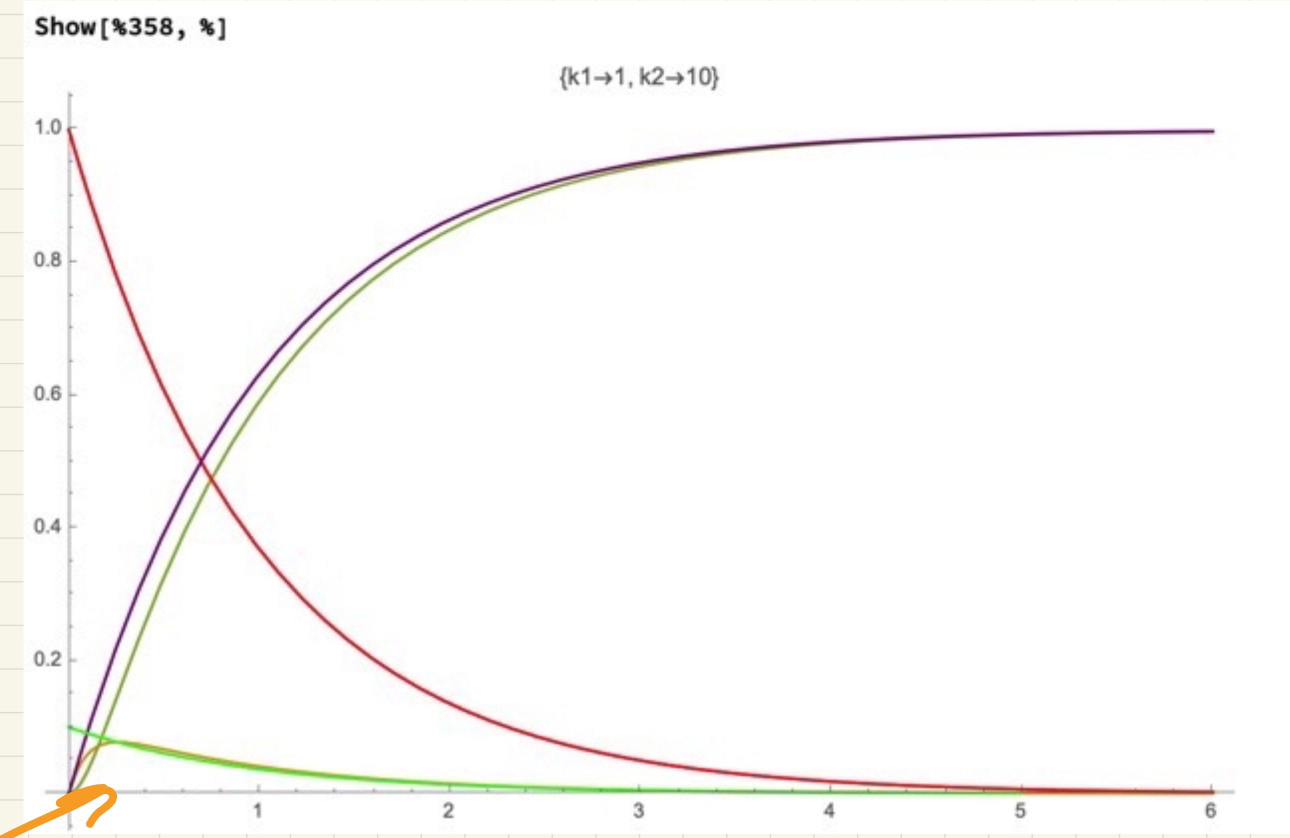


x(t)

w(t)

↑ FULL EQ's

SAME ANSWER FOR BOTH



Show[%358, %]

IF WE INCLUDE $y(t) = \frac{k_1}{k_2} \exp\left(-k_1 t\right)$

CONCLUSION: IF THIS "ASSUMPTION" HELPS TO SIMPLIFY AND "ELUCIDATE" COMPLEX MECHANISMS...

GO AHEAD & TRY!!

CAVEAT: THERE IS AN INDUCTION TIME: "RELAXATION TIME"

WHILE THIS APPROXIMATION DOESN'T WORK BECAUSE THE CONCENTRATION IS BUILDING UP TO THE STEADY-STATE

LET'S TAKE A QUICK LOOK!...

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

WE WANT TO CONSIDER THIS REACTION WITH $\frac{dC_B}{dt} = 0$, $k_2 >> k_1$

STEADY STATE CONCENTRATION

FIRST ALLOW THAT C_B IS NOT AT C_B^*

$$C_B = C_B^*(1+\bar{\varepsilon})$$

THEN

$$\frac{dC_B}{dt} = C_B^* \frac{d\bar{\varepsilon}}{dt} + (1+\bar{\varepsilon})\frac{dC_B^*}{dt}$$

FROM REACTION MECHANISM:

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

FROM PREVIOUS ANALYSIS, THE STEADY STATE OF C_B

$$C_B^* = \frac{k_1}{k_2} C_A$$

$$\Rightarrow \frac{dC_B^*}{dt} = \frac{k_1}{k_2}\frac{dC_A}{dt} = -\frac{k_1^2}{k_2} C_A$$

USING $$\frac{dC_A}{dt} = -k_1 C_A$$

NOW FROM ABOVE: $\nearrow$ $$\frac{dC_B}{dt} = +k_1 C_A - k_2 C_B$$

$\searrow$ $$\frac{dC_B}{dt} = C_B^* \frac{d\bar{\varepsilon}}{dt} + (1+\bar{\varepsilon})\frac{dC_B^*}{dt}$$

EQUATE THESE:

$$C_B^* \frac{d\bar{\varepsilon}}{dt} + (1+\bar{\varepsilon})\frac{dC_B^*}{dt} = k_1 C_A - k_2 C_B$$

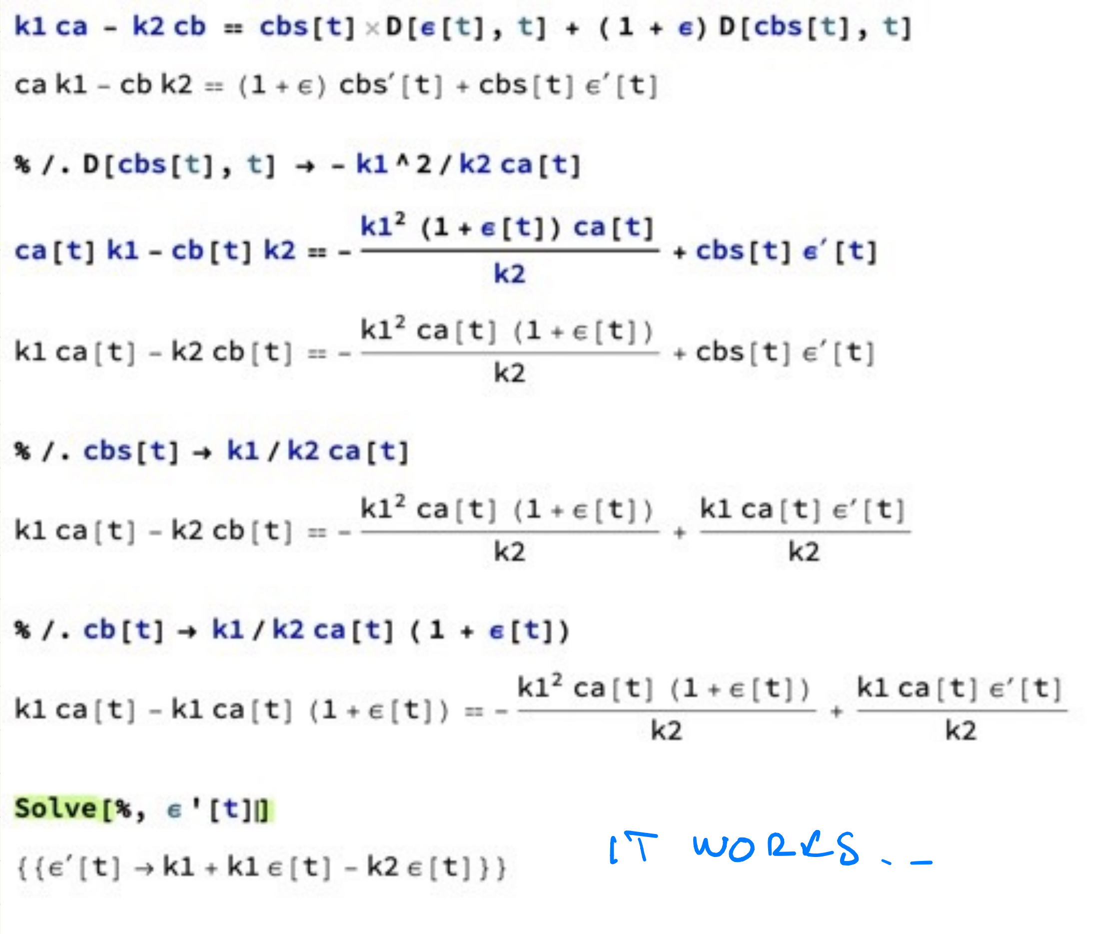
$$\frac{k_1 C_A}{k_2}\frac{d\bar{\varepsilon}}{dt} + (1+\bar{\varepsilon})\left(-\frac{k_1^2}{k_2} C_A\right) = k_1 C_A - k_2 C_B$$

$$\Rightarrow \frac{d\bar{\varepsilon}}{dt} + (k_2 - k_1)\bar{\varepsilon} - k_1 = 0$$

$\varepsilon = -1$ $\quad C_B = 0$

$t = 0$

CHECK...



```
k1 ca - k2 cb == cbs[t] × D[ϵ[t], t] + (1 + ϵ) D[cbs[t], t]
```

$$\mathrm{ca}\,\mathrm{k1}-\mathrm{cb}\,\mathrm{k2}=(1+\epsilon)\,\mathrm{cbs}'[t]+\mathrm{cbs}[t]\,\epsilon'[t]$$

```
% /. D[cbs[t], t] → - k1^2 / k2 ca[t]
```

$$\mathrm{ca}[t]\,\mathrm{k1}-\mathrm{cb}[t]\,\mathrm{k2}=-\frac{\mathrm{k1}^2\,(1+\epsilon[t])\,\mathrm{ca}[t]}{\mathrm{k2}}+\mathrm{cbs}[t]\,\epsilon'[t]$$

$$\mathrm{k1}\,\mathrm{ca}[t]-\mathrm{k2}\,\mathrm{cb}[t]=-\frac{\mathrm{k1}^2\,\mathrm{ca}[t]\,(1+\epsilon[t])}{\mathrm{k2}}+\mathrm{cbs}[t]\,\epsilon'[t]$$

```
% /. cbs[t] → k1 / k2 ca[t]
```

$$\mathrm{k1}\,\mathrm{ca}[t]-\mathrm{k2}\,\mathrm{cb}[t]=-\frac{\mathrm{k1}^2\,\mathrm{ca}[t]\,(1+\epsilon[t])}{\mathrm{k2}}+\frac{\mathrm{k1}\,\mathrm{ca}[t]\,\epsilon'[t]}{\mathrm{k2}}$$

```
% /. cb[t] → k1 / k2 ca[t] (1 + ϵ[t])
```

$$\mathrm{k1}\,\mathrm{ca}[t]-\mathrm{k1}\,\mathrm{ca}[t]\,(1+\epsilon[t])=-\frac{\mathrm{k1}^2\,\mathrm{ca}[t]\,(1+\epsilon[t])}{\mathrm{k2}}+\frac{\mathrm{k1}\,\mathrm{ca}[t]\,\epsilon'[t]}{\mathrm{k2}}$$

```
Solve[%, ϵ'[t]]
```

```
{{ϵ'[t] → k1 + k1 ϵ[t] - k2 ϵ[t]}}
```

IT WORKS...

$$\varepsilon = - \frac{1}{\overline{K}-1} \left\{ \overline{K} - \exp\left((\overline{K}-1) k_2 t \right) \right\}$$

$$K \equiv k_1 / k_2 < 1$$

AT SUFFICIENTLY LARGE TIME:

$$\overline{\varepsilon} = \overline{K} \quad .$$

THIS TIME IS OBTAINED FROM:

$$\exp(-k_2 t) \sim \exp(-4)$$

$$t \hat{=} \frac{4}{k_2}$$

EXAMPLE OF ENZYME CATALYSIS

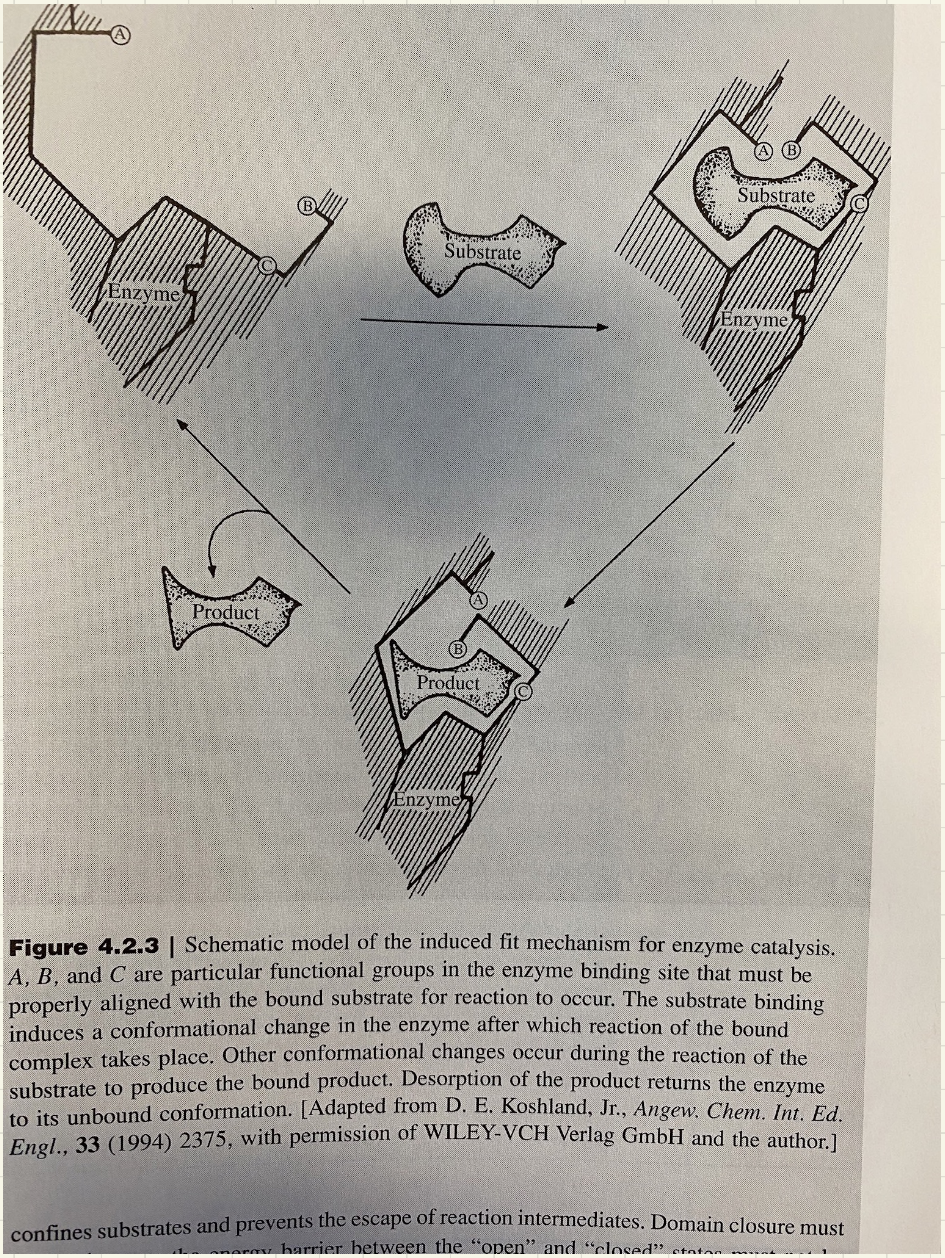


Figure 4.2.3 | Schematic model of the induced fit mechanism for enzyme catalysis. *A*, *B*, and *C* are particular functional groups in the enzyme binding site that must be properly aligned with the bound substrate for reaction to occur. The substrate binding induces a conformational change in the enzyme after which reaction of the bound complex takes place. Other conformational changes occur during the reaction of the substrate to produce the bound product. Desorption of the product returns the enzyme to its unbound conformation. [Adapted from D. E. Koshland, Jr., *Angew. Chem. Int. Ed. Engl.*, **33** (1994) 2375, with permission of WILEY-VCH Verlag GmbH and the author.]

confines substrates and prevents the escape of reaction intermediates. Domain closure must

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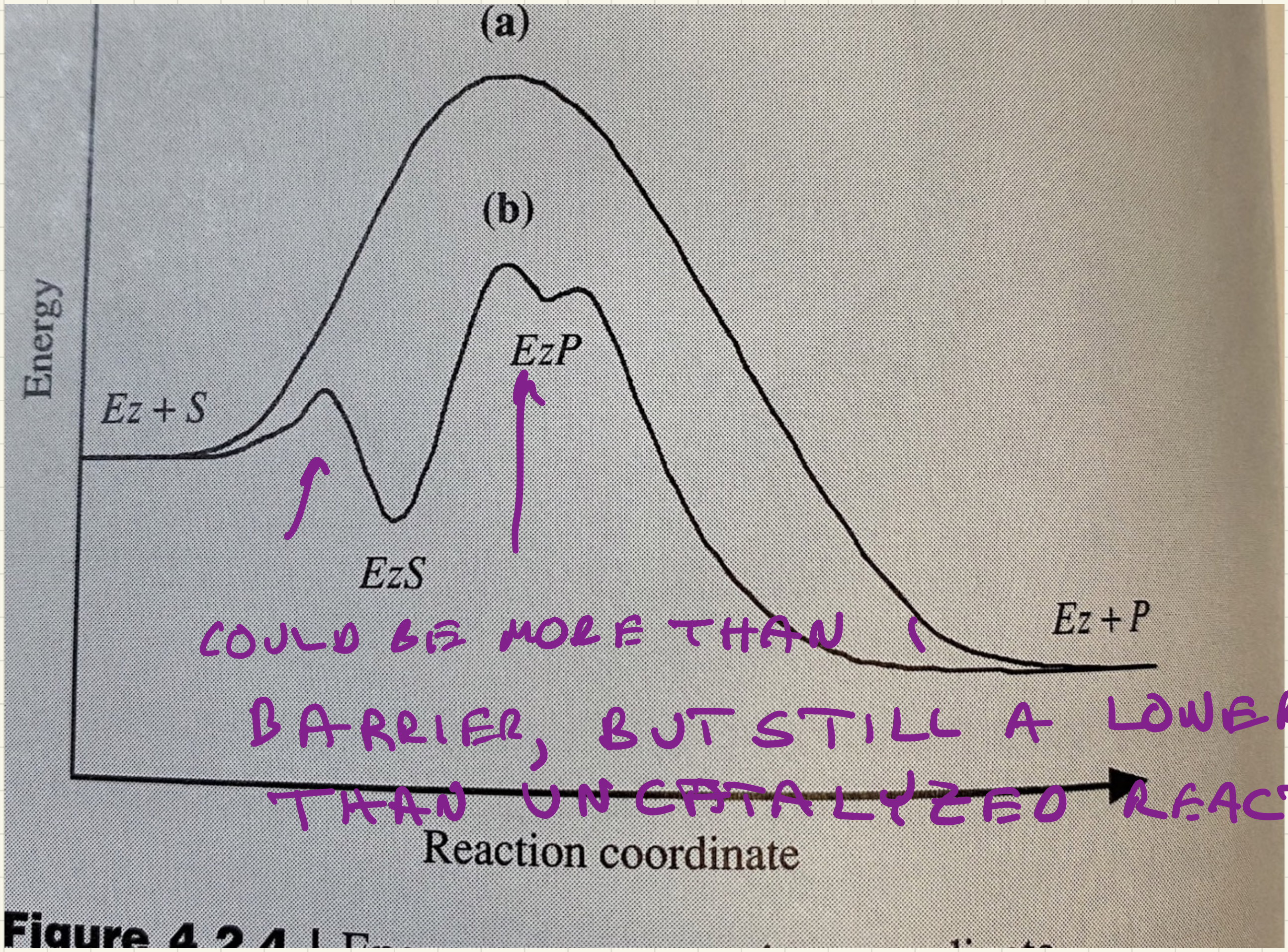


COULD BE MORE THAN 1 BARRIER, BUT STILL A LOWER E THAN UNCATALYZED REACTION

Figure 4.2.4 |

$$Ez + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} EzS \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} EzP \xrightarrow{k_3} Ez + P$$

$$\frac{dC_S}{dt} = -k_1 C_{Ez} C_S + k_{-1} C_{EzS}$$

$$\frac{dC_{EzS}}{dt} = k_1 C_{Ez} C_S - k_{-1} C_{EzS} - k_2 C_{EzS} + k_{-2} C_{EzP}$$

$$\frac{dC_{EzP}}{dt} = k_2 C_{EzS} - k_{-2} C_{EzP} - k_3 C_{EzP}$$

THIS IS THE "RATE" YOU NEED: →

$$\frac{dC_P}{dt} = k_3 C_{EzP} \Rightarrow F(S, Ez^0)$$

BUT MANY CASES ARE SUCH THAT $k_3 \gg k_2 + k_{-1}$

$$Ez + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} EzS \xrightarrow{k_3} Ez + P$$

$$\frac{dC_s}{dt} = -k_1 C_s C_{Ez} + k_{-1} C_{EzS}$$

LOOK HERE

$$\frac{dC_{EzS}}{dt} = k_1 C_s C_{Ez} - k_{-1} C_{EzS} - k_3 C_{EzS}$$

WORK BACKWARDS

NEED C_{EzS}

$$\frac{dC_p}{dt} = k_3 C_{EzS}$$

$$C_E^0 = C_{Ez} + C_{EzS}$$

$$\frac{dC_{EzS}}{dt} = 0 = k_1 C_s C_{Ez} - k_{-1} C_{EzS} - k_3 C_{EzS}$$

SOLVE: $C_{EzS} = \dfrac{k_1 C_s C_{Ez}}{k_{-1} + k_3} = \dfrac{C_s C_{Ez}}{K_m}$

MEASURE OF BINDING AFFINITY

$$K_m \equiv \frac{k_{-1} + k_3}{k_1}$$

PART OF RATIONALE! WE CAN'T GET ALL CONSTANTS ANYWAY!

$$C_{EZ}^{0} = C_{EZ} + C_{EZS}$$

$$C_{EZS} = \frac{C_S C_{EZ}}{K_m}$$

ELIMINATE C_{EZ}

$$C_{EZS} = \frac{C_{EZ}^{0} C_S - C_{EZS} C_S}{K_m}$$

SOLVE

$$C_{EZS} = \frac{C_{EZ}^{0} C_S}{K_m + C_S}$$

WHICH GIVES...

$$\frac{dC_P}{dt} = \frac{k_3 C_{EZ}^{0} C_S}{K_m + C_S}$$

OR

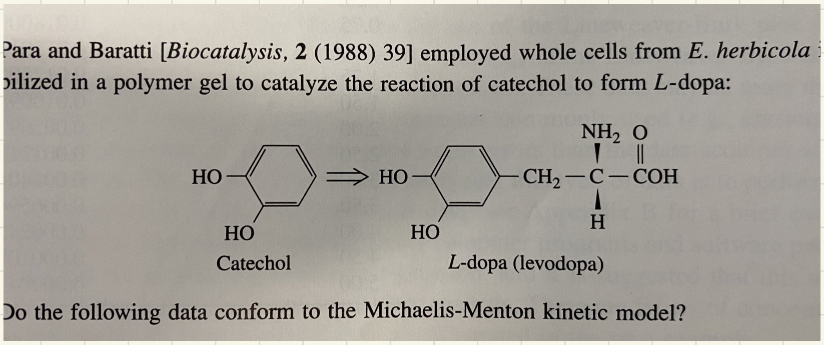
$$\frac{dC_P}{dt} = -\frac{dC_S}{dt} = \frac{\Lambda_{MAX} C_S}{K_m + C_S}$$

$$\Lambda_{MAX} = k_3 C_{EZ}^{0}$$

STANDARD FORM

D + D EXAMPLE 4.2.4

CATECHOL → L-dopa



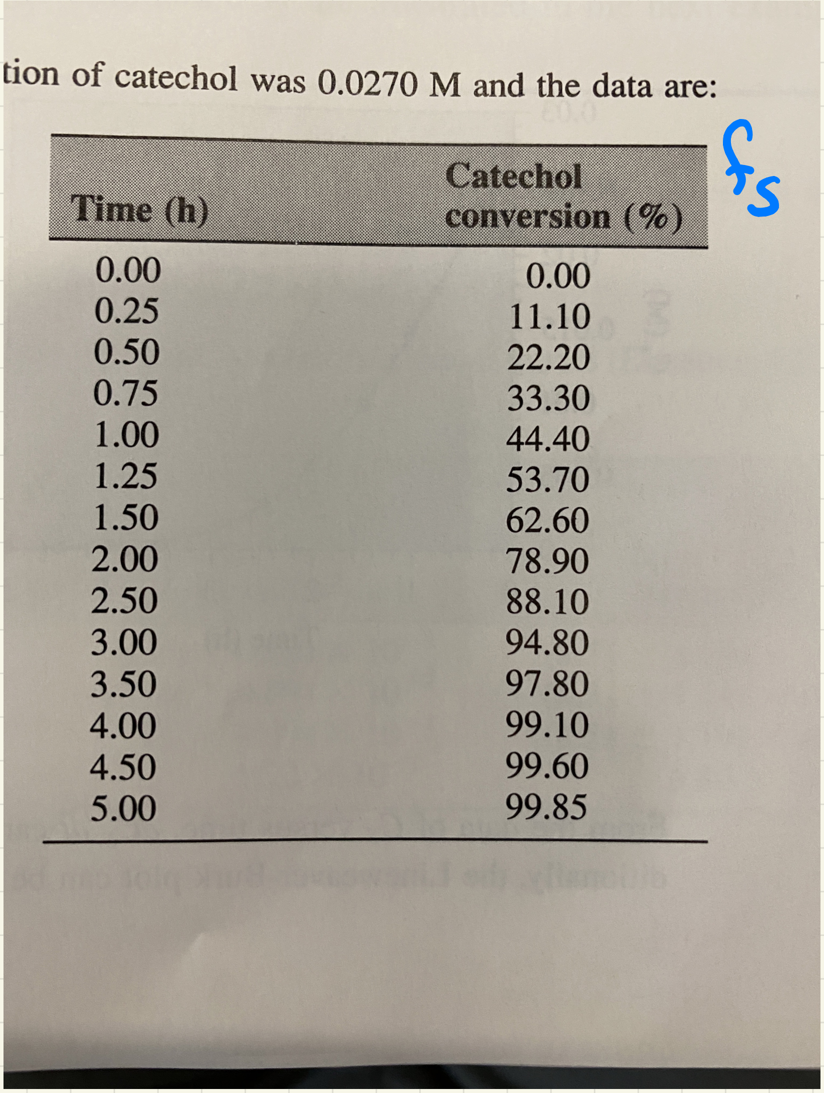
Para and Baratti [*Biocatalysis*, **2** (1988) 39] employed whole cells from *E. herbicola*
ilized in a polymer gel to catalyze the reaction of catechol to form *L*-dopa:

Catechol

L-dopa (levodopa)

Do the following data conform to the Michaelis-Menton kinetic model?

DOES MICHALIS-MENTON WORK??



tion of catechol was 0.0270 M and the data are:

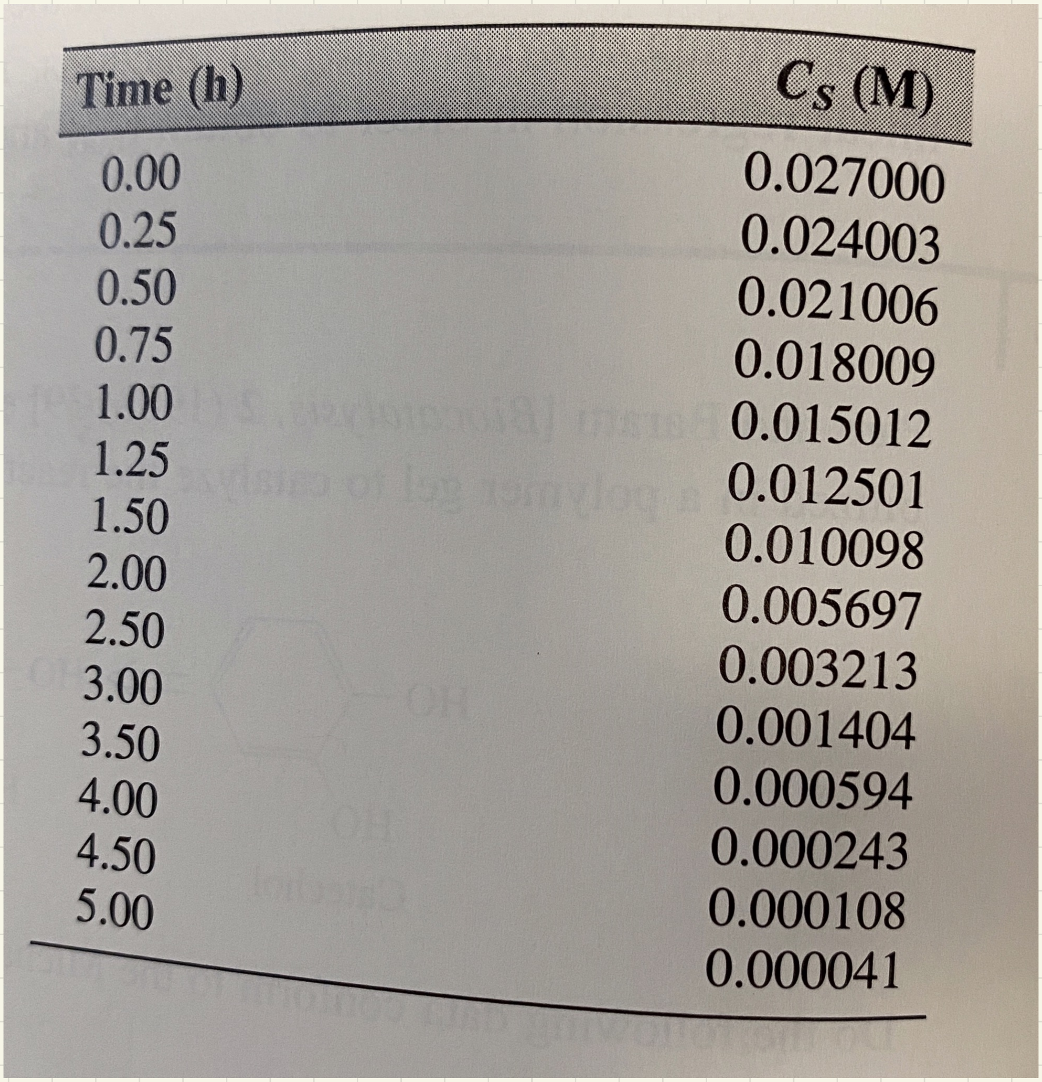
Time (h)	Catechol conversion (%)
0.00	0.00
0.25	11.10
0.50	22.20
0.75	33.30
1.00	44.40
1.25	53.70
1.50	62.60
2.00	78.90
2.50	88.10
3.00	94.80
3.50	97.80
4.00	99.10
4.50	99.60
5.00	99.85

f_s

RATE: $$\frac{dC_s}{dt} = -\frac{r_{MAX} C_s}{K_m + C_s}$$

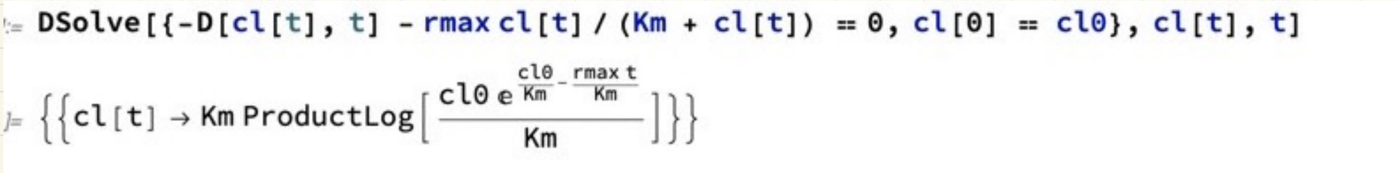
START WITH GETTING

$$C_s(t) = C_s^{\circ}(1 - f_s)$$



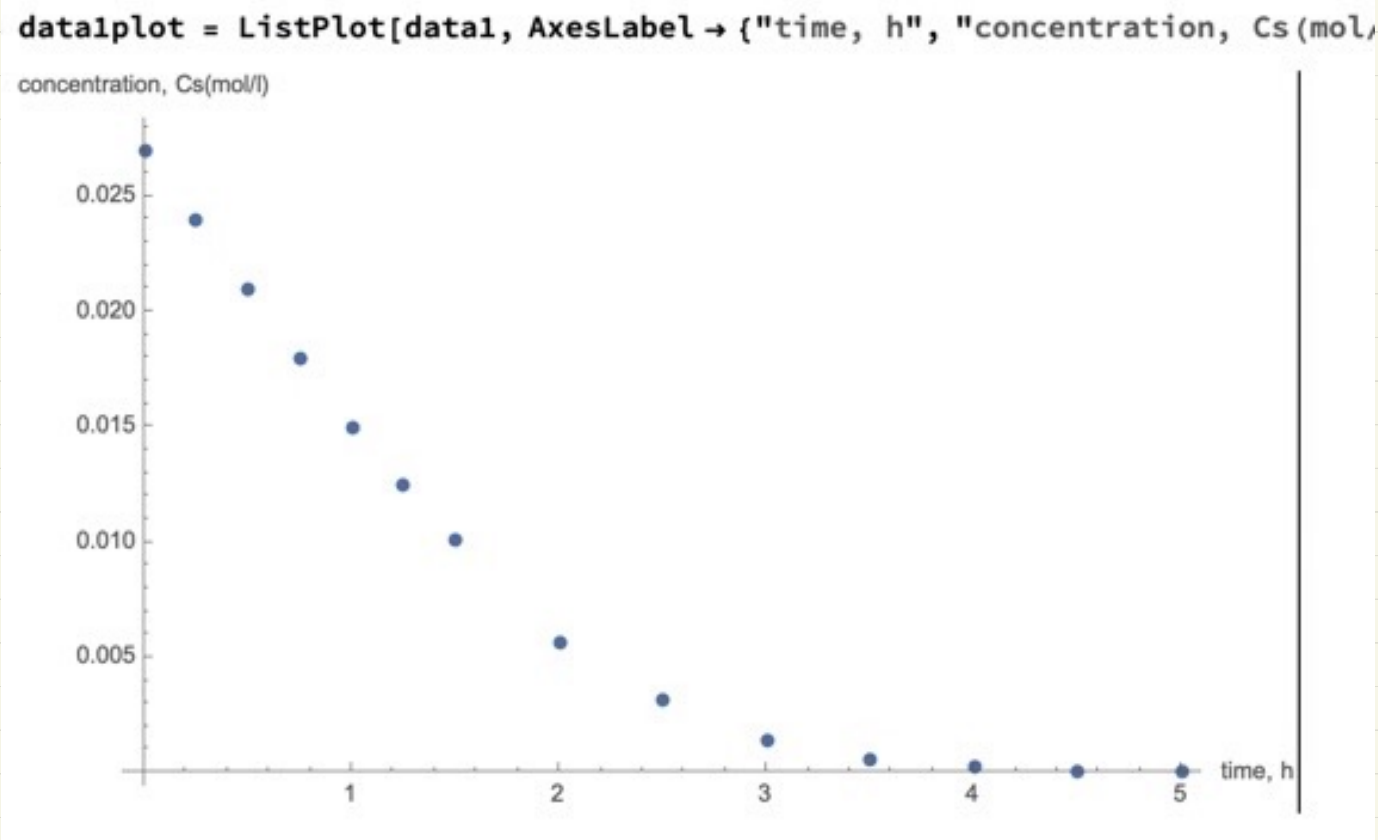
Time (h)	C_S (M)
0.00	0.027000
0.25	0.024003
0.50	0.021006
0.75	0.018009
1.00	0.015012
1.25	0.012501
1.50	0.010098
2.00	0.005697
2.50	0.003213
3.00	0.001404
3.50	0.000594
4.00	0.000243
4.50	0.000108
5.00	0.000041

LET'S FIT THIS DIRECTLY:

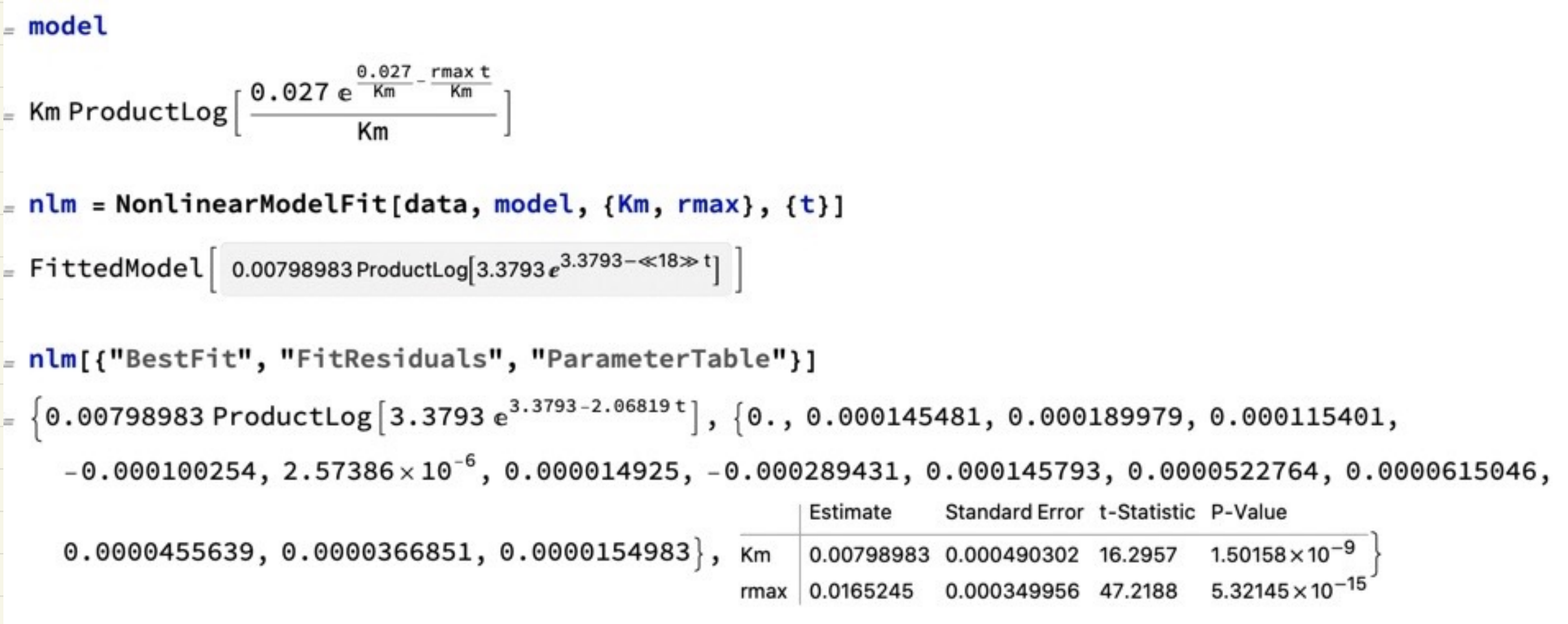


```
DSolve[{-D[cl[t], t] - rmax cl[t] / (Km + cl[t]) == 0, cl[0] == cl0}, cl[t], t]
```

$$\left\{\left\{\text{cl}[t] \to \text{Km ProductLog}\left[\frac{\text{cl0}\, e^{\frac{\text{cl0}}{\text{Km}}-\frac{\text{rmax}\, t}{\text{Km}}}}{\text{Km}}\right]\right\}\right\}$$



```
data1plot = ListPlot[data1, AxesLabel → {"time, h", "concentration, Cs(mol/
```



```
model
```

$$\text{Km ProductLog}\left[\frac{0.027\, e^{\frac{0.027}{\text{Km}}-\frac{\text{rmax}\, t}{\text{Km}}}}{\text{Km}}\right]$$

```
nlm = NonlinearModelFit[data, model, {Km, rmax}, {t}]
```

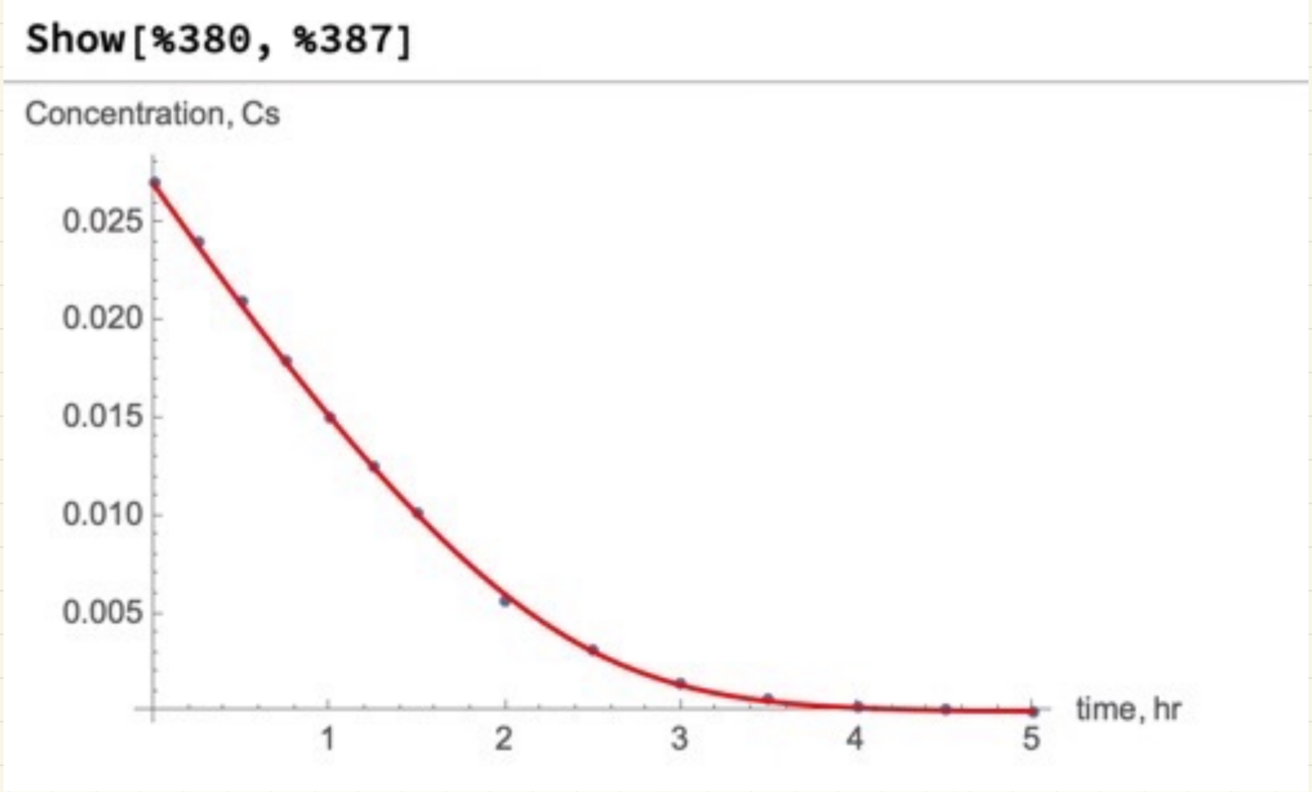
$$\text{FittedModel}\left[\ 0.00798983\ \text{ProductLog}\left[3.3793\, e^{3.3793-\ll 18\gg t}\right]\ \right]$$

```
nlm[{"BestFit", "FitResiduals", "ParameterTable"}]
```

$$\left\{0.00798983\ \text{ProductLog}\left[3.3793\, e^{3.3793-2.06819\, t}\right],\ \{0.,\ 0.000145481,\ 0.000189979,\ 0.000115401,\ -0.000100254,\ 2.57386\times 10^{-6},\ 0.000014925,\ -0.000289431,\ 0.000145793,\ 0.0000522764,\ 0.0000615046,\ 0.0000455639,\ 0.0000366851,\ 0.0000154983\},\right.$$

	Estimate	Standard Error	t-Statistic	P-Value
Km	0.00798983	0.000490302	16.2957	1.50158×10^{-9}
rmax	0.0165245	0.000349956	47.2188	5.32145×10^{-15}

$\}$



```
Show[%380, %387]
```

I GOT $K_m = .007989$

$r_{MAX} = .0165$

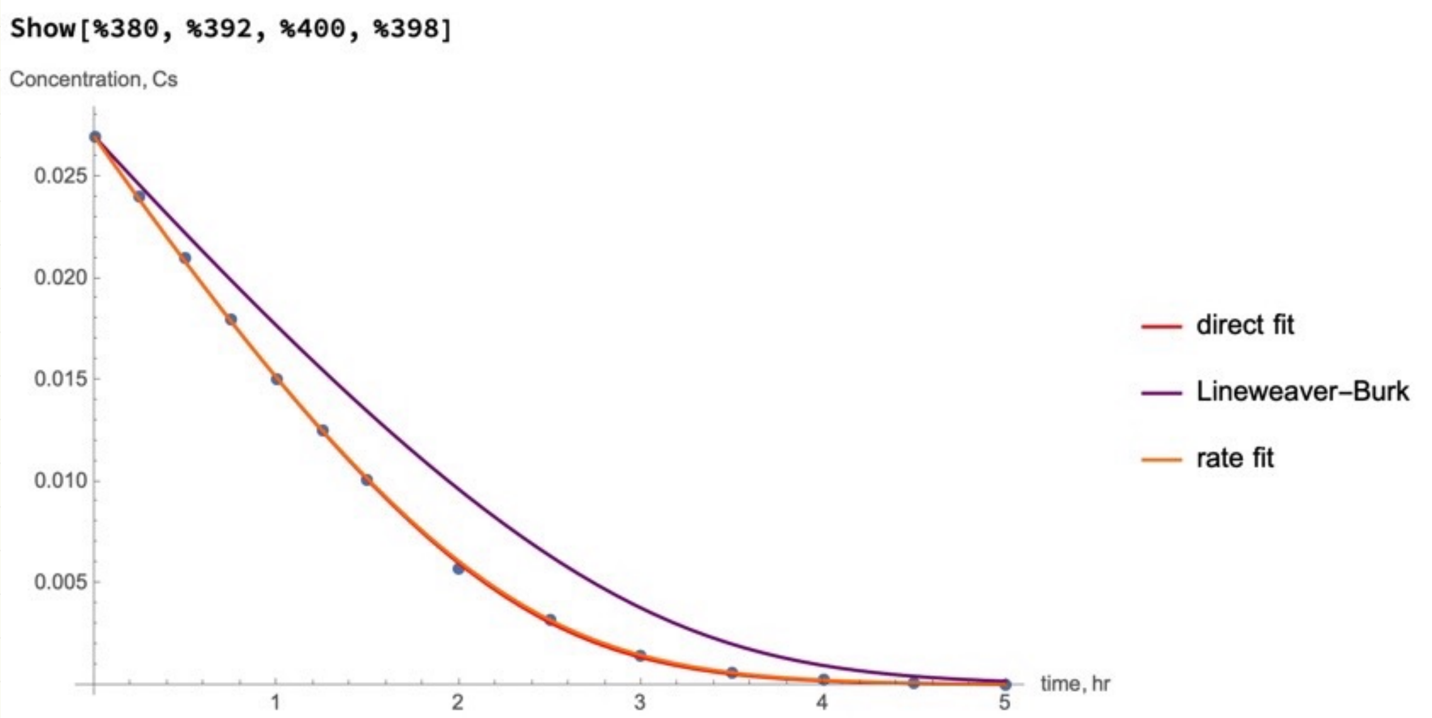
IF YOU TAKE DATA AND GET RATE: $K_m = .00851 \pm .00119$

$r_{MAX} = .0168 \pm .009$

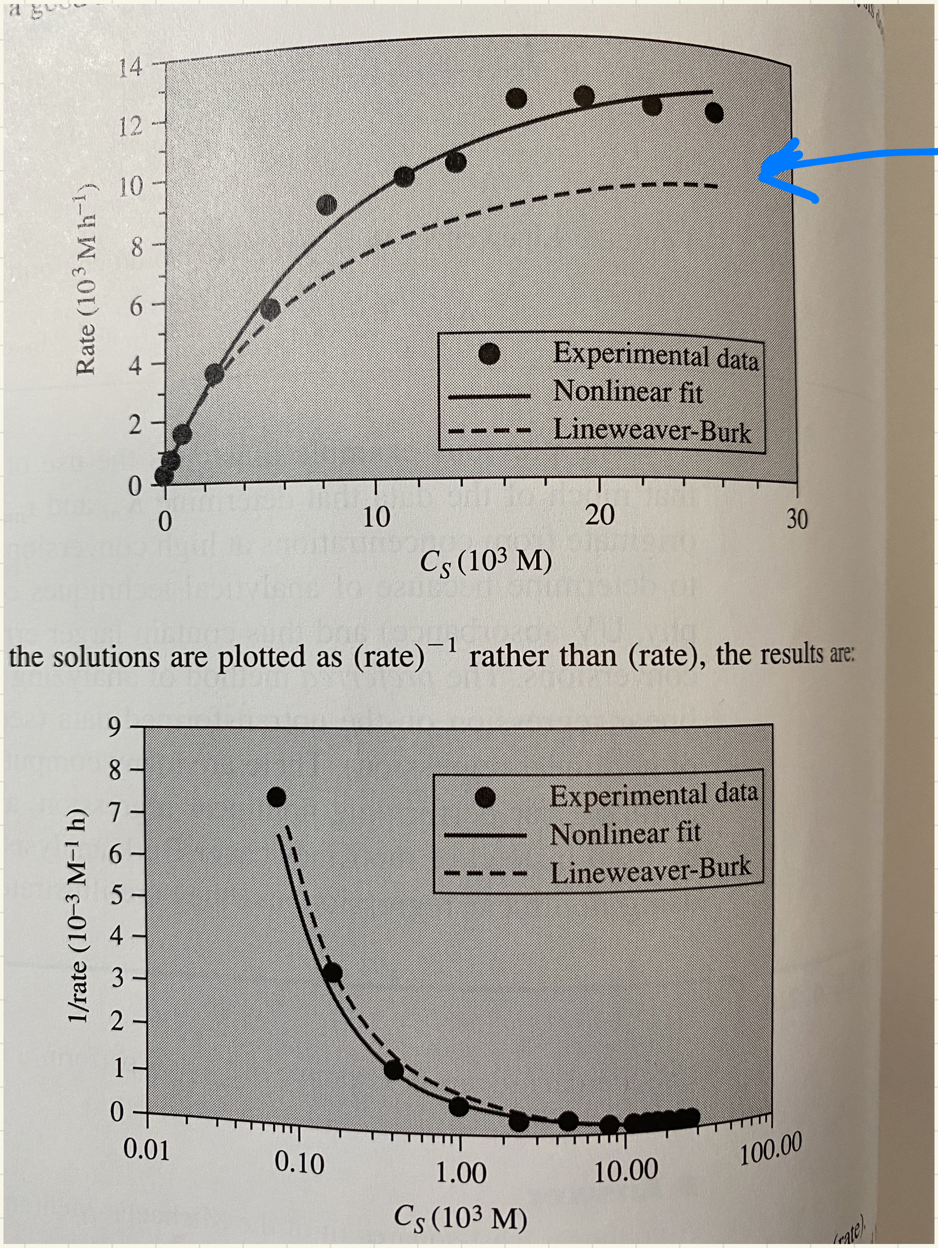
IF YOU DO LINE WEAVER-BURK

$K_m = .0068$

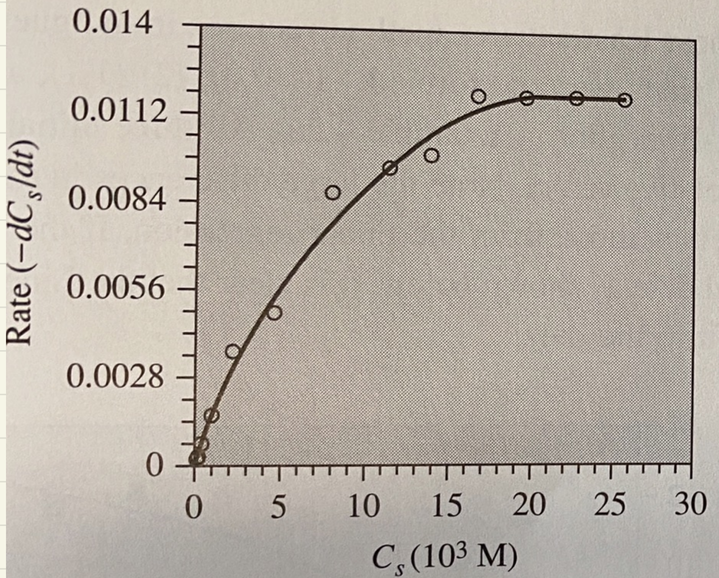
$r_{MAX} = .0122$

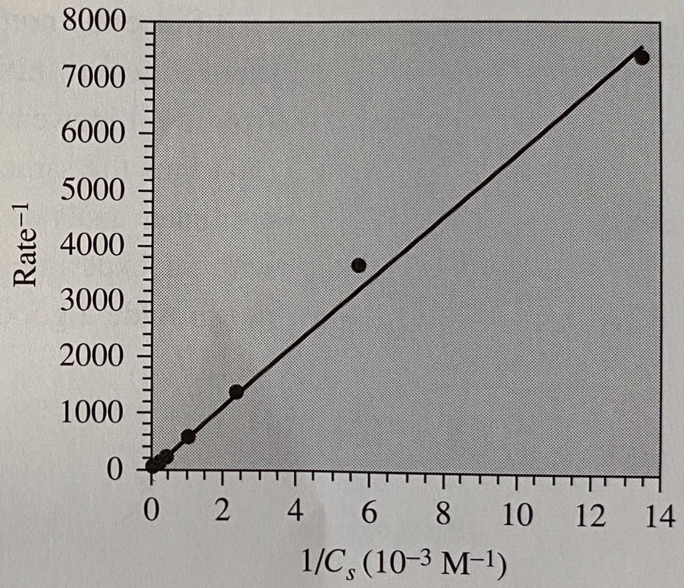


```
Show[%380, %392, %400, %398]
```



the solutions are plotted as (rate)$^{-1}$ rather than (rate), the results are:



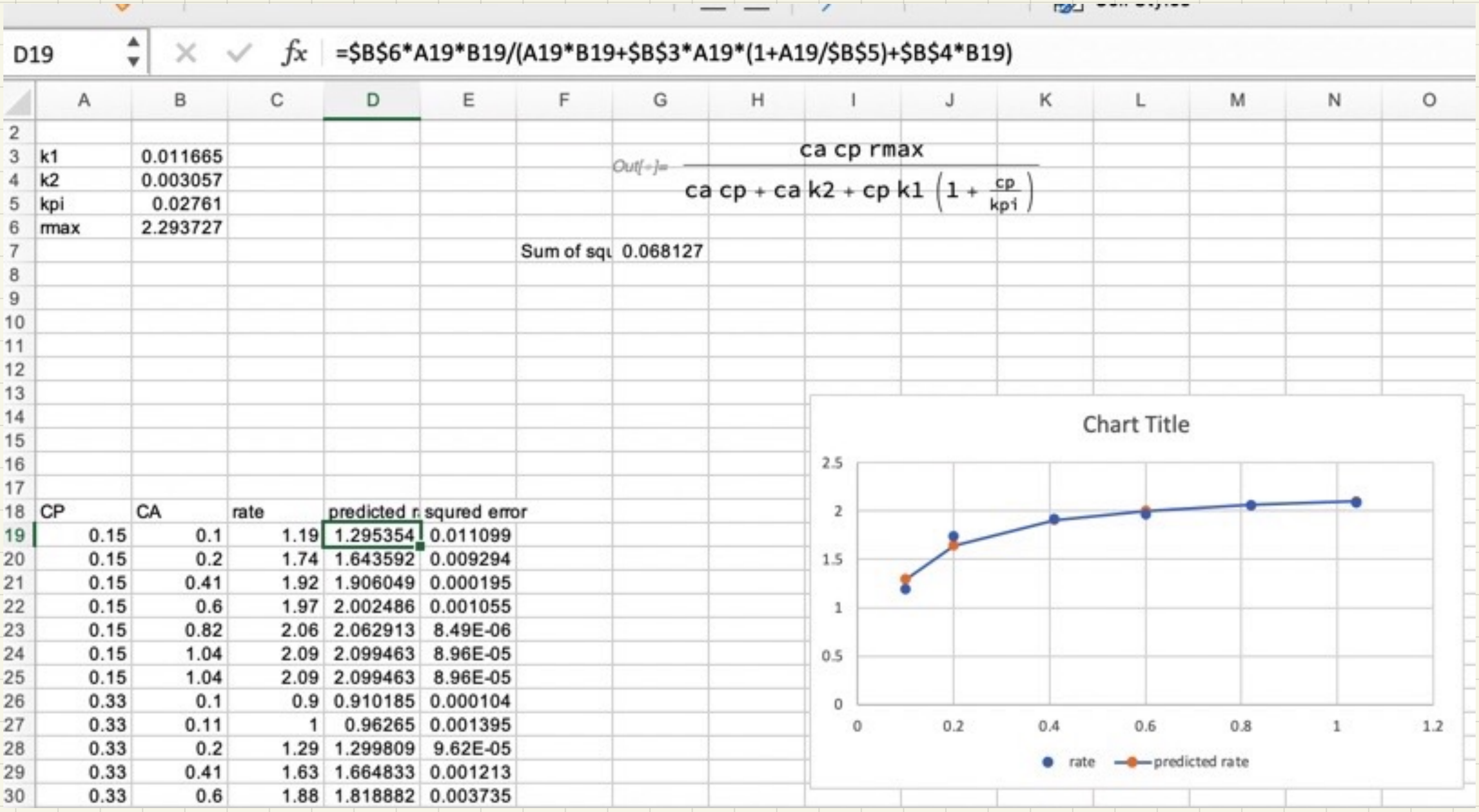


From the Lineweaver-Burk plot, the data do conform to the Michaelis-Menton rate law and

$$K_m = 6.80 \times 10^{-3}\ \frac{\text{kmol}}{\text{m}^3} \quad \text{and} \quad r_{\text{max}} = 1.22 \times 10^{-2}\ \frac{\text{kmol}}{\text{m}^3\text{-hr}}$$

The previous example illustrates the use of the Lineweaver-Burk plot. Notice

data that determine K_m and r_{max} in the Lineweaver-Burk analysis

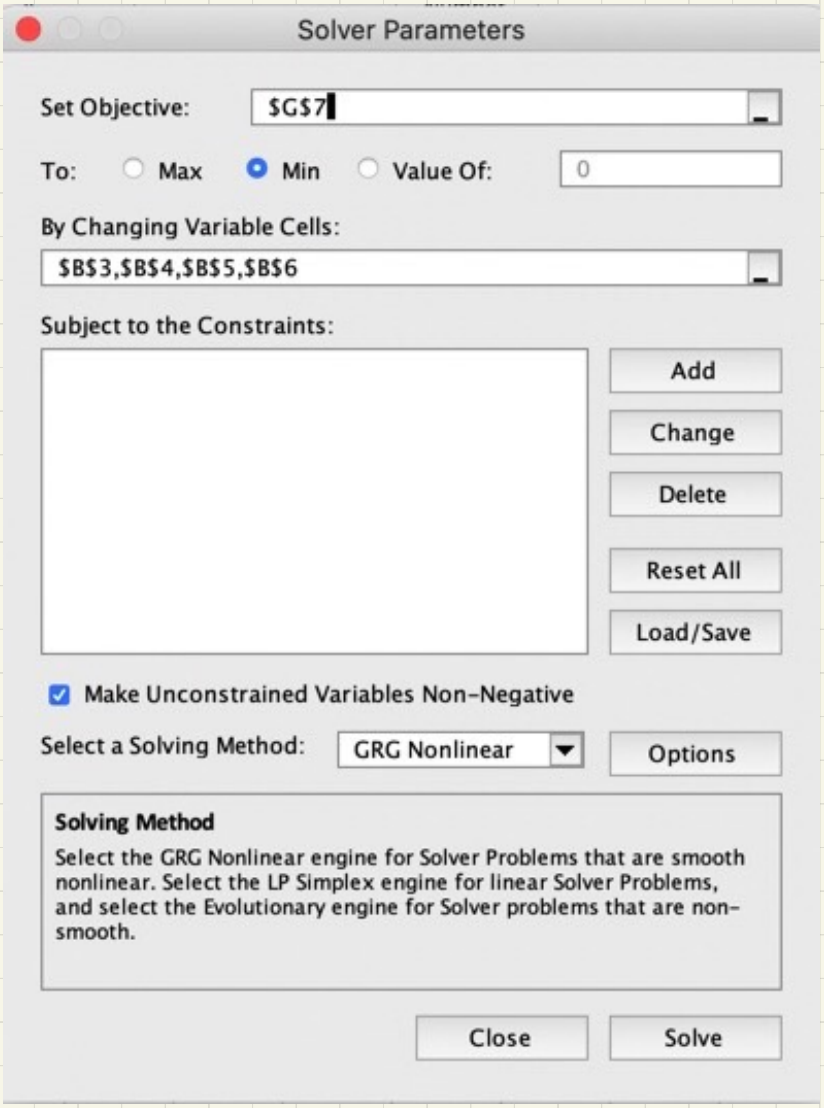


D19

```
=$B$6*A19*B19/(A19*B19+$B$3*A19*(1+A19/$B$5)+$B$4*B19)
```

	A	B	C	D	E	F	G
2							
3	k1	0.011665					
4	k2	0.003057					
5	kpi	0.02761					
6	rmax	2.293727					
7						Sum of squ	0.068127
18	CP	CA	rate	predicted r	squred error		
19	0.15	0.1	1.19	1.295354	0.011099		
20	0.15	0.2	1.74	1.643592	0.009294		
21	0.15	0.41	1.92	1.906049	0.000195		
22	0.15	0.6	1.97	2.002486	0.001055		
23	0.15	0.82	2.06	2.062913	8.49E-06		
24	0.15	1.04	2.09	2.099463	8.96E-05		
25	0.15	1.04	2.09	2.099463	8.96E-05		
26	0.33	0.1	0.9	0.910185	0.000104		
27	0.33	0.11	1	0.96265	0.001395		
28	0.33	0.2	1.29	1.299809	9.62E-05		
29	0.33	0.41	1.63	1.664833	0.001213		
30	0.33	0.6	1.88	1.818882	0.003735		

Out[=]= $$\frac{ca\ cp\ rmax}{ca\ cp + ca\ k2 + cp\ k1\left(1 + \frac{cp}{kpi}\right)}$$



Solver Parameters

Set Objective: $G$7

To: ○ Max ● Min ○ Value Of: 0

By Changing Variable Cells: $B$3,$B$4,$B$5,$B$6

Subject to the Constraints:

☑ Make Unconstrained Variables Non-Negative

Select a Solving Method: GRG Nonlinear

Solving Method

Select the GRG Nonlinear engine for Solver Problems that are smooth nonlinear. Select the LP Simplex engine for linear Solver Problems, and select the Evolutionary engine for Solver problems that are non-smooth.