Chapter 3 Summary
Analysis of rate data

Rate measurements and old topic

General approach

- Initiate reaction
- measure concentration vs time
- fit data to calculate rates

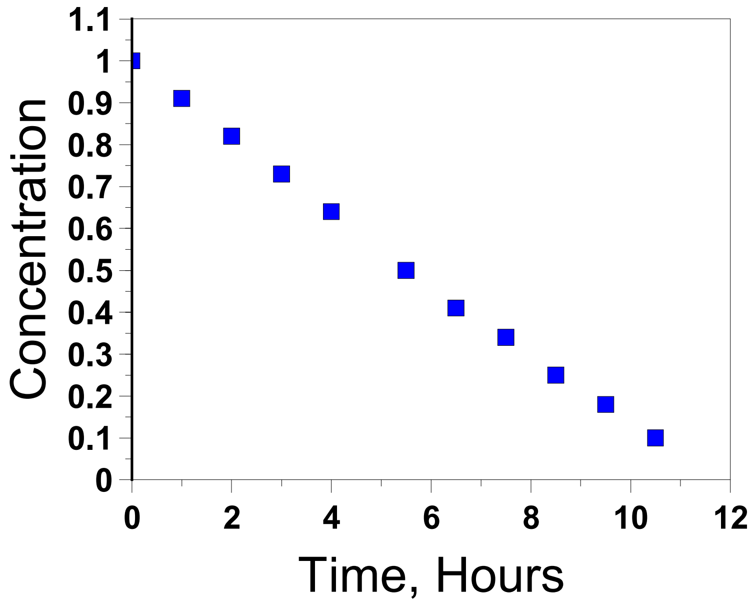


Figure 3.2 Wilhelmy's [1850] measurements of the changes in sucrose concentration in grape juice after acid is added.

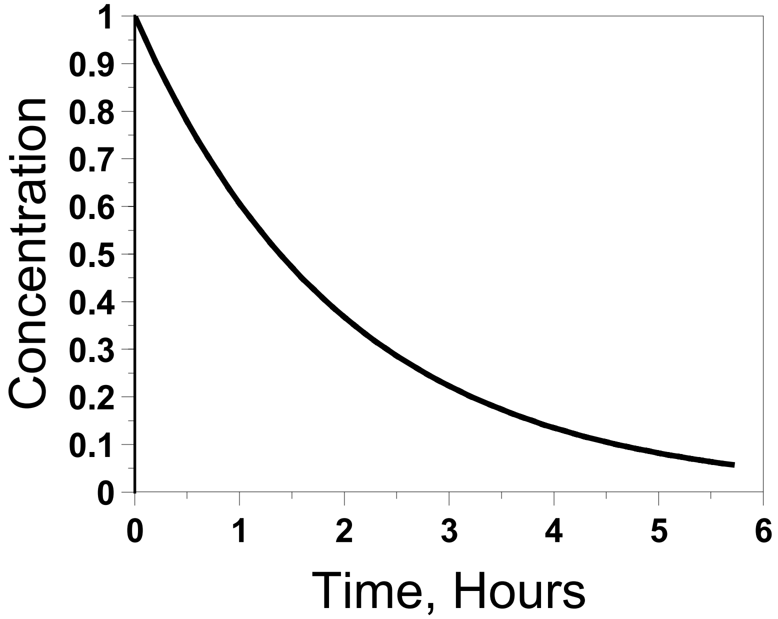


Figure 3.3 Concentration vs time for a simple reaction.

These types of measurements started in 1820. Still done today. (now do them faster).

Table 3.1 Some techniques used to measure rates of reaction.

Method	Description	Time Scale
Batch Methods		
Conventional	1) Mix reactants together in a batch reactor 2) Measure concentration versus time	10 sec or more
Stopped flow	1) Set of continuous flow systems where reactants are fed into the reactor, and flow out again so quickly that there is negligible reaction 2) Stop the flow so the reactants can react 3) Measure conversion versus time	10^{-1} sec or more
Temperature jump	1) Mix reactants at such a low temperature that the reaction rate is negligible 2) Use CO_2 laser to suddenly heat reaction 3) Measure concentration vs time	10^{-6} sec or more
Shock tube	1) Put 10^{-1} atm of one reactant and 10 atm at helium on one side of a diaphragm 2) Put 10^{-3} atm of the other reactant on the other side of the diaphragm 3) Suddenly break the diaphragm so the gas flows from the high pressure side to the low pressure side Measure the reactant concentration vs time	10^{-3} to 10^{-5} sec
Flash photolysis	1) Put the reactants into a vessel under conditions where reaction is negligible 2) Pulse a laser or flash lamp to start reaction 3) Measure the reactant concentration vs time	10^{-9} to 10^{-1} sec
NMR	1) Initiate a change with a magnetic pulse 2) Measure the decay of spins with the NMR	10^{-2} to 10^{-9} sec
Flow Methods		
Conventional flow system	1) Continuously feed reactants into a reactor - CSTR or plug flow 1) Measure the steady state reaction rate	10^{-3} sec or more
Molecular beam	1) Direct beams of reactants toward each together in a vacuum system 2) Measure the steady state reaction rate	10^{-13} to 10^{-9} sec

If you have to do an experiment which do you choose?

- Direct vs indirect methods
- Choose method with appropriate time scale

Direct vs indirect methods

recall - rate equation is the rate as a function of the concentrations

- Direct method - any method where you actually measure the rate as a function of concentration
- Indirect method - a method where you measure some other property (i.e. concentration vs time) and infer a rate equation.

Example of a direct method:

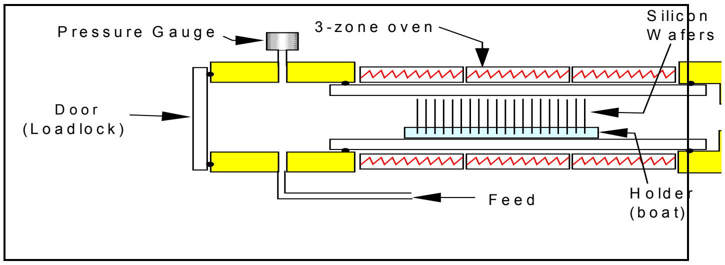


Figure 3.7 A typical arsine decomposition reactor.

$$2\mathrm{AsH}_3 \Rightarrow 2\mathrm{As} + 3\mathrm{H}_2$$

(3.6)

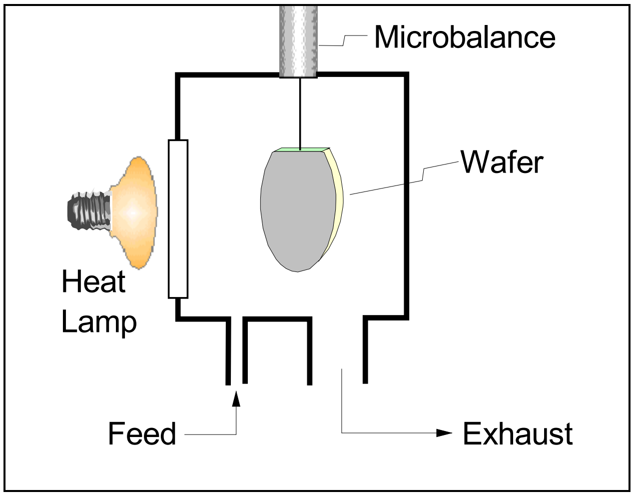


Figure 3.8 A possible apparatus to examine the decomposition of arsine (AsH_3) on silicon.

$$P_{AsH_3} = P^0_{AsH_3} \times e^{-k_1 t}$$

(3.8)

Indirect measurement to do the same thing

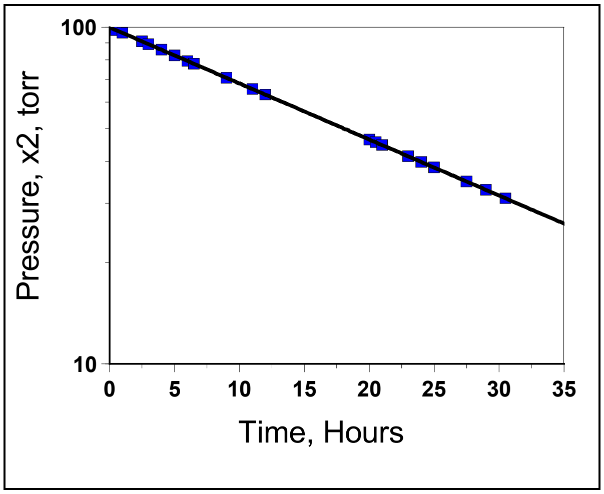


Figure 3.9 Typical batch data for reaction(3.7). Data of Tamaru[1955].

Table 3.2 A Comparison of the Advantages and Disadvantages of Direct and Indirect Methods

Direct Method	**Indirect Method**
Advantages • Get rate equation directly • Easy to fit data to a rate law • High confidence on final rate equation	**Disadvantages** • Must infer rate equation • Hard to analyze rate data • Low confidence on final rate equation
Disadvantages • Difficult experiment • Need many runs • Not suitable for very fast or very slow reactions	**Advantages** • Easier experiment • Can do a few runs and get important information • Suitable for all reactions including very fast or very slow ones

Other notation

direct method - differential method
-differential reactor
indirect method - integral method

Next: start analysis of data from indirect reactors:

Which is easier to analyze?
- Direct method (rate vs concentration)
- Indirect method (concentration vs time)

Direct is easier to analyze.

Analysis of data from a differential reactor

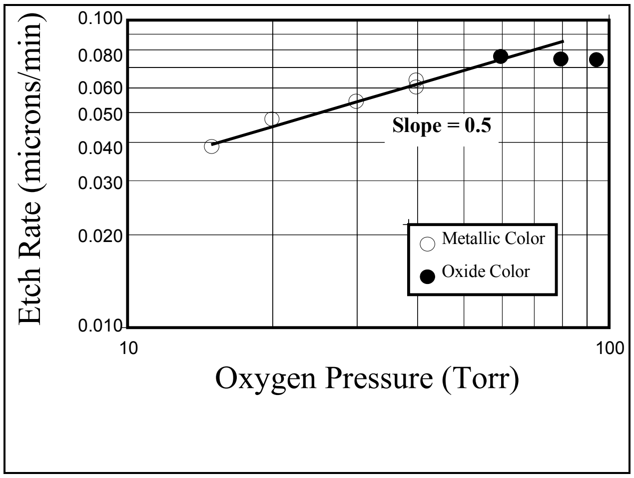


Figure 3.11 The rate of copper etching as a function of the oxygen concentration. Data of Steger and Masel [1998].

General method - least squares with rate vs time data.

Pitfalls

- It is not uncommon for more than one rate equation may fit the measured kinetics within the experimental uncertainties, just because data fits, does not mean rate equation is correct.

- The quality of kinetic data vary with the equipment used and the method of temperature measurement and control. Data taken on one apparatus is often not directly comparable to data taken on different apparatus.
- It is not uncommon to observe 10-30% variations in rate taken in the same apparatus on different days. Usually, these variations can be traced to variations in the temperature, pressure, or flow rate in the reactor.
- The procedure used to fit the data can have a major effect on the values of the parameters obtained in the data analysis.
- The quality of the regression coefficient (r^2) does not tell you how well a model fits your data.

Example 3.A Fitting data to Monod's Law

Table 3.A.1 shows some data for the growth rate of paramecium as a function of the paramecium concentration. Fit the data to Monod's Law:

$$r_p = \frac{k_1 K_2 [\text{par}]}{1 + K_2 [\text{par}]}$$

(3.A.1)

where [par] is the paramecium concentration, and k_1 and K_2 are constants.

Table 3.A.1 The rate of paramecium reproduction as a function of the paramecium concentration. Data of Meyers, J. Experimental Zoology, **49** (1927) 1

Paramecium concentration #/CC	rate, #/CC-hr	Paramecium concentration #/CC	rate, #/CC-hr	Paramecium concentration #/CC	rate, #/CC-hr
2	10.4	16	36	46	96
3.6	12.8	16.6	46.4	46.2	124.8
4	23.2	19	59.2	47.4	117.6
5.2	17.6	20	62.4	55	112
7.8	46.4	23.8	62.4	57	127.2
8	23.2	26	57.6	61	116
8	46.4	30.4	108.8	61.6	111.2
11	32	31	80	71	124
14.4	34.4	31.2	61.6	74	116
15.6	44.8	31.6	109.6	76.4	116
15.6	63.2	39.2	103.2		

There are two methods that people use to solve problems like this:

- Rearranging the equations to get a linear fit and using least squares
- Doing non-linear least squares

I prefer the latter, but I wanted to give a picture of the former.

There are two versions of the linear plots:

- Lineweaver-Burk Plots
- Eadie-Hofstee Plots

In the Lineweaver-Burk method, one plots 1/rate vs. 1/concentration. Rearranging equation (3.A.1) shows:

$$\frac{1}{r_p} = \frac{1}{k_1 K_2 [\mathrm{par}]} + \frac{1}{k_1}$$

(3.A.2)

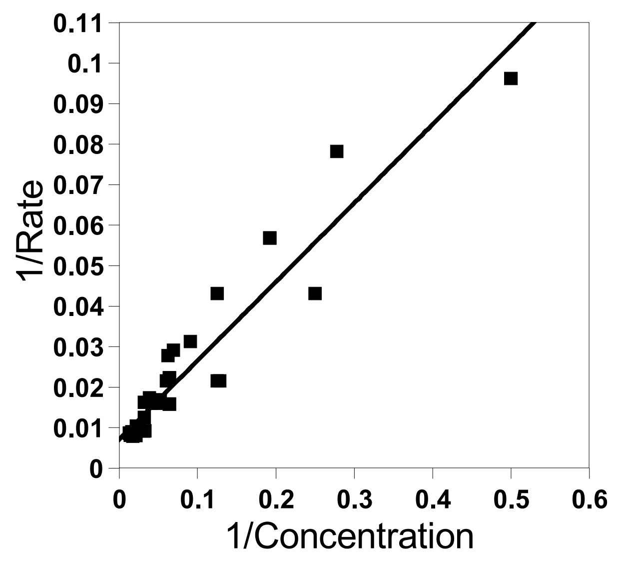


Figure 3.A.1 A Lineweaver-Burk plot of the data in Table 3.A.1

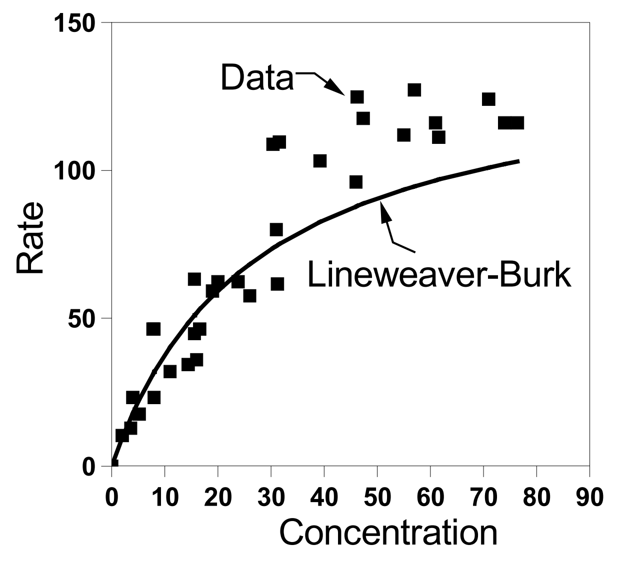


Figure 3.A.2 The Lineweaver-Burk fit of the data in Table 3.A.1

Table 3.A.2 The formulas in the spreadsheet for the Lineweaver Burke plot

	A	B	C	D	E	F
01		k_1	=1/D2	=SLOPE(D6:D35,C6:C35)		2
02		K_2	=1/C1/D1	=INTERCEPT(D6:D36,C6:C36)		=SUM(F5:F37)
03			r^2	=RSQ(D6:D36,C6:C36)		
04	conc	rate	1/conc	1/rate	rate calculated from rate equation	error
05	0	0			=C$1*C$2*$A5/(1+C$2*$A5)	=ABS(E5-$B5)^$F$1
06	2	10.4	=1/A6	=1/B6	=C$1*C$2*$A6/(1+C$2*$A6)	=ABS(E6-$B6)^$F$1
07	3.6	12.8	=1/A7	=1/B7	=C$1*C$2*$A7/(1+C$2*$A7)	=ABS(E7-$B7)^$F$1

Comparison of equations (3.A.2) and (3.A.3) shows:

$$k_1 = 1/.00717=139.4,$$

$$k_2=1/(0.194*k_1)=0.037,$$

$$r^2=0.930$$

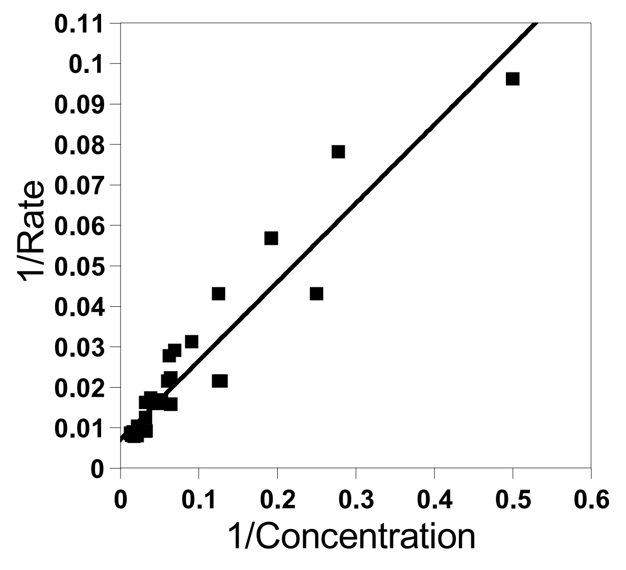


Figure 3.A.1 A Lineweaver-Burk plot of the data in Table 3.A.1

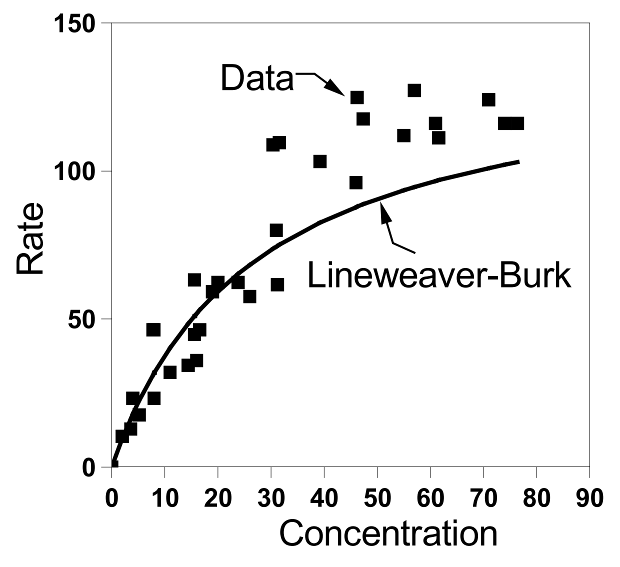


Figure 3.A.2 The Lineweaver-Burk fit of the data in Table 3.A.1

The Eadie-Hofstee plot

Rearranging equation (3.A.1):

$$r_p\left(1 + K_2[\mathrm{par}]\right) = k_1 K_2 [\mathrm{par}]$$

(3.A.4)

Further rearrangement yields:

$$\frac{r_p}{[\mathrm{par}]} = k_1 K_2 - \qquad K_2 r_p$$

(3.A.5)

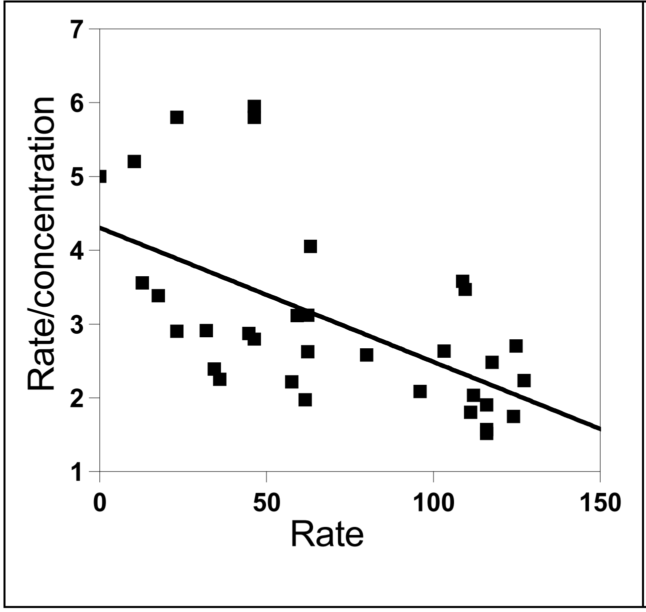


Figure 3.A.3 An Eadie-Hofstee plot of the data in Table 3.A.1

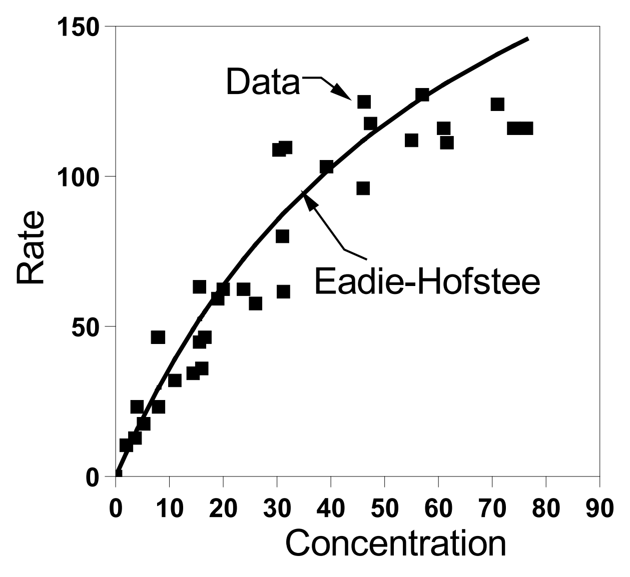


Figure 3.A.4 The Eadie-Hofstee fit of the data in Table 3.A.1

$$\frac{r_p}{[\text{par}]} = 4.18 - 0.0156 r_p$$

(3.A.6)

$$r^2 = 0.34$$

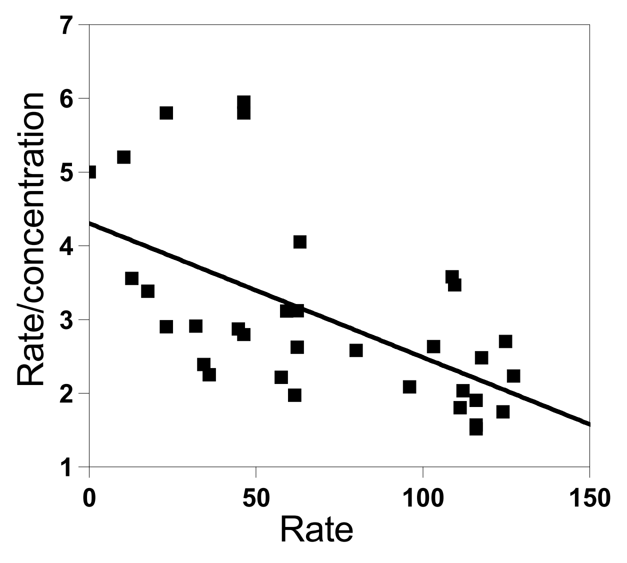


Figure 3.A.3 An Eadie-Hofstee plot of the data in Table 3.A.1

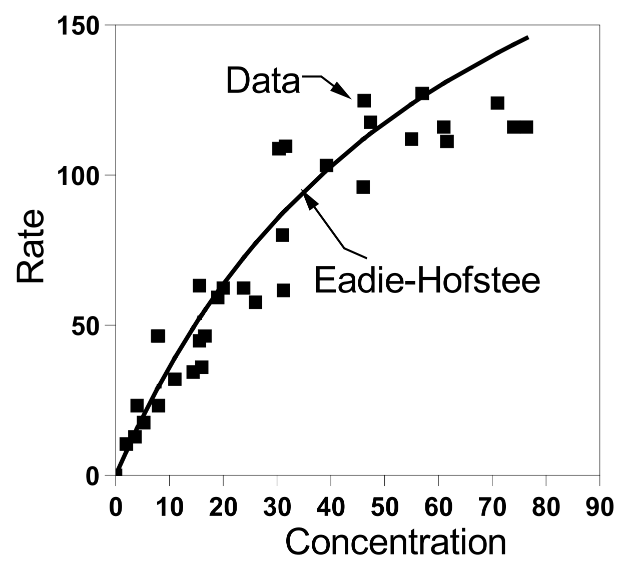


Figure 3.A.4 The Eadie-Hofstee fit of the data in Table 3.A.1

Eadie-Hofstee gives much lower r^2 but better fit to data!

The last way to fit the data is with a non-linear least squares.

The idea in nonlinear least squares is to use the solver function of a spreadsheet to calculate the best values of the coefficients based on some criterion. A common criterion is to minimize the total error, where the total error is defined by:

$$\text{Total Error} = \sum_{\text{Data}} \left[\text{abs}\left(r_p - \frac{k_1 K_2 [\text{par}]}{1 + K_2 [\text{par}]} \right) \right]^2$$

(3.A.7)

One often uses powers other than 2 to do the fitting.

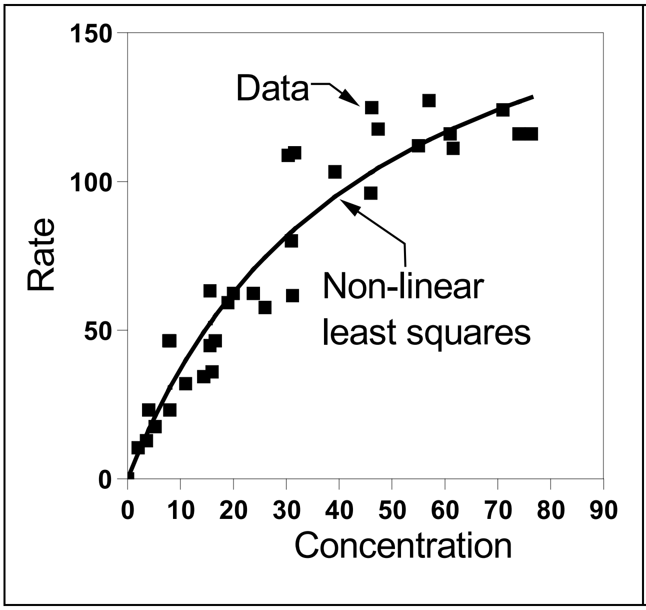


Figure 3.A.5 A nonlinear least squares fit to the data in Table 3.A.1

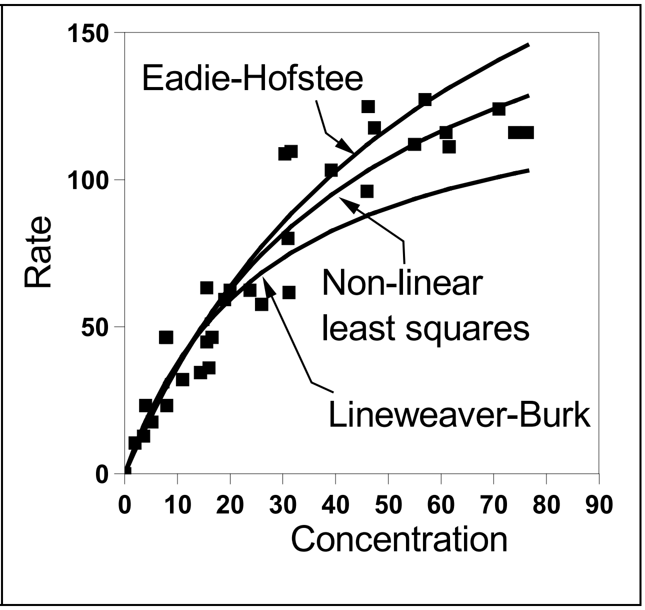


Figure 3.A.6 A comparison of the three fits to the data

Table 3.A.5 A comparison of the various fits to the data in Table 3.A.1

Method	k_1	K_2	Total error	R-squared
Lineweaver-Burk	139	0.0370	9643	0.910 (linear plot)
Eadie-Hofstee	267	0.0156	6809	0.344 (linear plot)
non-linear least squares	204	0.0221	4919	0.905 (non-linear)

Table 3.A.7 The values of R-squared calculated using the different methods

Method	R-squared from linear regression	R-squared from equation (2.B.9)	R-squared from equation (2.B.10)
Lineweaver-Burk	0.910	0.814	0.552
Eadie-Hofstee	0.344	0.869	0.516
nonlinear least squares	0.905	0.905	0.558

Example 3.B - Tests of Statistical Significance: Analysis of Variance

Table 3.B.1 Fits to the data in Example 3.A

Concentration	Experimental Rate	Calculated rate Non-linear least squares	Calculated rate Lineweaver-Burk	Calculated rate Eadie-Hofstee
0	0	0	0	0
2	10.4	8.65	9.6	8.10
3.6	12.8	15.06	16.38	14.24
4	23.2	16.60	17.69	15.73
5.2	17.6	21.07	22.49	20.10
7.8	46.4	30.05	31.21	29.06
8	32	30.71	31.83	29.72
8	34.4	30.71	31.83	29.72
		Continued		
Variance		164	230	321

Which model fits best? Is the difference statistically significant?

First let us see which model fits best. We do that by calculating the variance of the data and seeing which model has the lowest variance. The variance V_i is defined by

$$V_i = \frac{\sum\limits_{\text{po int s}} \left(\left(\text{experimental rate}\right) - \left(\text{calculated rate}\right)\right)^2}{\left(\text{number of samples}\right) - \left(\text{number of independent parameters in model}\right)}$$

(3.B.1)

substituting in equation (3.A.7) yields

$$V_i = \frac{\text{total error from Equ. 3.A.7}}{\text{number of samples} - \text{number of parameters}}$$

(3.B.2)

It is important to calculate the variance as shown in (3.B.1) and not for example the variance of one over the rate. In order to use the statistical tests below, one will have to assume that the error in the data follows what statisticians call a "χ^2 distribution." If you calculate the errors in the rate, the errors usually do follow a "χ^2 distribution".
I used Excel to calculate

1-FDIST (1.96, 30, 30) = 0.97

so I am 97% sure that the non-linear least squares fit better than the Lineweaver-Burk plot. Excel also has a FINV function that calculates F_{inverse} via

Analysis of batch reactor data

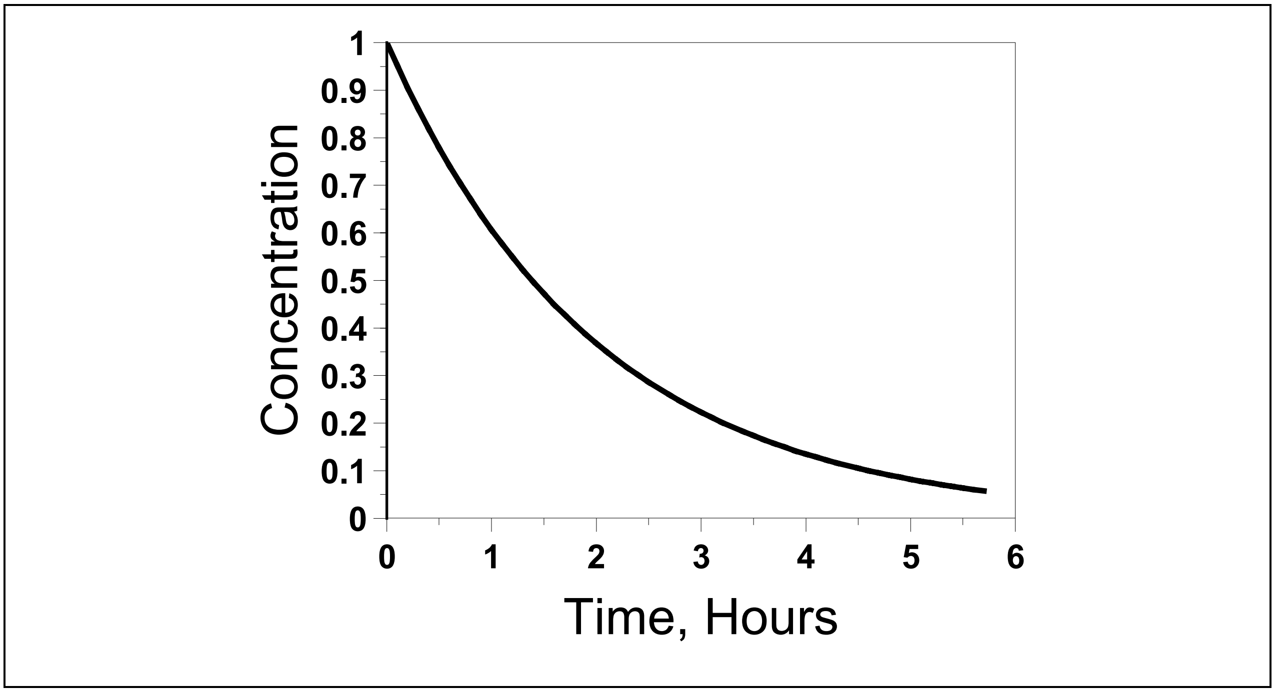
$$\int_{C_A^f}^{C_A^o} \frac{d\,C_A}{(-r_A)} = \tau$$

(3.31)

$$\boxed{\frac{1}{(n-1)k_n\left(C_A^o\right)^{n-1}}\left[\left(\frac{C_A^o}{C_A^f}\right)^{n-1} - 1\right] = \tau}$$

$$\boxed{\frac{1}{k_1}\mathrm{Ln}\left(\frac{C_A^o}{C_A^f}\right) = \tau}$$

Typical batch reactor data looks like



Two methods to analyze data
Essen's method
Van't Hoffs Method

Essen's method:

Essen's Method

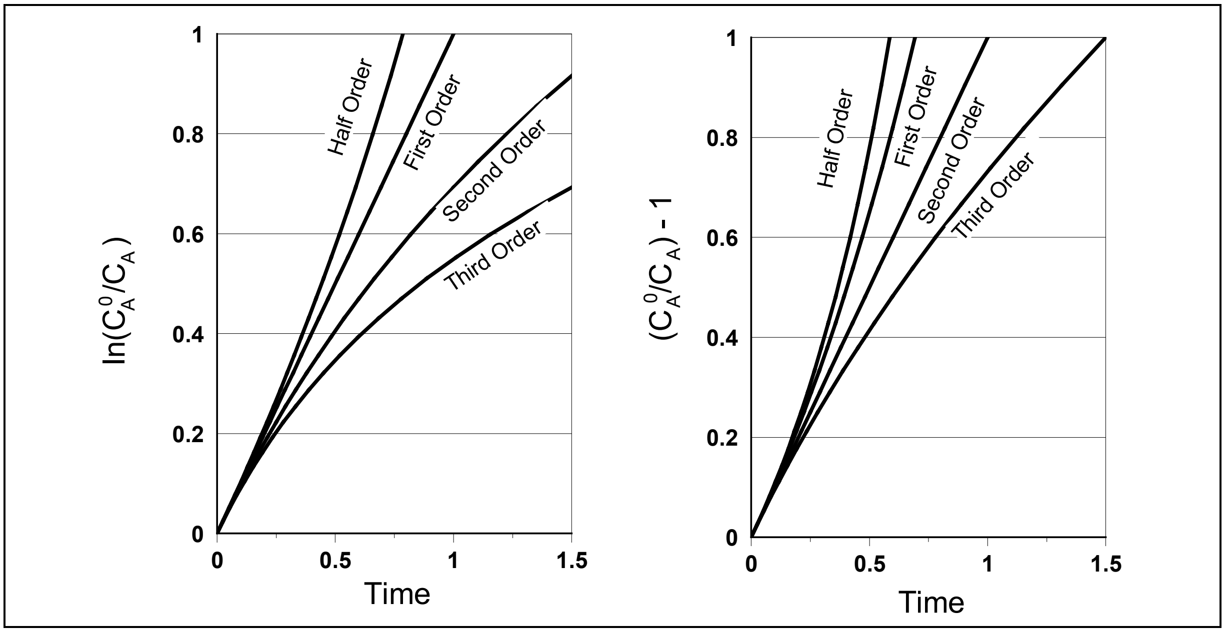


Figure 3.15 A replot of the data from Figure 3.14 as a function of ln $\left(C_A / C_A^0\right)$ and $\left(C_A^0 / C_{A.}\right)$.

Never works in practice

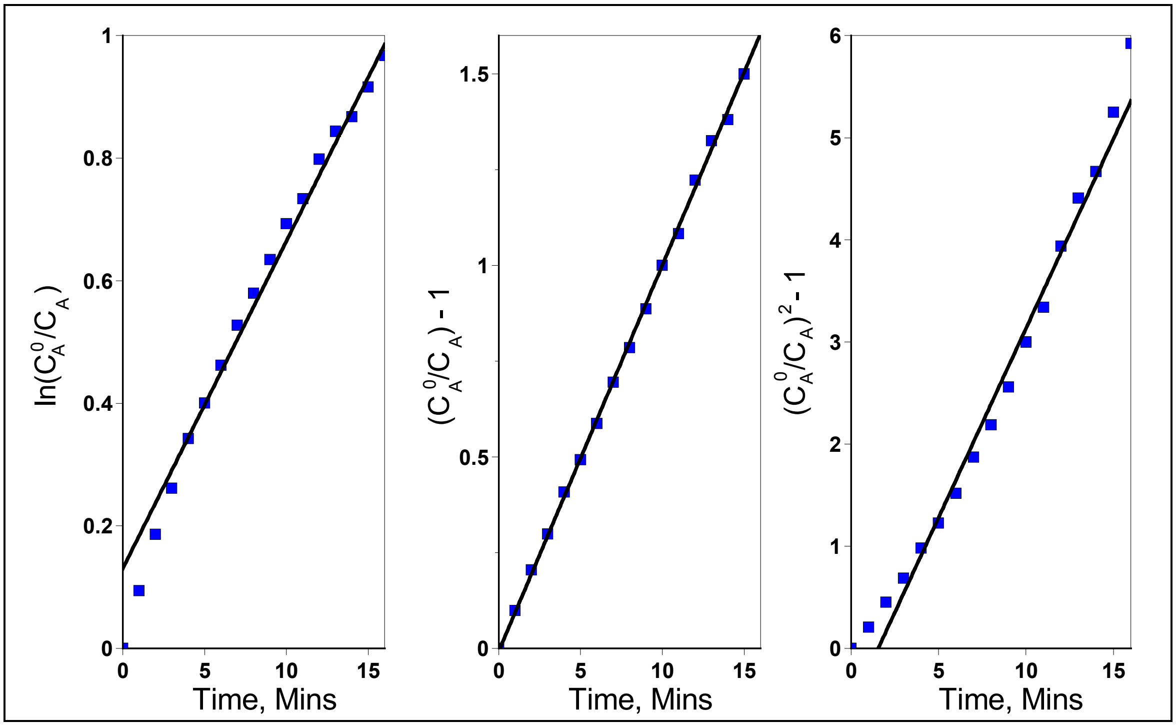


Figure 3.16 An Essen plot of the data in Table 3.5.

Van't hoff's method

Calculate k - is it constant

$$k_1 = \frac{1}{\tau} \mathrm{Ln}\left(\frac{C_A^0}{C_A}\right)$$

(3.51)

$$\boxed{\frac{1}{(n-1)k_n\left(C_A^0\right)^{n-1}}\left[\left(\frac{C_A^0}{C_A}\right)^{n-1} - 1\right] = \tau}$$

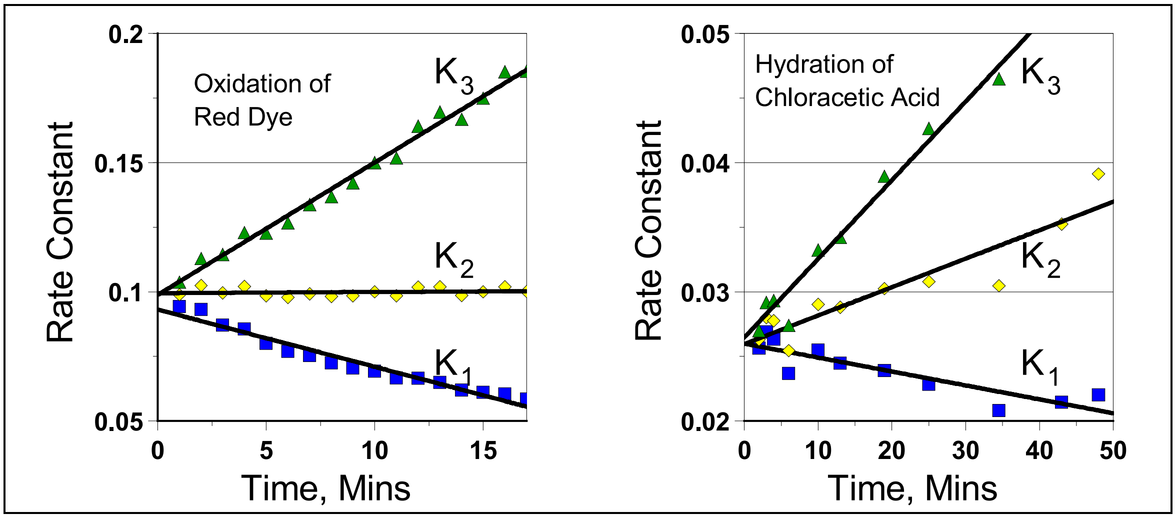


Figure 3.18 Van’t Hoff Plot of the data from Table 3.5 and Table 3.6

Another interesting thing in the chapter

Table 3.D.3 Module used to calculate k1, k2, k3, where k1, k2 and k3 are defined by equation (3.D.2)

```
Public Function kone(ca0, ca, tau) As Variant
kone = Log(ca0 / ca) / tau
End Function

Public Function ktwo(ca0, ca, tau) As Variant
ktwo = ((1# / ca) - (1# / ca0)) / tau
End Function

Public Function kthree(ca0, ca, tau) As Variant
kthree = ((1# / ca) ^ 2 - (1# / ca0) ^ 2) / tau
End Function
```

Table.1 Summary of key concepts.

Two methods to measure rates: Direct and Indirect

Direct	Indirect
High Accuracy Need many runs	Lower Accuracy Fewer experiments

Methods to analyze direct data

- Least squares
- Non-linear least squares

Non-linear least squares easier and more accurate

Methods to analyze indirect data

Essen

- construct plots of $\mathrm{Ln}\left(C_A^O / C_A\right), \left(C_A^O / C_A\right)^n - 1$

- see if linear

Van't Hoff

- calc k_1, k_2, k_3

- see if constant

Van't Hoff - easier and more accurate

Key equations for indirect data

$$N_A^0 \int_0^{X_A} \frac{dX_A}{V\left(-r_A\right)} = \tau \tag{3.26}$$

$$C_A^0 \int_0^{X_A} \frac{dX_A}{-r_A} = \tau \tag{3.28}$$

$$\int_{C_A^F}^{C_A^0} \frac{d\,C_A}{-\,r_A} = \tau \tag{3.31}$$

$$\frac{1}{k_1} \mathrm{Ln}\left(\frac{C_A^0}{C_A}\right) = \tau \tag{3.39}$$

$$\frac{1}{(n-1)k_n\left(C_A^0\right)^{n-1}}\left[\left(\frac{C_A^0}{C_A}\right)^{n-1} - 1\right] = \tau \tag{3.42}$$