CBE 40445
8/19/20

- REVERSIBLE REACTIONS
- FITTING MONOD KINETICS
- GETTING ACTIVATION ENERGY FROM DATA.

BESIDES WHAT DID THE STUDENT HAVE FOR LUNCH, THERE IS MORE TO THE STORY OF:

H_2SO_4 + DIETHYLSULFATE $(C_2H_5)_2SO_4$ $\longrightarrow 2\,C_2H_5SO_4H$

...

IT'S REVERSIBLE:

$$H_2SO_4 + (C_2H_5)_2SO_4 \rightleftharpoons 2\,C_2H_5SO_4H$$

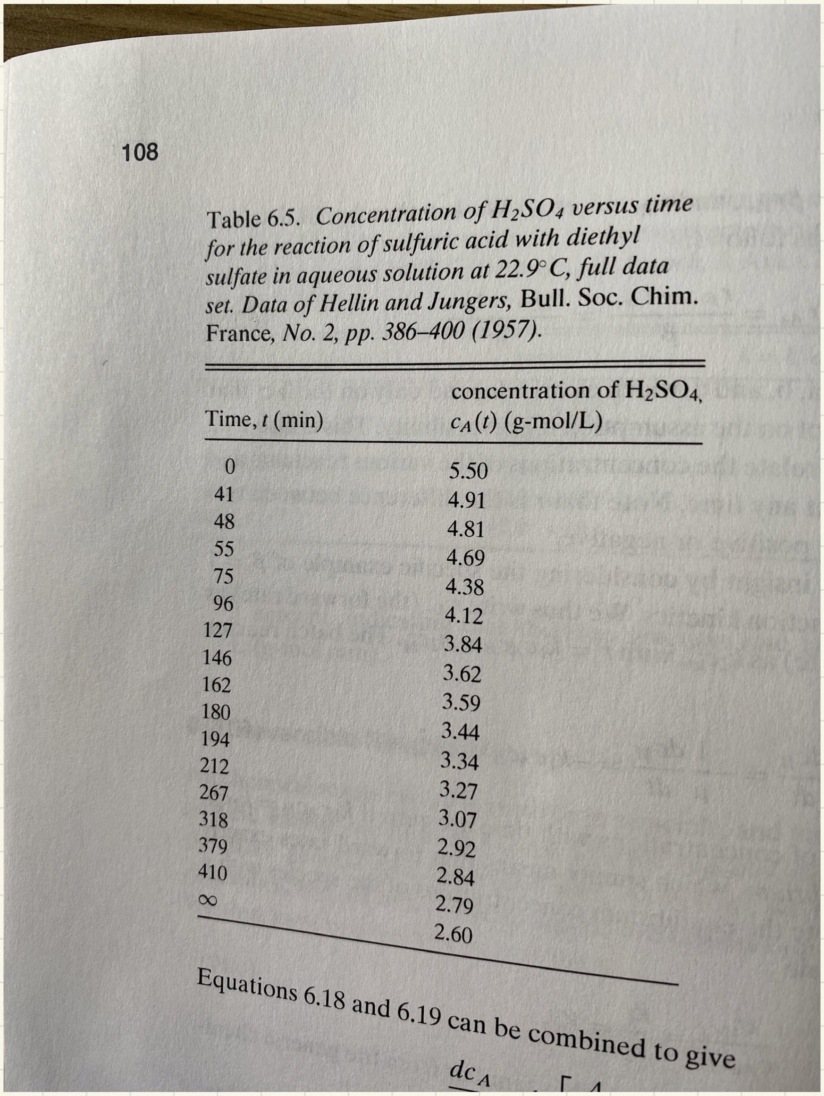

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Table 6.5. *Concentration of H_2SO_4 versus time for the reaction of sulfuric acid with diethyl sulfate in aqueous solution at 22.9°C, full data set. Data of Hellin and Jungers,* Bull. Soc. Chim. France, *No. 2, pp. 386–400 (1957).*

Time, t (min)	concentration of H_2SO_4, $c_A(t)$ (g-mol/L)
0	5.50
41	4.91
48	4.81
55	4.69
75	4.38
96	4.12
127	3.84
146	3.62
162	3.59
180	3.44
194	3.34
212	3.27
267	3.07
318	2.92
379	2.84
410	2.79
∞	2.60

Equations 6.18 and 6.19 can be combined to give

dc_A

$$\frac{d}{dt} C_{H_2SO_4} = -k_1 C_{H_2SO_4} C_{DIS} + k_2 C_{DSH}^2$$

WE PICKED $C^\circ_{H_2SO_4} = C^\circ_{DIS}$

AND : $C^\circ_{DSH} = 0$

$C_{H_2SO_4} = C_A$!

A+B = 2M

$$\frac{dC_A}{dt} = -k_1 C_A^2 + k_2 \left(2(C_A^\circ - C_A)\right)^2$$

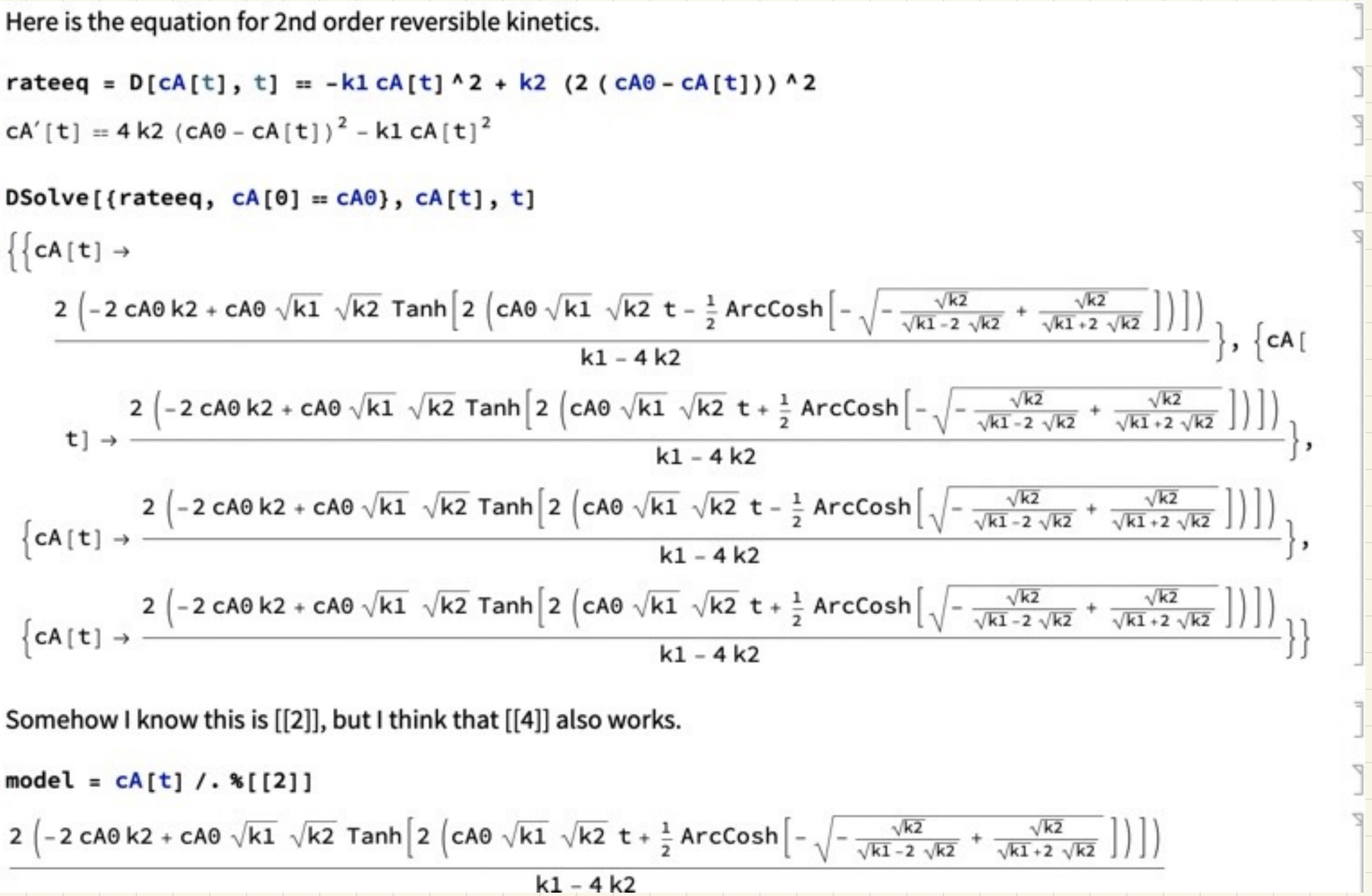
WE WOULD LIKE TO GET k_1 + k_2 + HENCE K_C

WE CAN ARRANGE THIS INTO:

$$\frac{K_C\, dC_A}{4(C_{A0} - C_A)^2 - K_C C_A^2} = k_1\, dt$$

THEN WE COULD INTEGRATE...

I THINK IT IS JUST EASIER TO SOLVE THE ODE DIRECTLY:



Here is the equation for 2nd order reversible kinetics.

```
rateeq = D[cA[t], t] == -k1 cA[t]^2 + k2 (2 (cA0 - cA[t]))^2
```

$$cA'[t] == 4\,k2\,(cA0 - cA[t])^2 - k1\,cA[t]^2$$

```
DSolve[{rateeq, cA[0] == cA0}, cA[t], t]
```

$$\left\{\left\{cA[t] \to \frac{2\left(-2\,cA0\,k2 + cA0\sqrt{k1}\,\sqrt{k2}\,\mathrm{Tanh}\left[2\left(cA0\sqrt{k1}\,\sqrt{k2}\,t - \frac{1}{2}\mathrm{ArcCosh}\left[-\sqrt{-\frac{\sqrt{k2}}{\sqrt{k1}-2\sqrt{k2}} + \frac{\sqrt{k2}}{\sqrt{k1}+2\sqrt{k2}}}\right]\right)\right]\right)}{k1 - 4\,k2}\right\}, \left\{cA[t] \to \frac{2\left(-2\,cA0\,k2 + cA0\sqrt{k1}\,\sqrt{k2}\,\mathrm{Tanh}\left[2\left(cA0\sqrt{k1}\,\sqrt{k2}\,t + \frac{1}{2}\mathrm{ArcCosh}\left[-\sqrt{-\frac{\sqrt{k2}}{\sqrt{k1}-2\sqrt{k2}} + \frac{\sqrt{k2}}{\sqrt{k1}+2\sqrt{k2}}}\right]\right)\right]\right)}{k1 - 4\,k2}\right\},$$

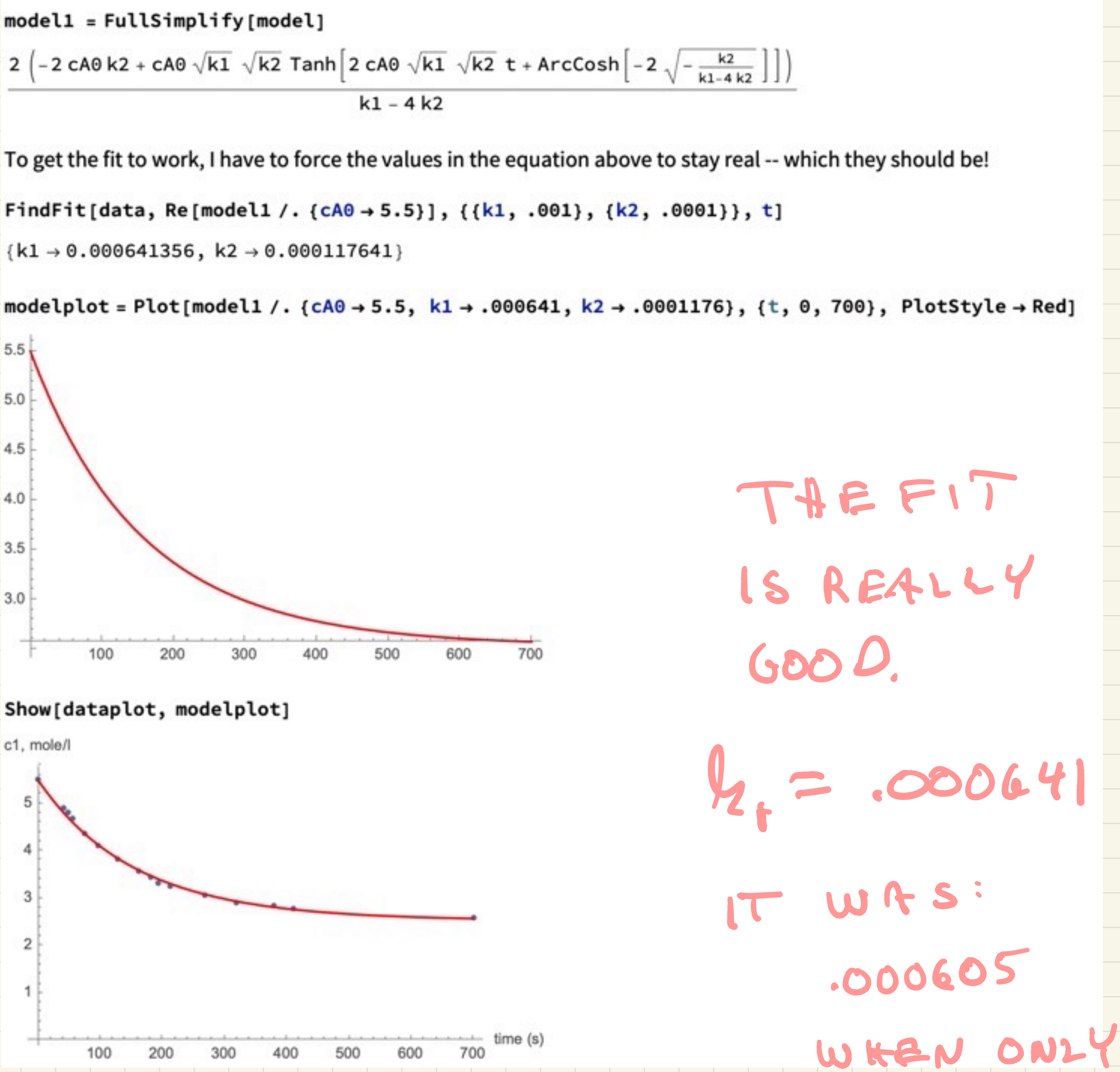
$$\left\{cA[t] \to \frac{2\left(-2\,cA0\,k2 + cA0\sqrt{k1}\,\sqrt{k2}\,\mathrm{Tanh}\left[2\left(cA0\sqrt{k1}\,\sqrt{k2}\,t - \frac{1}{2}\mathrm{ArcCosh}\left[\sqrt{-\frac{\sqrt{k2}}{\sqrt{k1}-2\sqrt{k2}} + \frac{\sqrt{k2}}{\sqrt{k1}+2\sqrt{k2}}}\right]\right)\right]\right)}{k1 - 4\,k2}\right\},$$

$$\left\{cA[t] \to \frac{2\left(-2\,cA0\,k2 + cA0\sqrt{k1}\,\sqrt{k2}\,\mathrm{Tanh}\left[2\left(cA0\sqrt{k1}\,\sqrt{k2}\,t + \frac{1}{2}\mathrm{ArcCosh}\left[\sqrt{-\frac{\sqrt{k2}}{\sqrt{k1}-2\sqrt{k2}} + \frac{\sqrt{k2}}{\sqrt{k1}+2\sqrt{k2}}}\right]\right)\right]\right)}{k1 - 4\,k2}\right\}\right\}$$

Somehow I know this is [[2]], but I think that [[4]] also works.

```
model = cA[t] /. %[[2]]
```

$$\frac{2\left(-2\,cA0\,k2 + cA0\sqrt{k1}\,\sqrt{k2}\,\mathrm{Tanh}\left[2\left(cA0\sqrt{k1}\,\sqrt{k2}\,t + \frac{1}{2}\mathrm{ArcCosh}\left[-\sqrt{-\frac{\sqrt{k2}}{\sqrt{k1}-2\sqrt{k2}} + \frac{\sqrt{k2}}{\sqrt{k1}+2\sqrt{k2}}}\right]\right)\right]\right)}{k1 - 4\,k2}$$



```
model1 = FullSimplify[model]
```

$$\frac{2\left(-2\,\text{cA0}\,\text{k2}+\text{cA0}\sqrt{\text{k1}}\sqrt{\text{k2}}\,\text{Tanh}\left[2\,\text{cA0}\sqrt{\text{k1}}\sqrt{\text{k2}}\,t+\text{ArcCosh}\left[-2\sqrt{-\frac{\text{k2}}{\text{k1}-4\,\text{k2}}}\right]\right]\right)}{\text{k1}-4\,\text{k2}}$$

To get the fit to work, I have to force the values in the equation above to stay real -- which they should be!

```
FindFit[data, Re[model1 /. {cA0 → 5.5}], {{k1, .001}, {k2, .0001}}, t]
{k1 → 0.000641356, k2 → 0.000117641}
```

```
modelplot = Plot[model1 /. {cA0 → 5.5, k1 → .000641, k2 → .0001176}, {t, 0, 700}, PlotStyle → Red]
```

```
Show[dataplot, modelplot]
```

THE FIT IS REALLY GOOD.

k_1 = .000641

IT WAS: .000605 WHEN ONLY THE INITIAL DATA WERE USED.

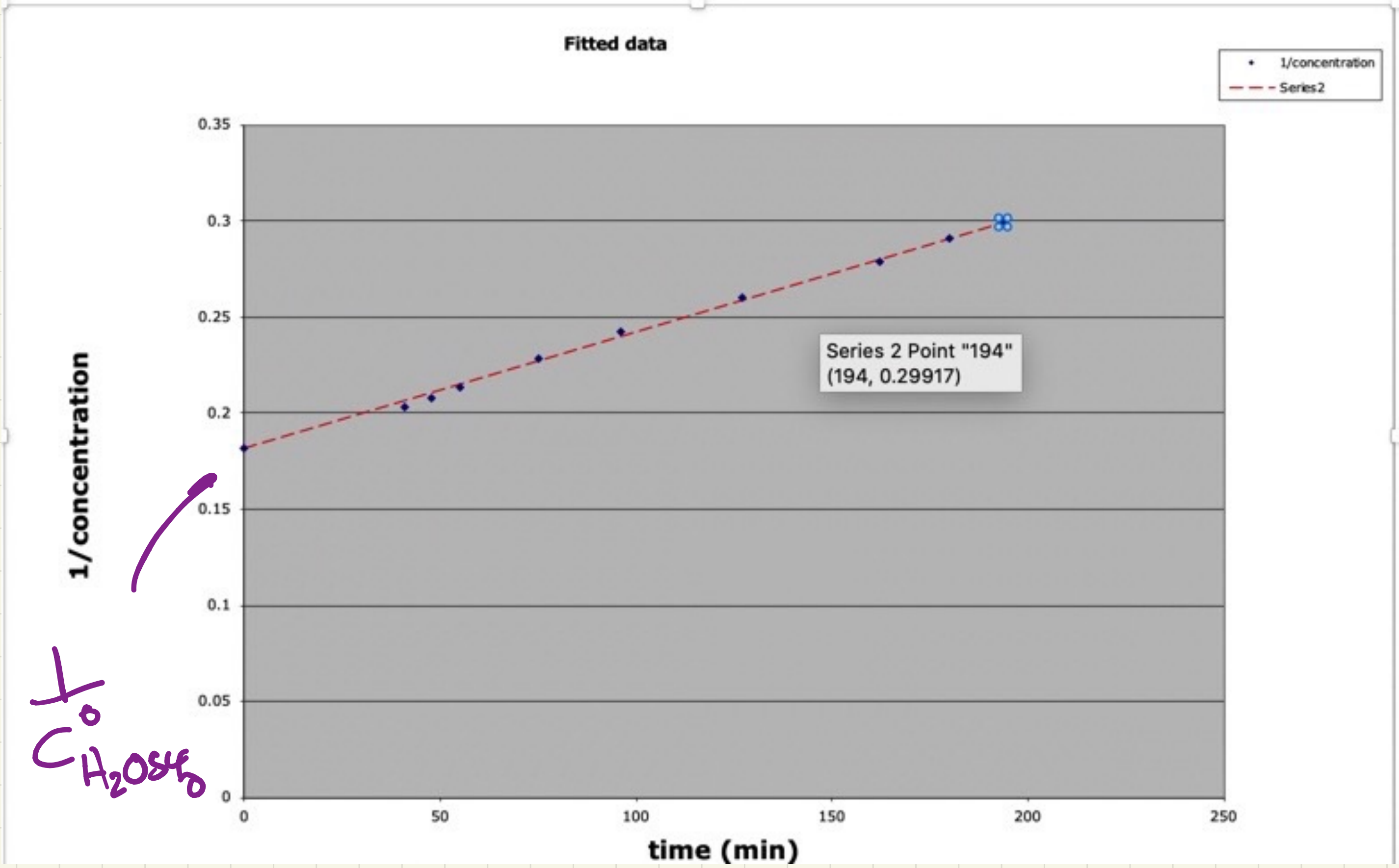
RECALL: LETS CONSIDER

$$C^0_{H_2OS4} = C^0_{DISO_4}$$

$$\frac{dC_{H_2SO_4}}{dt} = -k\, C_{H_2SO_4}^2$$

$$-\int_{C^0_{H_2SO_4}}^{C_{H_2SO_4}} \frac{dC_{H_2SO_4}}{C^2_{H_2SO_4}} = \int_0^t k\, dt$$

$$\left(\frac{1}{C_{H_2SO_4}} - \frac{1}{C^0_{H_2SO_4}}\right) = kt$$



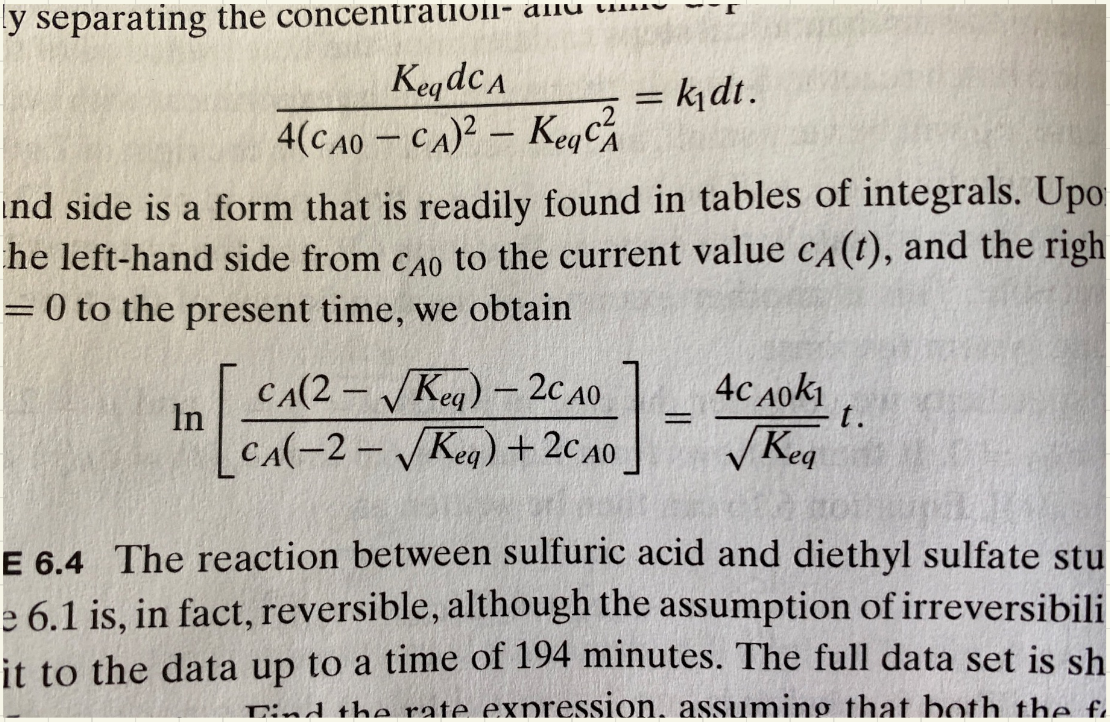
$\frac{1}{C^{o}_{H_2O8H_8}}$

$$k = \text{SLOPE}$$

$$= 6.05 \times 10^{-4} \left(\frac{l}{\text{MOL-MIN}}\right)$$

ANOTHER LOOK AT REVERSIBLE RXN.

EXCEL "SOLVER" FIT OF



ly separating the concentration- and time-dep

$$\frac{K_{eq}\,dc_A}{4(c_{A0}-c_A)^2 - K_{eq}c_A^2} = k_1\,dt.$$

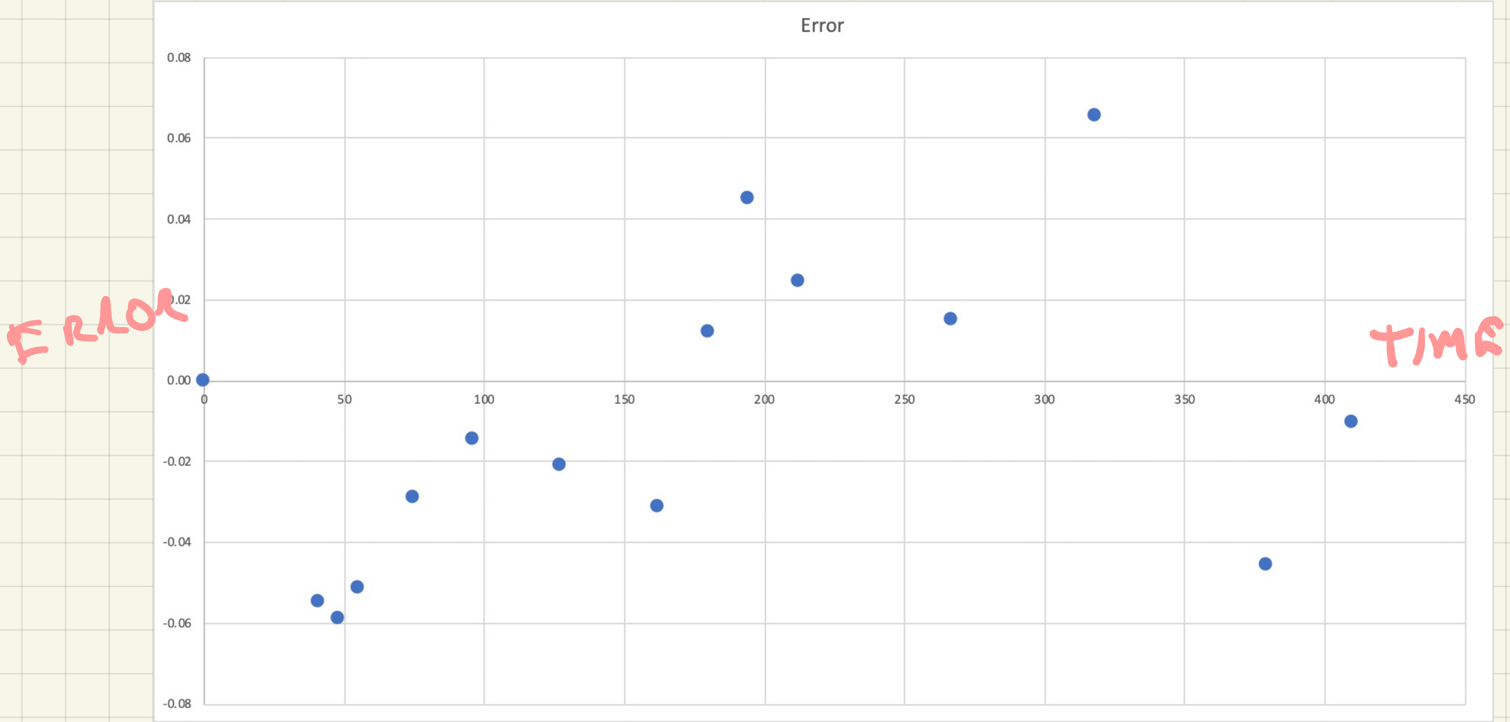
nd side is a form that is readily found in tables of integrals. Upo he left-hand side from c_{A0} to the current value $c_A(t)$, and the righ $= 0$ to the present time, we obtain

$$\ln\left[\frac{c_A(2-\sqrt{K_{eq}}) - 2c_{A0}}{c_A(-2-\sqrt{K_{eq}}) + 2c_{A0}}\right] = \frac{4c_{A0}k_1}{\sqrt{K_{eq}}}\,t.$$

E 6.4 The reaction between sulfuric acid and diethyl sulfate stu e 6.1 is, in fact, reversible, although the assumption of irreversibili it to the data up to a time of 194 minutes. The full data set is sh Find the rate expression, assuming that both the f

$k_1 = .00067$

$K_{EQ} = 4.922$ $k_2 = .000136$



ARRHENIUS TEMPERATURE DEPENDENCE

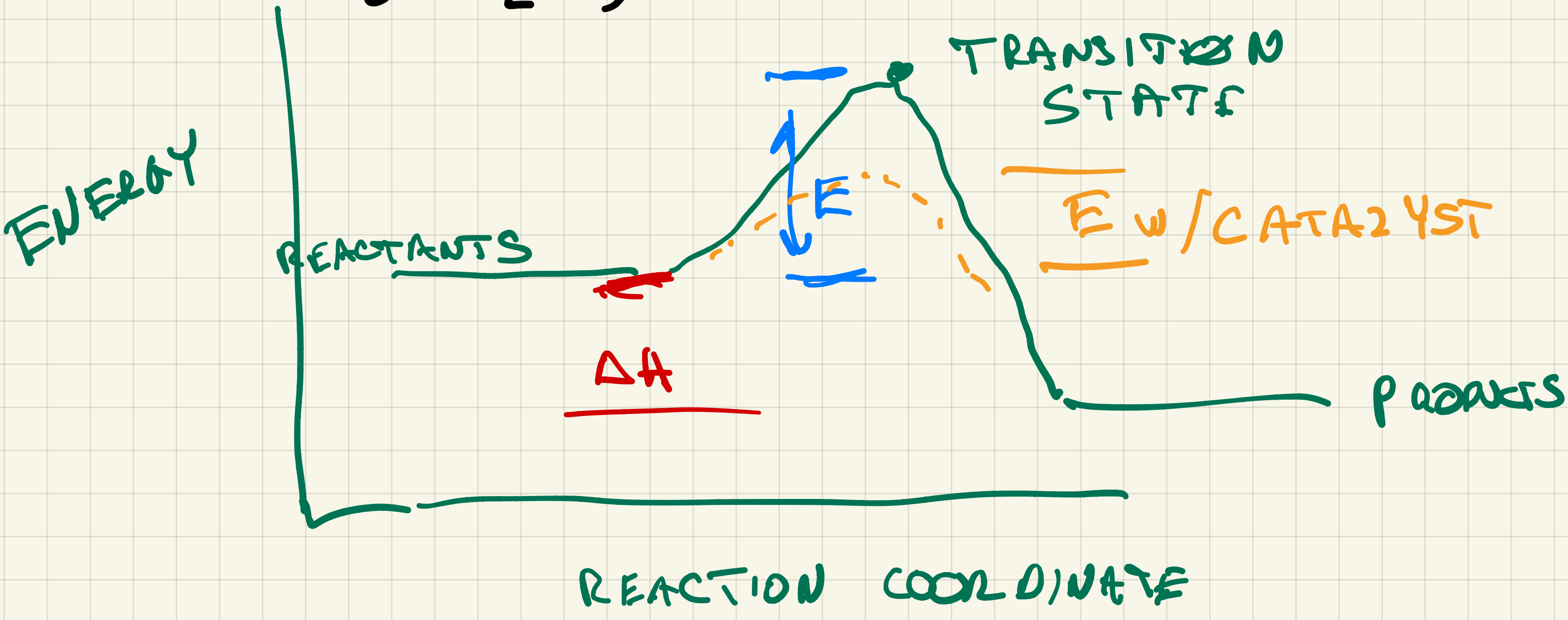
ONE OF THE BASIC RULES OF KINETICS WAS TO EXPECT ARRHENIUS BEHAVIOR

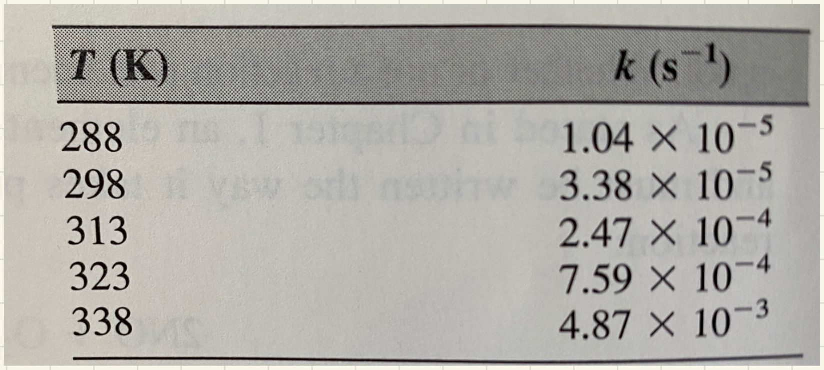
$$k = \bar{A} \exp\left[-\frac{E_A}{RT}\right]$$

IDEALLY NOT A FUNCTION OF T

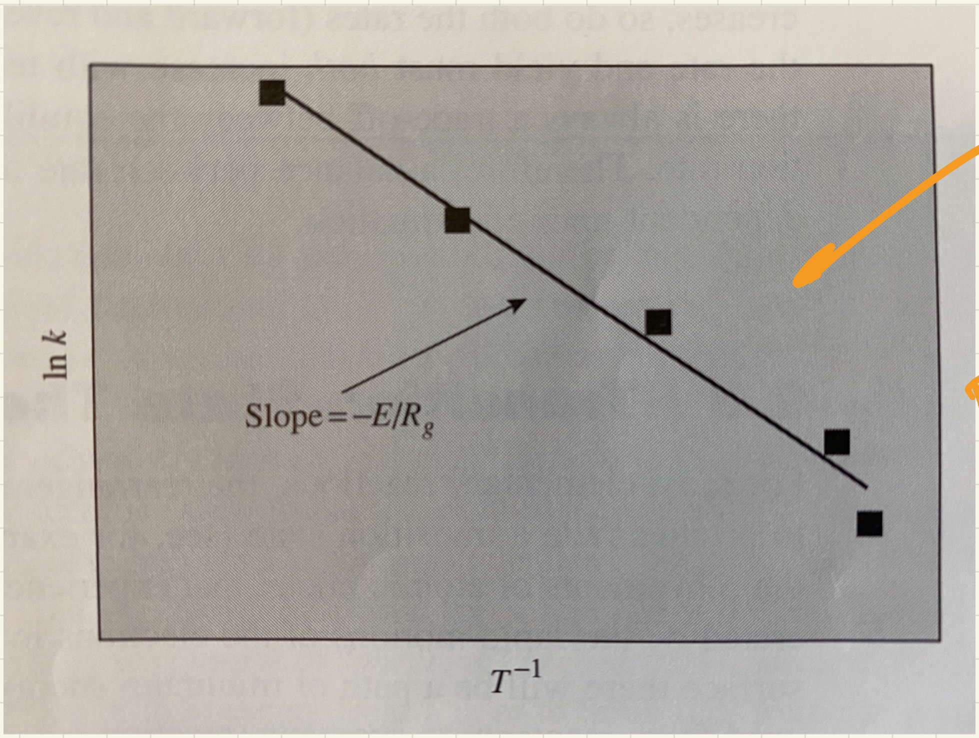
OFTEN VERY SIGNIFICANT TEMP DEPENDENCE

$$2N_2O_5 \rightleftharpoons 2N_2O_4 + O_2$$





T (K)	k (s^{-1})
288	1.04×10^{-5}
298	3.38×10^{-5}
313	2.47×10^{-4}
323	7.59×10^{-4}
338	4.87×10^{-3}



= -11981

$E_a \sim 99{,}000 \frac{J}{MO}$

$\cong 24 \frac{KCAL}{MOLE}$

A CATALYST IS USED TO REDUCE E.

AN OBVIOUS REASON FOR E TO VARY IS INTERNAL BONDING OF MOLECULE

WHILE 'A' CAN ALSO CHANGE FOR DIFFERENT SYSTEMS,

A SUFFICIENTLY HIGH T IS NECESSARY TO MAKE REACTION OCCUR AT FINITE RATE.

REACTION TIME SCALES FOR DIFFERING ACTIVATION ENERGY

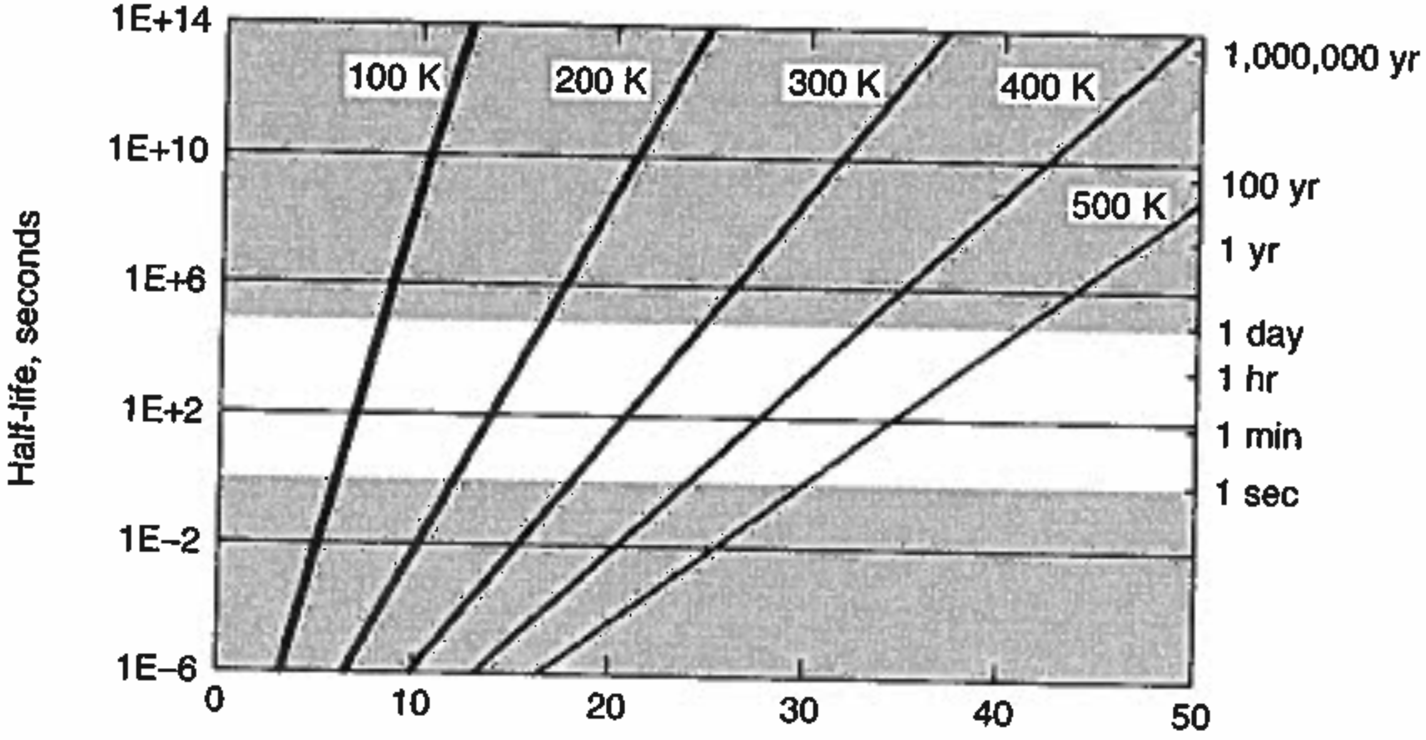


Figure 2.8 A plot of $\tau_{1/2}$ versus. E$_a$ at 100, 200, 300, 400, and 500 K.

"MONOD KINETICS"

HOW WOULD WE FIT DATA FOR A FORM LIKE:

$$\frac{dC_A}{dt} = -\frac{k_1 k_2 C_A C_E^0}{k_1 C_A + k_2 + k_r}$$

LOOKS LIKE:

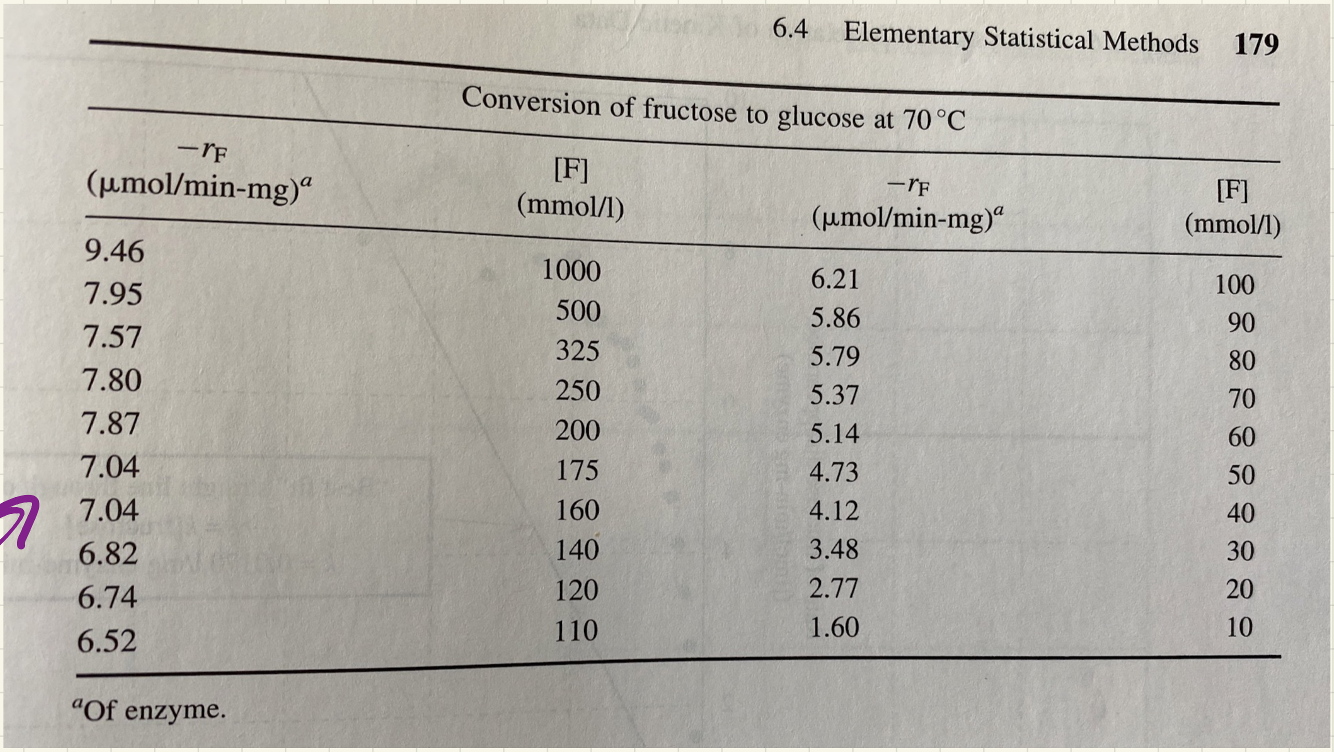
$$\text{RATE} = \frac{(k_2 C_E^0)\, C_A}{C_A + \left(\frac{k_2 + k_r}{k_1}\right)}$$

$$= \frac{V_{max}\, C_A}{C_A + K_m}$$

USE RATE v. C_A TO GET V_{max} + K_m

SOME DATA FOR FRUCTOSE → GLUCOSE

$$A + E \underset{k_r}{\overset{k_1}{\rightleftharpoons}} AE \xrightarrow{k_2} M + E$$

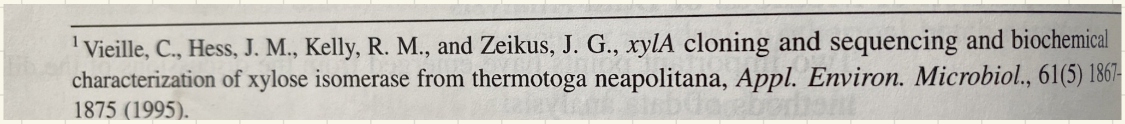


6.4 Elementary Statistical Methods 179

Conversion of fructose to glucose at 70 °C

$-r_F$ (μmol/min-mg)[a]	[F] (mmol/l)	$-r_F$ (μmol/min-mg)[a]	[F] (mmol/l)
9.46	1000	6.21	100
7.95	500	5.86	90
7.57	325	5.79	80
7.80	250	5.37	70
7.87	200	5.14	60
7.04	175	4.73	50
7.04	160	4.12	40
6.82	140	3.48	30
6.74	120	2.77	20
6.52	110	1.60	10

[a] Of enzyme.



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[1] Vieille, C., Hess, J. M., Kelly, R. M., and Zeikus, J. G., *xylA* cloning and sequencing and biochemical characterization of xylose isomerase from thermotoga neapolitana, *Appl. Environ. Microbiol.*, 61(5) 1867-1875 (1995).

$$\text{rate} = \frac{V_{max}\, C_A}{C_A + K_m}$$

$$\frac{1}{\text{rate}} = \frac{C_A + K_m}{V_{max}\, C_A} = \underbrace{\frac{1}{V_{max}} + \frac{K_m}{V_{max}} \frac{1}{C_A}}$$

COULD DO A LINEWEAVER BURK PLOT

THIS MIGHT BE OK, BUT...

- WHERE DID 'RATE' COME FROM ?

  → IS THIS A FINITE DIFFERANCE DERIVATIVE OF CONCENTRATION V. TIME DATA?

  → ADDS TO "NOISE"

- LINEARIZATION WILL SKEW WHICH POINTS ARE EMPHASIZED.

SO TRY A NONLINEAR FIT IN EXCEL....

FOR THIS DATA SET,

INITIAL GUESSES

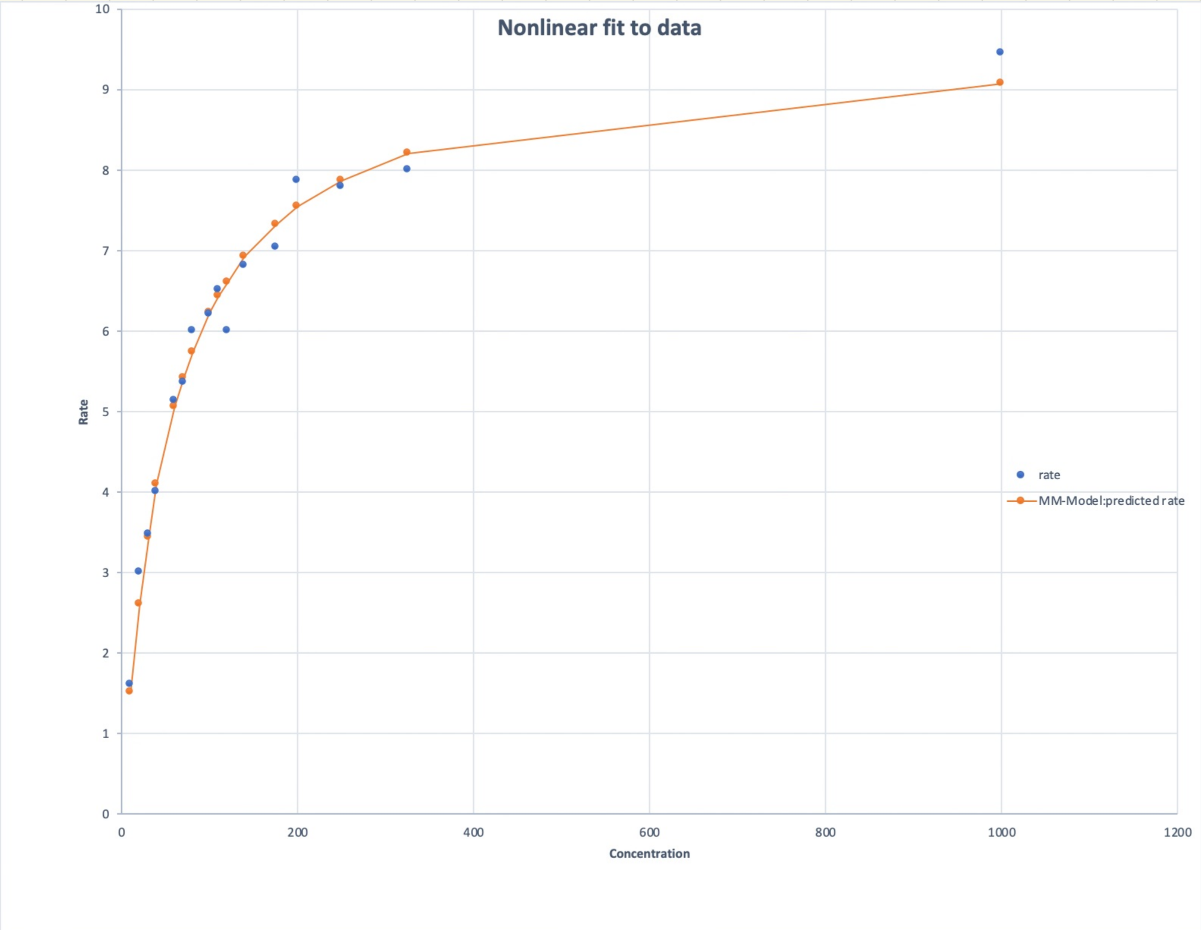
OF $V_{MAX} = 5$

$K_m = 40$

ARE RESOLVED TO

$V_{MAX} = 9.55$

$K_m = 53.29$



ISSUES RELATED TO DATA & DATA ANALYSIS

MATHEMATICA INSIGHTS...