

where  $P_T$  is the total pressure of the reactor,  $V$  is the volume in the reactor,  $N_T$  is the number of moles in the reactor,  $R$  is the gas law constant, and  $T$  is the temperature. At the start of the reaction

$$P_T^0 V = N_T^0 RT \quad (3.90)$$

where  $P_T^0$  is the initial pressure of the reactor and  $N_T^0$  is the total number of moles in the reactor at the start of the reactions. Dividing equation (3.89) by equation (3.90) and rearranging yields

$$P_T = P_T^0 \left( \frac{N_T}{N_T^0} \right) \quad (3.91)$$

Substituting  $N_T$  and  $N_T^0$  from the stoichiometric table into equation (3.91) and rearranging yields

$$\frac{P_T}{P_T^0} = 1 + \left( \frac{N_A^0}{N_T^0} \right) \left( \frac{\Delta \text{mol}}{a} \right) X_A \quad (3.92)$$

Therefore, if one knows the pressure in a vessel as a function of time, one can calculate the conversion as a function of time.

Figure 3.28 shows a plot of the pressure calculated from equation (3.92) as a function of conversion for various values of the  $\Delta \text{mol}$ . Notice that the pressure always varies linearly with conversion. The pressure goes up when  $\Delta \text{mol}$  is positive, while the pressure goes down when  $\Delta \text{mol}$  is negative. Consequently, whenever  $\Delta \text{mol}$  is nonzero, one can use the pressure to estimate the conversion.

Examples 3.B and 3.C illustrate the use of the stoichiometric table to calculate the conversion as a function of time.

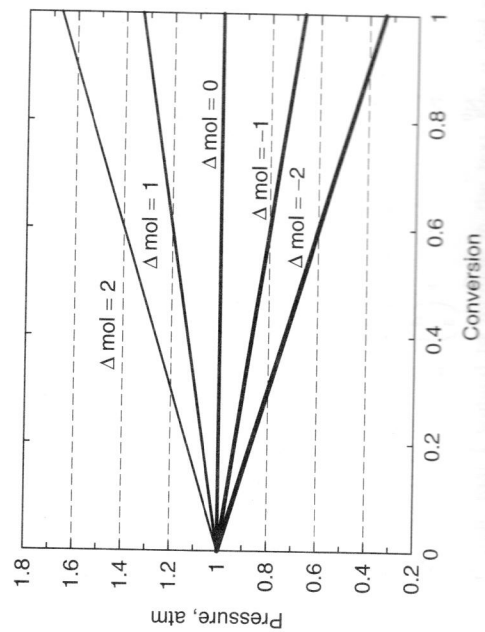


Figure 3.28 A plot of the pressure versus conversion calculated from equation (3.92) with  $N_A^0 = 1$  mol,  $N_T^0 = 3$  mol, and  $a = 1.0$ .

### 3.17 SOLVED EXAMPLES

**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 (Monod [1942]).

$$r_p = \frac{k_1 K_2 [\text{par}]}{1 + K_2 [\text{par}]} \quad (3.A.1)$$

where  $[\text{par}]$  is the paramecium concentration and  $k_1$  and  $K_2$  are constants.

**Solution** 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 nonlinear 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–Burke plots
- Eadie–Hofstee plots

In the Lineweaver–Burke method, one plots  $1/r$  against  $1/\text{concentration}$ . Rearranging equation (3.A.1) shows

$$\frac{1}{r_p} = \frac{1}{k_1 K_2 [\text{par}]} + \frac{1}{k_1} \quad (3.A.2)$$

Therefore, a plot of  $1/r_p$  versus  $1/[\text{par}]$  should be a straight line. The intercept should be  $\frac{1}{k_1}$ . The slope should be  $\frac{1}{k_1 K_2}$ . Once  $k_1$  is determined from the intercept,  $K_2$  can be

Table 3.A.1 The rate of paramecium reproduction as a function of the paramecium concentration

Paramecium concentration, $N/\text{cm}^3$	Rate, $N/\text{cm}^3\text{-hour}$	Paramecium concentration, $N/\text{cm}^3$	Rate, $N/\text{cm}^3\text{-hour}$
2	10.4	16	36
3.6	12.8	16.6	46.4
4	23.2	19	59.2
5.2	17.6	20	62.4
7.8	46.4	23.8	62.4
8	23.2	26	57.6
8	46.4	30.4	108.8
11	32	31	80
14.4	34.4	31.2	61.6
15.6	44.8	31.6	109.6
15.6	63.2	39.2	103.2

Source: Data of Meyers (1927).

determined from the slope. Figure 3.A.1 shows the plot. This is not a wonderful linear relationship, but such a result is typical.

Next, I want to calculate the rate constants using a least-squares procedure. Table 3.A.2 shows the formulas used to do the least-squares fit. I listed the concentration in column A and the rate data in column B. Column C is one over the concentration; column D is one over the rate. I then used the SLOPE, INTERCEPT and RSQ Functions in Excel to calculate the slope of the line.

Table 3.A.3 shows the numerical values in the plot. From the least-squares fit

$$\frac{1}{r_p} = \frac{0.194}{[\text{par}]} + 0.00711 \quad (3.A.3)$$

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

$$k_1 = \frac{1}{0.00711} = 140.5, \quad K_2 = \frac{1}{(0.194 * k_1)} = 0.037.$$

Figure 3.A.2 is a plot taking  $k_1 = 140.4$  and  $K_2 = 0.0366$ . The curve does not do a bad job of fitting the data, although there is a systematic error at high concentrations. This is typical. One can even get cases where the Lineweaver-Burke plot misses the trends in the data.

We got the systematic error because we fit to  $1/r_p$ . A plot of  $1/r_p$  gives greater weight to data taken at small concentrations, and that is usually where the data are the least accurate.

The Eadie-Hofstee plot avoids the difficulty at low concentrations by instead finding a way to linearize the data without calculating  $1/r_p$ .

Rearranging equation (3.A.1), we have

$$r_p(1 + K_2[\text{par}]) = k_1 K_2 [\text{par}] \quad (3.A.4)$$

Further rearrangement yields

$$\frac{r_p}{[\text{par}]} = k_1 K_2 - K_2 r_p \quad (3.A.5)$$

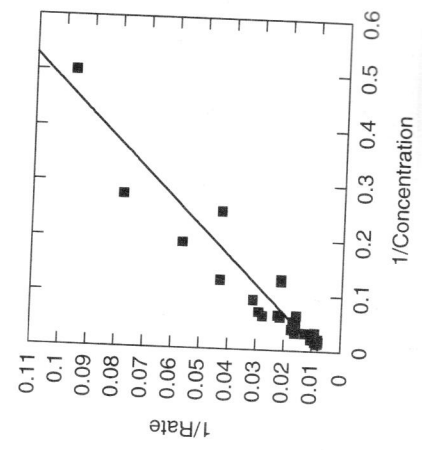


Figure 3.A.1 A Lineweaver-Burke plot of the data in Table 3.A.1.

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:D37, C6:C37)		2
02		K_2	=1/C1/D1	=INTERCEPT(D6:D37, C6:C37)		=SUM(F5:F37)
03				=RSQ(D6:D37, C6:C37)		
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)
06	2	10.4	=1/A6	=1/B6	=C\$1*C\$2*\$A6/(1+C\$2*\$A6)	=ABS(E6-\$B6)
07	3.6	12.8	=1/A7	=1/B7	=C\$1*C\$2*\$A7/(1+C\$2*\$A7)	=ABS(E7-\$B7)
08	4	23.2	=1/A8	=1/B8	=C\$1*C\$2*\$A8/(1+C\$2*\$A8)	=ABS(E8-\$B8)
09	5.2	17.6	=1/A9	=1/B9	=C\$1*C\$2*\$A9/(1+C\$2*\$A9)	=ABS(E9-\$B9)
10	7.8	46.4	=1/A10	=1/B10	=C\$1*C\$2*\$A10/(1+C\$2*\$A10)	=ABS(E10-\$B10)
11	8	23.2	=1/A11	=1/B11	=C\$1*C\$2*\$A11/(1+C\$2*\$A11)	=ABS(E11-\$B11)
12	8	46.4	=1/A12	=1/B12	=C\$1*C\$2*\$A12/(1+C\$2*\$A12)	=ABS(E12-\$B12)
13	11	32	=1/A13	=1/B13	=C\$1*C\$2*\$A13/(1+C\$2*\$A13)	=ABS(E13-\$B13)

Table 3.A.3 The numerical values in the spreadsheet for the Lineweaver-Burke plot

	A	B	C	D	E	F
01		k 1	140.5	0.194		2.000
02		K 2	0.037	0.00711		9454.2
03				0.901		
04	conc	rate	1/conc	1/rate	rate	error
05	0.000	0.000	0.000	0.000	0.000	0.000
06	2.000	10.400	0.500	0.096	9.58	0.664
07	3.600	12.800	0.278	0.078	16.35	12.67
08	4.000	23.200	0.250	0.043	17.94	27.62
09	5.200	17.600	0.192	0.057	22.47	23.69
10	7.800	46.400	0.128	0.022	31.20	230.87
11	8.000	23.200	0.125	0.043	31.82	74.37
12	8.000	46.400	0.125	0.022	31.82	212.45
13	11.000	32.000	0.091	0.031	40.33	69.42

Note! These numbers are from Excel 98. Excel 95 gives slightly different results.

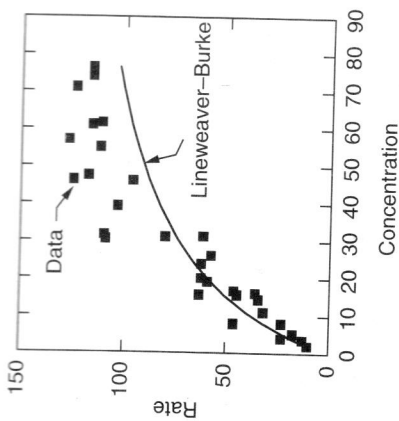


Figure 3.A.2 The Lineweaver-Burke fit of the data in Table 3.A.1.

Therefore a plot of  $r_p/[par]$  versus  $r_p$  should yield a straight line. Figure 3.A.3 shows the plot. In this case, the line does not fit the data very well. I did a least-squares fit through the data using a spreadsheet like that in Table 3.A.3. The results showed

$$\frac{r_p}{[par]} = 4.21 - 0.0171r_p \quad (3.A.6)$$

Comparing equation (3.A.6) and (3.A.5) shows  $K_2 = 0.0171$ ,  $k_1 = 4.20/0.0171 = 246$ . Figure 3.A.4 shows how well the data actually fit's the line. Notice that there is still an error at high concentration. In this case the predicted rate is slightly too high. When you divide by  $[par]$ , you give lower weight to the high concentration points. The result is that there are still errors. Still, the Eadie-Hofstee method fits better than the Lineweaver-Burke fit, even though  $R^2$  is 0.34 in Figure 3.A.3 while  $R^2$  is 0.90 in Figure 3.A.1. The last way to fit the data are with a nonlinear 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

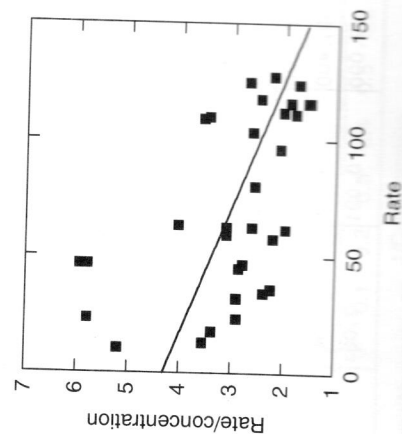


Figure 3.A.3 An Eadie-Hofstee plot of the data in Table 3.A.1.

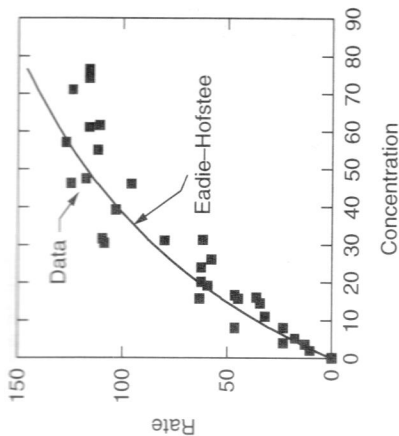


Figure 3.A.4 The Eadie-Hofstee fit of the data in Table 3.A.1.

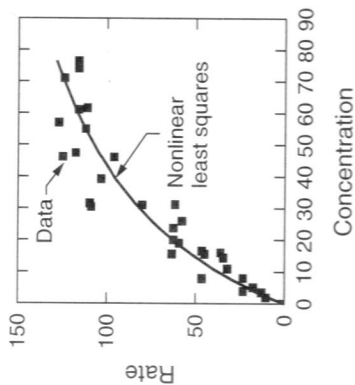


Figure 3.A.5 A nonlinear least-squares fit to the data in Table 3.A.1.

is to minimize the total error, where the total error is defined by

$$\text{Total error} = \sum_{\text{data}} \{(\text{abs}[(\text{measured rate}) - (\text{calculated rate})])^2\}$$

where abs is absolute value. For our example, this becomes

$$\text{Total error} = \sum_{\text{data}} \left[ \text{abs} \left( r_p - \frac{k_1 K_2 [par]}{1 + K_2 [par]} \right) \right]^2 \quad (3.A.7)$$

One often uses powers other than 2 to do the fitting. Table 3.A.4 shows a spreadsheet for the fitting. The spreadsheet calculates the rate in column C. The error is calculated in column D. Element \$D\$2 is the total error. I then used the solver function in Microsoft

Table 3.A.4 Part of the spreadsheet used to calculate values of  $k_1$  and  $K_2$  to minimize the total error

A	B	C	D
01	$k_1=204.3$ (Calculated by solver)		
02	$K_2=0.0221$ (Calculated by solver)		=SUM(D4:D50)
03	conc	rate	error
04	0	= $k_1 * K_2^2 * A4 / (1 + K_2^2 * A4)$	=ABS(C4 - \$B4) * \$D\$1
05	10.4	= $k_1 * K_2^2 * A5 / (1 + K_2^2 * A5)$	=ABS(C5 - \$B5) * \$D\$1
06	12.8	= $k_1 * K_2^2 * A6 / (1 + K_2^2 * A6)$	=ABS(C6 - \$B6) * \$D\$1
07	23.2	= $k_1 * K_2^2 * A7 / (1 + K_2^2 * A7)$	=ABS(C7 - \$B7) * \$D\$1
08	17.6	= $k_1 * K_2^2 * A8 / (1 + K_2^2 * A8)$	=ABS(C8 - \$B8) * \$D\$1
09	46.4	= $k_1 * K_2^2 * A9 / (1 + K_2^2 * A9)$	=ABS(C9 - \$B9) * \$D\$1
10	23.2	= $k_1 * K_2^2 * A10 / (1 + K_2^2 * A10)$	=ABS(C10 - \$B10) * \$D\$1
11	46.4	= $k_1 * K_2^2 * A11 / (1 + K_2^2 * A11)$	=ABS(C11 - \$B11) * \$D\$1
12	32	= $k_1 * K_2^2 * A12 / (1 + K_2^2 * A12)$	=ABS(C12 - \$B12) * \$D\$1
13	34.4	= $k_1 * K_2^2 * A13 / (1 + K_2^2 * A13)$	=ABS(C13 - \$B13) * \$D\$1
14	15.6	= $k_1 * K_2^2 * A14 / (1 + K_2^2 * A14)$	=ABS(C14 - \$B14) * \$D\$1
15	15.6	= $k_1 * K_2^2 * A15 / (1 + K_2^2 * A15)$	=ABS(C15 - \$B15) * \$D\$1
16	36	= $k_1 * K_2^2 * A16 / (1 + K_2^2 * A16)$	=ABS(C16 - \$B16) * \$D\$1
17	16.6	= $k_1 * K_2^2 * A17 / (1 + K_2^2 * A17)$	=ABS(C17 - \$B17) * \$D\$1

Excel<sup>1</sup> to minimize \$D\$2 by varying  $k_1$  and  $K_2$ . The result is that  $k_1=204.3$  and  $K_2=0.0221$ .

Next, it is useful to compare the numerical values of the parameters calculated via the various methods. Figure 3.A.6 shows the fits to the data, and all three lines are reasonable. Still, the Lineweaver-Burke method is too low at high concentrations while the Eadie-Hofstee method is too high. The nonlinear least-squares method gives the best balance in the fit.

Next, it is useful to compare the parameters calculated via the various methods. Notice that the three methods give  $k_1$  values between 140 and 246 and  $K_2$  values between 0.0171 and 0.0366. Yet all three curves fit the data. This example illustrates the difficulty in fitting kinetic data in that when you have lots of parameters, you can use different values of the parameters and still fit the data pretty well.

Well, which fits best? That is not an easy question. In the literature, people often assess the "goodness of fit" by looking at the  $R^2$  values. They are given in Table 3.A.5. Table 3.A.5 also shows the errors created by each method. Where the total error is defined by equation (3.A.7). The Lineweaver-Burke plot has an excellent value of  $R^2$  as measured

<sup>1</sup> One needs to be very careful with the solver programs in Excel. In my experience, the solver programs often goes to a local minimum in the error rather than a global minimum. Therefore it is important to start the algorithm at several sets of initial guesses for  $k_1$  and  $K_2$ , minimize and then take the best answer. There are also global minimizers, such as Sahinidi's BARON program. They are the best chance when you want to be sure you minimize the error.

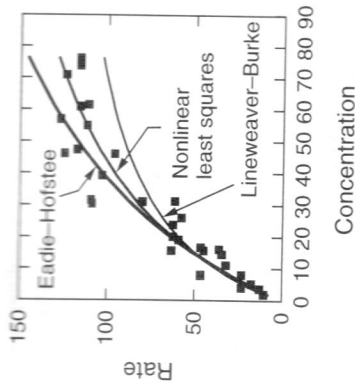


Figure 3.A.6 A comparison of the three fits to the data.

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	$R^2$
Lineweaver-Burke	140	0.0366	9454	0.901 (linear plot)
Eadie-Hofstee	246	0.0171	5648	0.344 (linear plot)
Nonlinear least-squares	204	0.0221	4919	0.905 (nonlinear)

by the linear regression, but the highest total error. The Eadie-Hofstee method has the worst  $R^2$ , but a lesser total error. The nonlinear least-squares method has the lowest total error but a value of  $R^2$  similar to that for Lineweaver-Burke.

My own view is that one has to be very careful in using  $R^2$  as a measure of the goodness of fit. In linear regression,  $R^2$  measures the uncertainty in the slope of the line. However, it does not give you any uncertainty in the intercept, or the relative importance of the slope and intercept in fitting your data. If you fit some data  $Y$  to a function  $f(x)$ , then  $R^2$  is defined by

$$R^2 = 1 - \frac{\sum_{\text{data}} [\text{abs}(Y - f(x))]^2}{\sum_{\text{data}} [\text{abs}(Y - \bar{Y})]^2} \quad (3.A.8)$$

where  $\bar{Y}$  is the average value of  $Y$ . When you use a least-squares technique, you define a function that you are fitting to a variable  $Y$ . According to how you define  $Y$ , you can get wildly different values of  $R^2$ . The Lineweaver-Burke, Eadie-Hofstee, and nonlinear least-squares methods define  $Y$  differently, as indicated in Table 3.A.6. The net result is that the values of  $R^2$  are not comparable.

In the homework set, we have an example where we fit two different models to a single data set. The first model fits the data to two significant figures even though  $R^2$  is  $10^{-5}$ . The second model does not fit the data at all. (It sometimes gets the wrong sign.) Yet,  $R^2$  is 0.75. This example clearly illustrates the ideas that  $R^2$  does not tell you how well a given model fits your data.

**Table 3.A.6** The values of Y and f(x) used to calculate R<sup>2</sup> using the different methods

Method	Y	f(x)
Lineweaver-Burke	$\frac{1}{r_p}$	$\frac{1 + K_2[\text{par}]}{k_1 K_2[\text{par}]}$
Eadie-Hofstee	$\frac{r_p}{[\text{par}]}$	$k_1 K_2 - K_2 r_p$
Nonlinear least-squares	$r_p$	$\frac{k_1 K_2 [\text{par}]}{1 + K_2 [\text{par}]}$

One way around the difficulty is to define a uniform value of R<sup>2</sup>. For example, two definitions that we can use are

$$R^2 = 1 - \frac{\sum_{\text{data}} \left[ \text{abs} \left( r_p - \frac{k_1 K_2 [\text{par}]}{1 + K_2 [\text{par}]} \right) \right]^2}{\sum_{\text{data}} [\text{abs}(r_p - \bar{r}_p)]^2} \tag{3.A.9}$$

where  $\bar{r}_p$  is the average value of the rate.

$$R^2 = 1 - \frac{\sum_{\text{data}} \left[ \text{abs} \left( \frac{r_p}{[\text{par}]} - \frac{k_1 K_2}{1 + K_2 [\text{par}]} \right) \right]^2}{\sum_{\text{data}} \left[ \text{abs} \left( \frac{r_p}{[\text{par}]} - \left( \frac{r_p}{[\text{par}]} \right)_{\text{av}} \right) \right]^2} \tag{3.A.10}$$

where  $(r_p/[\text{par}])_{\text{av}}$  is the average value of  $(r_p/[\text{par}])$ . Table 3.A.7 shows the values. Notice that the different definitions of R<sup>2</sup> give wildly different values of R<sup>2</sup>.

In the literature, people often use R<sup>2</sup> as a measure of the goodness of fit and to distinguish between various models. One has to be very careful when doing that. After all, Table 3.A.7 shows that you can calculate wildly different values of R<sup>2</sup> according to how you do the calculations. Still, in the literature people often ignore these complexities and naively use the R<sup>2</sup> values that come out of their linear regression to assess how well their model fits the data. Readers can judge for themselves whether that is a valid approach.

**Example 3.B Tests of Statistical Significance: Analysis of Variance** The next question is how can one really tell if one model fits a given data set better than another.

**Table 3.A.7** The values of R<sup>2</sup> calculated using the different methods

Method	R <sup>2</sup> from		R <sup>2</sup> from equation (2.B.10)
	linear regression	equation (2.B.9)	
Lineweaver-Burke	0.901	0.818	0.552
Eadie-Hofstee	0.344	0.890	0.525
Nonlinear least-squares	0.905	0.905	0.558

The objective of this example is to provide an objective test. Let's consider the example in Example 3.A (see Table 3.B.1).

Which model fits best? Is the difference statistically significant?

**Solution** 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

$$V_i = \frac{\sum_{\text{points}} ((\text{experimental rate}) - (\text{calculated rate}))^2}{(\text{number of samples}) - (\text{number of independent parameters in model})} \tag{3.B.1}$$

Substituting in equation (3.A.7) yields

$$V_i = \frac{\text{total error from equation 3.A.7}}{\text{number of samples} - \text{number of parameters}} \tag{3.B.2}$$

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 *chi-square* ( $\chi^2$ ) distribution. If you calculate the errors in the rate, the errors usually do follow a  $\chi^2$  distribution. However, the errors in one over rate *do not* follow a  $\chi^2$  distribution. As a result, although the statistical measures below are meaningful for variances calculated via equation (3.B.1), they are not meaningful for variances in one over the rate.

The variances are easily calculated from the total errors in Table 3.A.5. For example, in the nonlinear least-squares case

$$V_i = \frac{4919}{(32 \text{ points} - 2 \text{ parameters})} = 164 \tag{3.B.3}$$

Similarly, for Eadie-Hofstee

$$V_i = \frac{5648}{32 - 2} = 188 \tag{3.B.4}$$

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

Concentration	Experimental Rate	Calculated Rate		
		Nonlinear Least Squares	Lineweaver-Burke	Eadie-Hofstee
0	0	0	0	0
2	10.4	8.65	9.6	8.14
3.6	12.8	15.06	16.36	14.26
4	23.2	16.60	17.94	15.75
5.2	17.6	21.07	22.46	20.08
7.8	46.4	30.05	31.20	28.95
8	32	30.71	31.82	29.60
8	34.4	30.71	31.82	29.60
Variance		164	164	188

$$V_1 = \frac{9454}{32 - 2} = 315 \quad (3.B.5)$$

So the nonlinear least-squares method fits the data best.

The next question is whether the difference is statistically significant. This is important, because one model could fit better, but the difference between the models could be within the noise in the data. Statisticians are still developing methods to test whether one model is better than another. It is easy to test what are called "nested models": two models that are the same except that one has one extra parameter. However, independent models are much harder to test. The Cox algorithm can do the testing rigorously. One can also do a test using a Bayesian maximum-likelihood or minimum-entropy algorithm. Both are beyond the scope of this book.

In this problem we will provide an approximation that is not mathematically rigorous but has the advantage that it can be used for practical calculations. The method is based on a statistical test called the *F test*. The idea in the *F test* is to compute  $F_{\text{inverse}}$  given by

$$F_{\text{inverse}} = \frac{\text{variance in weaker model}}{\text{variance in better model}} \quad (3.B.6)$$

So, if we want to compare the Lineweaver-Burke and nonlinear least-squares methods, we calculate

$$F_{\text{inverse}} = \frac{315}{164} = 1.91 \quad (3.B.7)$$

Statistically, if the two variances are independent and the value of  $F_{\text{inverse}}$  is large enough, we can say that the difference is statistically significant. Table 3.B.2 gives values of  $F_{\text{inverse}}$ . In the table,  $F_{\text{inverse}}$  is listed as a function of *nf* given by

$$nf = \text{number of data points} - \text{parameters in the model} \quad (3.B.8)$$

If you want to see if one model fits rate data better than another does, you should always do an *F test* to see if the difference between two models is statistically significant.

I want to say clearly that the *F test* is an approximation. It assumes that the two variances are independent, which is clearly not true. Still, it does give useful information even though the *F test* cannot be rigorously applied to this case.

To read Table 3.B.2, if *nf* is 30, then  $F_{\text{inverse}}$  must be 1.84 to have 95% confidence that one model is better than another and 2.39 to have 99% confidence that one model is better than another. We are between 95 and 99%, so we can say that we are between 95 and 99% and are certain that the nonlinear least-squares model fits the data better than does the Lineweaver-Burke model.

One can calculate a more accurate value for the confidence using the *FDIST* function in Excel. *FDIST* calculates the probability that a given value of  $F_{\text{inverse}}$  occurs by chance. So,  $1 - \text{FDIST}$  is the probability that it occurred by other than chance.

$$\% \text{confidence} = 1 - \text{FDIST}(F_{\text{inverse}}, nf \text{ for better model}, nf \text{ for worse model}) \quad (3.B.9)$$

I used Excel to calculate

$$1 - \text{FDIST}(1.91, 30, 30) = 0.96$$

**Table 3.B.2** Values of  $F_{\text{inverse}}$  as a function of *nf* when both models have the same value of *nf*

nf	Significance Level		
	90%	95%	99.5%
1	39.86	161.5	4052
2	9.0	19	99
3	5.39	9.28	29.46
4	4.11	6.39	15.98
5	3.45	5.05	10.97
6	3.05	4.28	8.42
7	2.78	3.79	6.99
8	2.59	3.44	6.03
9	2.44	3.18	5.35
10	2.32	2.98	4.85
20	1.79	2.12	2.84
30	1.61	1.84	2.39
40	1.51	1.69	2.11
50	1.44	1.60	1.95
			2.1

So I am 96% sure that the nonlinear least-squares fit better than the Lineweaver-Burke plot. Excel also has a *FINV* function that calculates  $F_{\text{inverse}}$  via

$$F_{\text{inverse}} = \text{FINV}(1 - \% \text{significance}, nf \text{ for better model}, nf \text{ for worse model})$$

So you do not have to use Table 3.B.2 to calculate  $F_{\text{inverse}}$ .

In the literature, people often use  $R^2$  values to see which model is better. I do not believe that is meaningful. There are other methods to compare models (see Bevington and Robinson, 1992).

**Example 3.C Fitting the Data in Example 3.A with Another Kinetic Model** The objective of this problem is to illustrate the difficulty in using kinetic data to distinguish between rate data. In order to illustrate the ideas, we will fit the data in Example 3.A with the model:

$$r_p = \frac{k_1 K_2 [\text{par}]}{1 + K_2 [\text{par}]^{1.5}} \quad (3.C.1)$$

and see if the difference is statistically significant.

**Solution** In Table 3.C.1, column A is the concentration, column B is the experimental rate data, Column C is the rate calculated from equation (3.C.1), whereas column D is the square of the difference between the calculated rate and the measured rate. I then used the solver function to minimize cell D2, by varying cells C1 and C2.

The spreadsheet is the same as in Example 3.A (see Table 3.C.1). When you solve the equation, you find that the total error is 4576, compared to 4919 with equation (3.A.1). Therefore, equation (3.C.1) fits the data slightly better than does equation (3.A.1).

Next, we will consider whether the difference is statistically significant. Again we can do an *F test*.

Table 3.C.1 Part of the spreadsheet used to calculate values of  $k_1$  and  $k_2$  to minimize the total error

A	B	C	D
01	$k_1=1944$	(Calculated by solver)	2
02	$K_2=0.00188$	(Calculated by solver)	=SUM(D4:D50)
03	conc	rate	error
04	0	equation 3.C.1*1.5	
05	2	$=k_1 * K_2 * A^4 / (1 + K_2 * A^4 * 1.5)$	$=ABS(C4 - \$B4) * \$D\$1$
06	3	$=k_1 * K_2 * A^5 / (1 + K_2 * A^5 * 1.5)$	$=ABS(C5 - \$B5) * \$D\$1$
07	4	$=k_1 * K_2 * A^6 / (1 + K_2 * A^6 * 1.5)$	$=ABS(C6 - \$B6) * \$D\$1$
08	5	$=k_1 * K_2 * A^7 / (1 + K_2 * A^7 * 1.5)$	$=ABS(C7 - \$B7) * \$D\$1$
09	7	$=k_1 * K_2 * A^8 / (1 + K_2 * A^8 * 1.5)$	$=ABS(C8 - \$B8) * \$D\$1$
10	8	$=k_1 * K_2 * A^9 / (1 + K_2 * A^9 * 1.5)$	$=ABS(C9 - \$B9) * \$D\$1$
11	8	$=k_1 * K_2 * A^{10} / (1 + K_2 * A^{10} * 1.5)$	$=ABS(C10 - \$B10) * \$D\$1$
12	11	$=k_1 * K_2 * A^{11} / (1 + K_2 * A^{11} * 1.5)$	$=ABS(C11 - \$B11) * \$D\$1$
13	14	$=k_1 * K_2 * A^{12} / (1 + K_2 * A^{12} * 1.5)$	$=ABS(C12 - \$B12) * \$D\$1$
14	15	$=k_1 * K_2 * A^{13} / (1 + K_2 * A^{13} * 1.5)$	$=ABS(C13 - \$B13) * \$D\$1$
15	15	$=k_1 * K_2 * A^{14} / (1 + K_2 * A^{14} * 1.5)$	$=ABS(C14 - \$B14) * \$D\$1$
16	16	$=k_1 * K_2 * A^{15} / (1 + K_2 * A^{15} * 1.5)$	$=ABS(C15 - \$B15) * \$D\$1$
17	16	$=k_1 * K_2 * A^{16} / (1 + K_2 * A^{16} * 1.5)$	$=ABS(C16 - \$B16) * \$D\$1$
18	16	$=k_1 * K_2 * A^{17} / (1 + K_2 * A^{17} * 1.5)$	$=ABS(C17 - \$B17) * \$D\$1$

$V_{3.A.1}$ , the variance of equation (3.A.1), is

$$V_{3.A.1} = \frac{4919}{32 \text{ points} - 2 \text{ parameters}} = 164$$

$V_{3.C.1}$ , the variance of equation (3.C.1), is

$$V_{3.C.1} = \frac{4576}{32 \text{ points} - 2 \text{ parameters}} = 152$$

The ratio of the variances is

$$F_{\text{inverse}} = \frac{164}{152} = 1.07$$

The probability that equation (3.C.1) is better than (3.A.1) is given by equation (3.B.8). Plugging in the numbers yields

$$\text{Probability} = 1 - \text{FDIST}(1.07, 30, 30) = 0.58$$

So there is a 58% chance that equation (3.C.1) fits better than does (3.A.1). Conversely, there is a 42% chance that equation (3.A.1) fits better than does equation (3.C.1).

Statisticians usually say that one needs a 95–99% chance to say that a difference is statistically significant. Here we see only a 58 : 42 chance. Consequently, we can say that

equations (3.A.1) and (3.C.1) both fit the data to within the error bars. This is important because people often say that one model fits data better than another. Often, however, multiple models are within the error bars in the data.

**Example 3.D Analysis of the data in Table 3.5** Use Essen's method, Van't Hoff's method, and Powell's method to analyze the data in Table 3.5.

**Solution**

**Essen's Method** According to equations (3.38) and (3.40)

$$\frac{1}{k_1} \ln \left( \frac{C_0}{C_A} \right) = \tau \tag{3.38}$$

$$\frac{1}{(n-1)k_n(C_0/C_A)^{n-1}} \left[ \left( \frac{C_0}{C_A} \right)^{n-1} - 1 \right] = \tau \tag{3.40}$$

First, let's start with Essen's method. According to Essen's method, one should make plots of  $\ln(C_0/C_A)$ ,  $(C_0/C_A) - 1$ ,  $(C_0/C_A)^2 - 1$  and see which plot is the most linear. I programmed an Excel spreadsheet to do the calculations.

Table 3.D.1 shows the formulas in the spreadsheet to do the calculations. Column A in the spreadsheet is the time, column B is concentration, column C is  $\ln(C_0/C_A)$ , column D is  $(C_0/C_A) - 1$ , and column E is  $(C_0/C_A)^2 - 1$ . Cell B6 is the concentration at time = 1. =LN(1/B6) computes  $\ln(C_0/C_A)$  at time = 1 with  $C_0 = 1$ . The regression statements at the bottom of the table compute the slope, the intercept, and  $\rho$  for a least-squares fit to the data.

Table 3.D.2 shows the numerical values for the plots. The regression coefficients are particularly interesting. Notice that the regression coefficients are always above 0.98, Plots of the data are given in Figure 3.18. Notice that all three lines fit the data reasonably well, which means that we could not distinguish between the various orders with an Essen plot. If we had much more data, going to above 90% conversion, we would be able to distinguish between the curves. However, there is no reason to do additional experiments since Van't Hoff's method allows one to distinguish between zero-, first-, and second-order kinetics using the existing data.

**Van't Hoff's Method** In Van't Hoff's method, one calculates  $k_1$ ,  $k_2$ , and  $k_3$  from

$$k_1 = \frac{1}{\tau} \ln \left( \frac{C_0}{C_A} \right) \tag{3.51}$$

$$k_n = \frac{1}{n^{(n-1)\tau}(C_0/C_A)^{n-1}} \left[ \left( \frac{C_0}{C_A} \right)^{n-1} - 1 \right] \tag{3.52}$$

When  $n \neq 1$ , I find it easier to plot a new function KN defined by

$$\text{KN} = k_n n^{n-1} (C_0/C_A)^{n-1} \tag{3.D.2}$$

Table 3.D.1 Formulas for the spreadsheet for Essen's method

A	B	C	D	E
Essen's Method				
time	conc	first	second	third
0		$\ln(\text{CaO}/\text{Ca})$	$(\text{CaO}/\text{Ca})-1$	$=(\text{CaO}/\text{Ca})^2-1$
1	0	$=\text{LN}(1/\text{B5})$	$=(1/\text{B5})-1$	$=(1/\text{B5})^2-1$
2	0.91	$=\text{LN}(1/\text{B6})$	$=(1/\text{B6})-1$	$=(1/\text{B6})^2-1$
3	0.83	$=\text{LN}(1/\text{B7})$	$=(1/\text{B7})-1$	$=(1/\text{B7})^2-1$
4	0.77	$=\text{LN}(1/\text{B8})$	$=(1/\text{B8})-1$	$=(1/\text{B8})^2-1$
5	0.71	$=\text{LN}(1/\text{B9})$	$=(1/\text{B9})-1$	$=(1/\text{B9})^2-1$
6	0.67	$=\text{LN}(1/\text{B10})$	$=(1/\text{B10})-1$	$=(1/\text{B10})^2-1$
7	0.63	$=\text{LN}(1/\text{B11})$	$=(1/\text{B11})-1$	$=(1/\text{B11})^2-1$
8	0.59	$=\text{LN}(1/\text{B12})$	$=(1/\text{B12})-1$	$=(1/\text{B12})^2-1$
9	0.56	$=\text{LN}(1/\text{B13})$	$=(1/\text{B13})-1$	$=(1/\text{B13})^2-1$
10	0.53	$=\text{LN}(1/\text{B14})$	$=(1/\text{B14})-1$	$=(1/\text{B14})^2-1$
11	0.5	$=\text{LN}(1/\text{B15})$	$=(1/\text{B15})-1$	$=(1/\text{B15})^2-1$
12	0.48	$=\text{LN}(1/\text{B16})$	$=(1/\text{B16})-1$	$=(1/\text{B16})^2-1$
13	0.45	$=\text{LN}(1/\text{B17})$	$=(1/\text{B17})-1$	$=(1/\text{B17})^2-1$
14	0.43	$=\text{LN}(1/\text{B18})$	$=(1/\text{B18})-1$	$=(1/\text{B18})^2-1$
15	0.42	$=\text{LN}(1/\text{B19})$	$=(1/\text{B19})-1$	$=(1/\text{B19})^2-1$
16	0.4	$=\text{LN}(1/\text{B20})$	$=(1/\text{B20})-1$	$=(1/\text{B20})^2-1$
17	0.38	$=\text{LN}(1/\text{B21})$	$=(1/\text{B21})-1$	$=(1/\text{B21})^2-1$
18	0.37	$=\text{LN}(1/\text{B22})$	$=(1/\text{B22})-1$	$=(1/\text{B22})^2-1$
Intercept	pt	$=\text{Intercept}$ $(\$C\$5.. \$C\$22,$ $A\$7.. A\$22)$	$=\text{Intercept}$ $(\$D\$5.. \$D\$22,$ $A\$5.. A\$22)$	$=\text{Intercept}$ $(\$E\$5.. \$E\$22,$ $A\$5.. A\$22)$
Slope		$=\text{slope}$ $(\$C\$5.. \$C\$22,$ $A\$5.. A\$22)$	$=\text{slope}$ $(\$D\$5.. \$D\$22,$ $A\$7.. A\$22, 110)$	$=\text{slope}$ $(\$E\$7.. \$E\$22,$ $A\$5.. A\$22)$
Rho		$=\text{RSQ}$ $(\$C\$5.. \$C\$22,$ $A\$5.. A\$22)$	$=\text{RSQ}$ $(\$D\$5.. \$D\$22,$ $A\$5.. A\$22)$	$=\text{RSQ}$ $(\$E\$5.. \$E\$22,$ $A\$5.. A\$22)$

Substituting

$$KN = \left[ \left( \frac{C_0}{C_A} \right)^{n-1} - 1 \right] \quad (3.D.3)$$

KN should be a constant!

Again, I used an Excel spreadsheet to do the calculations. When I solve this, I find it useful to use the module macro in Excel to set up all of the equations. The module macro capability allows you to define your own functions, in Visual BASIC.

Table 3.D.2 Numerical values for the Essen plots

A	B	C	D	E
Essen's Method				
time	conc	first	second	third
0		$\ln(1/\text{Ca})$	$(\text{CaO}/\text{Ca})-1$	$(\text{CaO}/\text{Ca})^2-1$
1	1.00	0.000	0.000	0.000
2	0.91	0.094	0.099	0.208
3	0.83	0.186	0.205	0.452
4	0.77	0.261	0.299	0.667
5	0.71	0.342	0.408	0.984
6	0.67	0.400	0.493	1.228
7	0.63	0.462	0.587	1.520
8	0.59	0.528	0.695	1.873
9	0.56	0.580	0.786	2.189
10	0.53	0.635	0.887	2.560
11	0.50	0.693	1.000	3.000
12	0.48	0.734	1.083	3.340
13	0.45	0.799	1.222	3.938
14	0.43	0.844	1.326	4.408
15	0.42	0.868	1.381	4.669
16	0.40	0.916	1.500	5.250
17	0.38	0.968	1.632	5.925
Intercept		0.994	1.703	6.905
Slope		0.087	-0.005	-0.477
Rho		0.057	0.100	0.373
		0.984	0.999	0.981

You can define your own functions by first inserting a module page into your workbook. In my version of Excel you do that by using the INSERT-MACRO-MODULE tab. Once you create a module, you can create your own functions by typing them onto the module page.

Table 3.D.3 shows the module to calculate  $k_1$ ,  $k_2$  and  $k_3$ , where  $k_1$  is given by equation (3.51) and  $k_2$  and  $k_3$  are given by equation (3.D.3). The first three lines define a function "kone" ( $k_1$ ). The first line defines kone as a public function. I called the function "kone", not  $k_1$  because of a limitation of Excel. The word "public" in the function definition makes the function available to Excel. The term "as variant" says that the return type is variant. "Variant" is a general return type that can be used for anything. Table 3.D.4 gives a list of other return types. The second line of the definition gives a value to "kone" according to equation 3.51. The third line tells the function to return. We use log in the function. In modules, log returns the natural log of a number while log10 returns a base 10 log



**Table 3.D.3** Module used to calculate  $k_1$ ,  $k_2$ ,  $k_3$ , where  $k_1$ ,  $k_2$ , and  $k_3$  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/2
End Function
```

**Table 3.D.4** Some Microsoft Excel/Visual BASIC return types

Type	Meaning	Type	Meaning
As variant	General return type (can be an integer, real, vector, matrix logical or text)	As Double	Double-precision real
As single	Single precision real	As Integer	Integer

Table 3.D.3 also shows the function definitions to calculate  $k_2$  and  $k_3$  according to equation (3.50). The only thing that is weird in the definition is that the "#" makes 1 a floating-point number.

Once you type in the module, you can then use the function kone like any other function in Excel. So if you want to calculate kone with  $Ca0 = 1.0$ ,  $Ca = 0.6$  and  $tau = 3$ , you enter

```
=kone(1, 0.6, 3)
```

in a cell in your spreadsheet.

I use these functions to calculate  $k_1$ ,  $k_2$ , and  $k_3$  in my spreadsheet. Table 3.D.5 shows my spreadsheet. I listed time in column B and concentration in column C, and I wanted to calculate  $k_1$  in column D,  $k_2$  in column E, and  $k_3$  in column F.

I used the following steps to get the answer:

1. I named cell e1 CaO, and set it equal to 1.
2. I used the kone, ktwo, and kthree functions to calculate  $k_1$ ,  $k_2$ , and  $k_3$ .

For example, row 6 is for time=1.  $Ca0=1$ ,  $Ca=c6$ ,  $tau=b6$ , so kone calculates  $k_1$  for  $Ca0=ca0$ ,  $ca=c6$ ,  $tau=b6$ .

I also included a spreadsheet (Table 3.D.6) that does not use the user-defined functions. Table 3.D.6 shows the formulas used in the spreadsheet. Column A is the time, column B is the concentration, column C is  $k_1$ , column D is  $k_2$ , and column E is  $k_3$ . At time = 2,  $Ca = B33$ ,  $\ln(C_A^0/C_A) = \ln(1/B33)$ . Also,  $\ln(C_A^0/C_A)/\tau = \ln(1/B33)/A33$ . The actual calculations are listed in Table 3.D.7.

**Table 3.D.5** The formulas in the spreadsheet for Van't Hoff's method

	B	C	D	E	F
1			Ca0=1.0		
2			Essen's Method		
3	time	conc	first	second	third
4			$\ln(Ca0/Ca)$	$(Ca0/Ca)-1$	$(Ca0/Ca)^2-1$
5	0	1	=kone(ca0,C5,B5)	=ktwo(ca0,C5,B5)	=kthree(ca0,C5,B5)
6	1	0.91	=kone(ca0,C6,B6)	=ktwo(ca0,C6,B6)	=kthree(ca0,C6,B6)
7	2	0.83	=kone(ca0,C7,B7)	=ktwo(ca0,C7,B7)	=kthree(ca0,C7,B7)
8	3	0.77	=kone(ca0,C8,B8)	=ktwo(ca0,C8,B8)	=kthree(ca0,C8,B8)
9	4	0.71	=kone(ca0,C9,B9)	=ktwo(ca0,C9,B9)	=kthree(ca0,C9,B9)
10	5	0.67	=kone(ca0,C10,B10)	=ktwo(ca0,C10,B10)	=kthree(ca0,C10,B10)
11	6	0.63	=kone(ca0,C11,B11)	=ktwo(ca0,C11,B11)	=kthree(ca0,C11,B11)
12	7	0.59	=kone(ca0,C12,B12)	=ktwo(ca0,C12,B12)	=kthree(ca0,C12,B12)
13	8	0.56	=kone(ca0,C13,B13)	=ktwo(ca0,C13,B13)	=kthree(ca0,C13,B13)
14	9	0.53	=kone(ca0,C14,B14)	=ktwo(ca0,C14,B14)	=kthree(ca0,C14,B14)
15	10	0.5	=kone(ca0,C15,B15)	=ktwo(ca0,C15,B15)	=kthree(ca0,C15,B15)
16	11	0.48	=kone(ca0,C16,B16)	=ktwo(ca0,C16,B16)	=kthree(ca0,C16,B16)
17	12	0.45	=kone(ca0,C17,B17)	=ktwo(ca0,C17,B17)	=kthree(ca0,C17,B17)
18	13	0.43	=kone(ca0,C18,B18)	=ktwo(ca0,C18,B18)	=kthree(ca0,C18,B18)
19	14	0.42	=kone(ca0,C19,B19)	=ktwo(ca0,C19,B19)	=kthree(ca0,C19,B19)
20	15	0.4	=kone(ca0,C20,B20)	=ktwo(ca0,C20,B20)	=kthree(ca0,C20,B20)
21	16	0.38	=kone(ca0,C21,B21)	=ktwo(ca0,C21,B21)	=kthree(ca0,C21,B21)
22	17	0.37	=kone(ca0,C22,B22)	=ktwo(ca0,C22,B22)	=kthree(ca0,C22,B22)

Notice that  $k_2$  is constant while  $k_1$  and  $k_3$  vary. Figure 3.18 also shows a plot of these data. According to Van't Hoff's analysis, if  $k_2$  is constant, the reaction is second-order; therefore, we conclude that the reaction is second-order.

**Powell's Method** In Powell's method (see formulas listed in Table 3.D.8), one uses plots of  $\log$  of  $\tau$  versus  $\ln C_A$ . One then shifts the curves left and right until things fit. In my spreadsheet, I defined a new variable shift to do the calculations. I then varied shift by hand. I put the top two points in the middles of the curves and then saw which curve fit best.

The values for Powell's method are shown in Table 3.D.9.

A plot of the data in Table 3.D.9 shows that these data follow second-order kinetics (see Figure 3.D.1).

**Example 3.E** Using the Stoichiometric Table to Solve Stoichiometric Problems Let's use the stoichiometric table to do a problem from page 118 in Felder and Rousseau, (1978). Ethylene is being made via the dehydrogenation of ethane.



Assume that 100 mol/minute are fed into a flow reactor. Analysis of the exit stream indicates that 40 mol/minute of hydrogen leave the reactor. Calculate the exit flow rate.

Table 3.D.6 The formulas used for Van't Hoff's method

A	B	C	D	E
30 time	conc	k1	k2	k3
31	0	$\ln(1/\text{Ca})/t$	$(\text{Ca}_0/\text{Ca}-1)/t$	$((\text{Ca}_0/\text{Ca})^2-1)/t/2$
32	1	$=\text{LN}(1/\text{B32})/\text{A32}$	$= (1/\text{B32}-1)/\text{A32}$	$= ((1/\text{B32})^2-1)/\text{A32}/2$
33	2	$=\text{LN}(1/\text{B33})/\text{A33}$	$= (1/\text{B33}-1)/\text{A33}$	$= ((1/\text{B33})^2-1)/\text{A33}/2$
34	3	$=\text{LN}(1/\text{B34})/\text{A34}$	$= (1/\text{B34}-1)/\text{A34}$	$= ((1/\text{B34})^2-1)/\text{A34}/2$
35	4	$=\text{LN}(1/\text{B35})/\text{A35}$	$= (1/\text{B35}-1)/\text{A35}$	$= ((1/\text{B35})^2-1)/\text{A35}/2$
36	5	$=\text{LN}(1/\text{B36})/\text{A36}$	$= (1/\text{B36}-1)/\text{A36}$	$= ((1/\text{B36})^2-1)/\text{A36}/2$
37	6	$=\text{LN}(1/\text{B37})/\text{A37}$	$= (1/\text{B37}-1)/\text{A37}$	$= ((1/\text{B37})^2-1)/\text{A37}/2$
38	7	$=\text{LN}(1/\text{B38})/\text{A38}$	$= (1/\text{B38}-1)/\text{A38}$	$= ((1/\text{B38})^2-1)/\text{A38}/2$
39	8	$=\text{LN}(1/\text{B39})/\text{A39}$	$= (1/\text{B39}-1)/\text{A39}$	$= ((1/\text{B39})^2-1)/\text{A39}/2$
40	9	$=\text{LN}(1/\text{B40})/\text{A40}$	$= (1/\text{B40}-1)/\text{A40}$	$= ((1/\text{B40})^2-1)/\text{A40}/2$
41	10	$=\text{LN}(1/\text{B41})/\text{A41}$	$= (1/\text{B41}-1)/\text{A41}$	$= ((1/\text{B41})^2-1)/\text{A41}/2$
42	11	$=\text{LN}(1/\text{B42})/\text{A42}$	$= (1/\text{B42}-1)/\text{A42}$	$= ((1/\text{B42})^2-1)/\text{A42}/2$
43	12	$=\text{LN}(1/\text{B43})/\text{A43}$	$= (1/\text{B43}-1)/\text{A43}$	$= ((1/\text{B43})^2-1)/\text{A43}/2$
44	13	$=\text{LN}(1/\text{B44})/\text{A44}$	$= (1/\text{B44}-1)/\text{A44}$	$= ((1/\text{B44})^2-1)/\text{A44}/2$
45	14	$=\text{LN}(1/\text{B45})/\text{A45}$	$= (1/\text{B45}-1)/\text{A45}$	$= ((1/\text{B45})^2-1)/\text{A45}/2$
46	15	$=\text{LN}(1/\text{B46})/\text{A46}$	$= (1/\text{B46}-1)/\text{A46}$	$= ((1/\text{B46})^2-1)/\text{A46}/2$
47	16	$=\text{LN}(1/\text{B47})/\text{A47}$	$= (1/\text{B47}-1)/\text{A47}$	$= ((1/\text{B47})^2-1)/\text{A47}/2$
48	17	$=\text{LN}(1/\text{B48})/\text{A48}$	$= (1/\text{B48}-1)/\text{A48}$	$= ((1/\text{B48})^2-1)/\text{A48}/2$

Table 3.E.1 Stoichiometric table for Example 3.E

Species	Flow-rate in Feed	Change Moles	Moles out of Reactor
Ethane	$F_{\text{C}_2\text{H}_6}^0$	$-F_{\text{C}_2\text{H}_6}^0 X_{\text{C}_2\text{H}_6}$	$F_{\text{C}_2\text{H}_6}^0 (1 - X_{\text{C}_2\text{H}_6})$
Ethylene	$F_{\text{C}_2\text{H}_4}^0$	$(b/a)F_{\text{C}_2\text{H}_6}^0 X_{\text{C}_2\text{H}_6}$	$F_{\text{C}_2\text{H}_4}^0 + (b/a)F_{\text{C}_2\text{H}_6}^0 X_{\text{C}_2\text{H}_6}$
Hydrogen	$F_{\text{H}_2}^0$	$(c/a)F_{\text{C}_2\text{H}_6}^0 X_{\text{C}_2\text{H}_6}$	$F_{\text{H}_2}^0 + (c/a)F_{\text{C}_2\text{H}_6}^0 X_{\text{C}_2\text{H}_6}$

Table 3.E.2 The results after substituting data into Table 3.E.1

Species	Flow Rate in Feed	Change Moles	Moles out of Reactor
Ethane	100 mol/minute	-100 mol/minute $X_{\text{C}_2\text{H}_6}$	100 mol/minute $(1 - X_{\text{C}_2\text{H}_6})$
Ethylene	0	100 mol/minute $X_{\text{C}_2\text{H}_6}$	100 mol/minute $X_{\text{C}_2\text{H}_6}$
Hydrogen	0	100 mol/minute $X_{\text{C}_2\text{H}_6}$	100 mol/minute $X_{\text{C}_2\text{H}_6}$

**Solution** Table 3.7 is a general stoichiometric table for the reaction. There are one reactant, two products, and no inerts in reaction (3.E.1). Therefore, the stoichiometric table will be in the format of Table 3.E.1.

In Table 3.7,  $a$  is the minus stoichiometric coefficient of  $\text{C}_2\text{H}_6$ ,  $b$  is the stoichiometric coefficient of  $\text{C}_2\text{H}_4$ , and  $c$  is the stoichiometric coefficient of  $\text{H}_2$ . Substituting  $a = b = c = 1$ ,  $F_{\text{C}_2\text{H}_6}^0 = 100$  mol/minute,  $F_{\text{H}_2}^0 = F_{\text{C}_2\text{H}_4}^0 = 0$  yields Table 3.E.2.

Table 3.D.7 The numerical values for Van't Hoff's method

B	C	D	E	F
3 time	conc	k1	k2	k3
4	0	$\ln(1/\text{Ca})/t$	$((\text{Ca}_0/\text{Ca}-1)/t$	$((\text{Ca}_0/\text{Ca})^2-1)/t/2$
5	1	0.91	0.094	0.099
6	2	0.83	0.093	0.102
7	3	0.77	0.087	0.100
8	4	0.71	0.086	0.102
9	5	0.67	0.080	0.099
10	6	0.63	0.077	0.098
11	7	0.59	0.075	0.099
12	8	0.56	0.072	0.098
13	9	0.53	0.071	0.099
14	10	0.5	0.069	0.100
15	11	0.48	0.067	0.098
16	12	0.45	0.067	0.102
17	13	0.43	0.065	0.102
18	14	0.42	0.062	0.099
19	15	0.4	0.061	0.100
20	16	0.38	0.060	0.102
21	17	0.37	0.058	0.100

Table 3.E.3 The results (in mol/minute) after substituting  $X_{\text{C}_2\text{H}_6} = 0.4$  into Table 3.E.2

Species	Flow Rate Feed	Change Moles	Moles out of Reactor
Ethane	100	-40	60
Ethylene	0	+40	40
Hydrogen	0	+40	40

But 40 mol/minute of hydrogen leave the reactor. Therefore

$$[100 \text{ mol/hour}]X_{\text{C}_2\text{H}_6} = 40 \text{ mol/minute} \quad (3.E.2)$$

$$X_{\text{C}_2\text{H}_6} = 0.4 \quad (3.E.3)$$

plugging  $X_{\text{C}_2\text{H}_6}$  into Table 3.E.2 yields Table 3.E.3.

**Example 3.F** Chuchani and Martin (1997) examined the pyrolysis of maleic acid:



by loading the maleic acid into a batch reactor and measuring the pressure as a function of time. The data in Table 3.F.1 were obtained at 320.1°C, after correcting for a side reaction.

- Calculate the concentration of maleic acid as a function of time.
- Fit the data to a simple rate equation.

Table 3.D.9 Numerical values of the data for the analysis of Powell's method

	A	B	C	D	E	F	G	H
63	time	conc	shift=	In time +	Ca/Ca0	Log Tau	Log Tau	Log Tau
64	0.000	1.000	In time	shift		First	Second	Third
65	1.000	0.910	0.000	-1.000	0.910	order	order	Order
66	2.000	0.830	0.301	-0.699	0.830	-1.025	-1.005	-0.984
67	3.000	0.770	0.477	-0.523	0.770	-0.730	-0.689	-0.646
68	4.000	0.710	0.602	-0.398	0.710	-0.583	-0.525	-0.464
69	5.000	0.670	0.699	-0.301	0.670	-0.465	-0.389	-0.308
70	6.000	0.630	0.778	-0.222	0.630	-0.397	-0.308	-0.212
71	7.000	0.590	0.845	-0.155	0.590	-0.335	-0.231	-0.119
72	8.000	0.560	0.903	-0.097	0.560	-0.278	-0.158	-0.029
73	9.000	0.530	0.954	-0.046	0.530	-0.237	-0.105	0.039
74	10.000	0.500	1.000	0.000	0.500	-0.197	-0.052	0.107
75	11.000	0.480	1.041	0.041	0.480	-0.159	0.000	0.176
76	12.000	0.450	1.079	0.079	0.450	-0.134	0.035	0.223
77	13.000	0.430	1.114	0.114	0.430	-0.098	0.087	0.294
78	14.000	0.420	1.146	0.146	0.420	-0.074	0.122	0.343
79	15.000	0.400	1.176	0.176	0.400	-0.062	0.140	0.368
80	16.000	0.380	1.204	0.204	0.380	-0.038	0.176	0.419
81	17.000	0.370	1.230	0.230	0.370	-0.014	0.213	0.472
82						-0.003	0.231	0.499

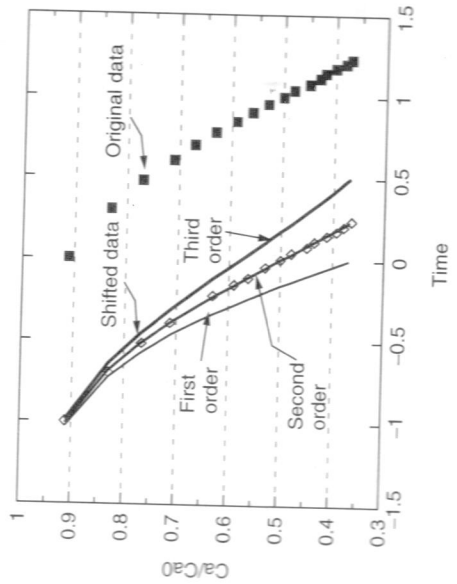


Figure 3.D.1 Plot of the data in the spreadsheet in Table 3.D.9.

	A	B	C	D	E	F	G	H
52			shift=-					
53	time	conc	Log time	In time +shift	Ca/Ca0	Log Tau	Log Tau	Log Tau
54	0	1						
55	1	0.91	=LOG10(A55)	=C55+SHIFT	+B55/1	=LOG(LN(1/B55))	Second Order	Third Order
56	2	0.83	=LOG10(A56)	=C56+SHIFT	+B56/1	=LOG(LN(1/B56))		
57	3	0.77	=LOG10(A57)	=C57+SHIFT	+B57/1	=LOG(LN(1/B57))		
58	4	0.71	=LOG10(A58)	=C58+SHIFT	+B58/1	=LOG(LN(1/B58))		
59	5	0.67	=LOG10(A59)	=C59+SHIFT	+B59/1	=LOG(LN(1/B59))		
60	6	0.63	=LOG10(A60)	=C60+SHIFT	+B60/1	=LOG(LN(1/B60))		
61	7	0.59	=LOG10(A61)	=C61+SHIFT	+B61/1	=LOG(LN(1/B61))		
62	8	0.56	=LOG10(A62)	=C62+SHIFT	+B62/1	=LOG(LN(1/B62))		
63	9	0.53	=LOG10(A63)	=C63+SHIFT	+B63/1	=LOG(LN(1/B63))		
64	10	0.5	=LOG10(A64)	=C64+SHIFT	+B64/1	=LOG(LN(1/B64))		
65	11	0.48	=LOG10(A65)	=C65+SHIFT	+B65/1	=LOG(LN(1/B65))		
66	12	0.45	=LOG10(A66)	=C66+SHIFT	+B66/1	=LOG(LN(1/B66))		
67	13	0.43	=LOG10(A67)	=C67+SHIFT	+B67/1	=LOG(LN(1/B67))		
68	14	0.42	=LOG10(A68)	=C68+SHIFT	+B68/1	=LOG(LN(1/B68))		
69	15	0.4	=LOG10(A69)	=C69+SHIFT	+B69/1	=LOG(LN(1/B69))		
70	16	0.38	=LOG10(A70)	=C70+SHIFT	+B70/1	=LOG(LN(1/B70))		
71	17	0.37	=LOG10(A71)	=C71+SHIFT	+B71/1	=LOG(LN(1/B71))		

Table 3.D.8 Formulas used to analyze the data using Powell's method

**Solution** According to equation (3.88)

$$\frac{P_T}{P_T^0} = 1 + \left( \frac{N_A^0}{N_T^0} \right) \left( \frac{\Delta \text{mol}}{a} \right) X_A \quad (3.F.1)$$

Solving

$$X = \left( \frac{P_T}{P_T^0} - 1 \right) \left( \frac{N_T^0}{N_A^0} \right) \left( \frac{a}{\Delta \text{mol}} \right)$$

But  $N_T^0 = N_A^0 a = 1$ ,  $\Delta \text{mol} = 2$ .  
Therefore

$$X = \frac{1}{2} \left( \frac{P_T}{P_T^0} - 1 \right)$$

$$C_M = \frac{N}{V} = \frac{P_A^0}{RT} (1 - X_A) = \frac{52.1 \text{ torr}}{\left( \frac{0.052 \text{ liter}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) (593.1 \text{ K})} (1 - X_A)$$

or

$$C_M = 1.4 \times 10^{-3} (1 - X_A)$$

Plugging in the numbers yields Table 3.F.2.

I analyzed these data using the spreadsheet in Table 3.C.3. The results are given in Table 3.F.3.

Notice that  $k_1$  is constant up until about 70% conversion, which implies that the reaction is first-order in that conversion range (the side reaction starts at about 60% conversion).

**Table 3.F.1 Data for Example 3.F**

Pressure, atm	$\tau$ , minutes	Pressure, atm	$\tau$ , minutes	Pressure, atm	$\tau$ , minutes
52.1	0	110.9	5.2	124.7	9
72.8	1.5	114.4	6.0	134.7	40
92.5	3.0	121.6	7.0	139.8	51

**Table 3.F.2 Concentration versus time for the data in Table 3.F.1**

Time, minutes	$X_A$	$C_M$ , mol/liter	Time, minutes	$X_A$	$C_M$ , mol/liter
0	0	$1.40 \times 10^{-3}$	9	0.667	$4.66 \times 10^{-4}$
1.5	0.199	$1.12 \times 10^{-3}$	10	0.697	$4.27 \times 10^{-4}$
3	0.388	$8.57 \times 10^{-4}$	40	0.763	$2.90 \times 10^{-4}$
5.2	0.564	$6.10 \times 10^{-4}$	51	0.842	$2.21 \times 10^{-4}$
6	0.598	$5.63 \times 10^{-4}$	—	—	—

**Example 3.G** Develop a stoichiometric table for the reaction



and show that the density is constant.

**Solution** Following the analysis in Section 3.12.1, Table 3.G.1 the stoichiometric table for this system becomes.

Since the number of moles is constant, the density is constant (for an isothermal ideal gas).

### Example 3.H Limiting Reactants

(a) Develop a stoichiometric table for the homogeneous gas-phase reaction:



(b) Develop an expression for the concentration of the oxygen as a function of the conversion of the nitrogen dioxide in a constant pressure reactor.

**Table 3.F.3 Numerical Values in Table 3.F.2**

	A	B	C	D	E
30 $t_{\text{lim}}$	$1 - X_A$	k1	k2	k3	
31	0	1	$\ln(1/\text{Ca})/t$	$((\text{Ca}0/\text{Ca})^2 - 1)/t/2$	
32	1.5	0.80	0.148	0.166	0.186
33	3.9	0.61	0.164	0.211	0.278
34	5.2	0.44	0.160	0.246	0.410
35	6	0.40	0.152	0.248	0.432
36	7	0.33	0.157	0.286	0.573
37	9	0.30	0.133	0.256	0.550
38	40	0.21	0.039	0.096	0.279
39	51	0.16	0.036	0.104	0.383

**Table 3.G.1 Stoichiometric table for Example 3.G**

Species	Initial Moles	Change Moles	Moles Unreacted
CO	$N_{\text{CO}}^0$	$-N_{\text{CO}}^0 X_{\text{CO}}$	$N_{\text{CO}}^0 (1 - X_{\text{CO}})$
H <sub>2</sub>	$N_{\text{H}_2}^0$	$-N_{\text{CO}}^0 X_{\text{CO}}$	$N_{\text{H}_2}^0 - N_{\text{CO}}^0 X_{\text{CO}}$
CO <sub>2</sub>	$N_{\text{CO}_2}^0$	$+N_{\text{CO}}^0 X_{\text{CO}}$	$N_{\text{CO}_2}^0 + N_{\text{CO}}^0 X_{\text{CO}}$
H <sub>2</sub>	$N_{\text{H}_2}^0$	$+N_{\text{CO}}^0 X_{\text{CO}}$	$N_{\text{H}_2}^0 + N_{\text{CO}}^0 X_{\text{CO}}$
Total	$N_{\text{CO}}^0 + N_{\text{H}_2}^0 + N_{\text{CO}_2}^0 + N_{\text{H}_2}^0$	0	$N_{\text{CO}}^0 + N_{\text{H}_2}^0 + N_{\text{CO}_2}^0 + N_{\text{H}_2}^0$

- (c) If we put 2 mol of nitrogen dioxide and 1 mol of oxygen into a closed reactor, will oxygen or nitrogen dioxide be used up first? We call the reactant that is used up first the **limiting reactant**.

### Solution

- (a) Refer to Table 3.H.1.  
 (b) The oxygen concentration: by definition

$$CO_2 = \frac{NO_2}{V} \quad (3.H.1)$$

where  $V$  is the volume. From the ideal-gas law

$$PV = N_{\text{total}}RT \quad (3.H.2)$$

Substituting  $V$  from equation (3.H.2) into equation (3.H.1) and substituting expressions for  $N_{\text{total}}$  and the concentration of  $NO_2$  from the stoichiometric table yields

$$CO_2 = \left( \frac{N_{NO_2}^0 - \frac{1}{4}X_{NO_2}N_{NO_2}^0}{N_{O_2}^0 + N_{NO_2}^0(1 - \frac{3}{4}X_{NO_2})} \right) \frac{P}{RT}$$

- (c) The  $NO_2$  is used up when  $X_{NO_2} = 1$ . At that point

$$NO_2 = N_{O_2}^0 - \frac{1}{4}X_{NO_2}N_{NO_2}^0 = 1 - \left(\frac{1}{4}\right)(1)(2) = 0.5 \text{ mol}$$

$NO_2$  is used up first. Therefore  $NO_2$  is the limiting reactant.

**Example 3.I** Using the Equations in Section 3.I.3.2 for Design Ethylbenzoate (E) is made by reacting benzoyl chloride (B) with ethyl alcohol (A) (see Figure 3.I.1).

**Table 3.H.1** Stoichiometric table for Example 3.H

Species	Initial Moles	Change Moles	Moles Unreacted
$NO_2$	$N_{NO_2}^0$	$-X_{NO_2}N_{NO_2}^0$	$N_{NO_2}^0(1 - X_{NO_2})$
$O_2$	$N_{O_2}^0$	$-\frac{1}{4}X_{NO_2}N_{NO_2}^0$	$N_{O_2}^0 - \frac{1}{4}X_{NO_2}N_{NO_2}^0$
$N_2O_5$	0	$+\frac{1}{2}X_{NO_2}N_{NO_2}^0$	$\frac{1}{2}X_{NO_2}N_{NO_2}^0$
Total	$N_{NO_2}^0 + N_{O_2}^0$	$-\frac{3}{4}X_{NO_2}N_{NO_2}^0$	$N_{NO_2}^0 + N_{O_2}^0(1 - \frac{3}{4}X_{NO_2})$



**Figure 3.I.1** The reaction to form ethylbenzoate.

Assume that you mix 1 mol of benzoyl chloride into 1 liter of ethyl alcohol and find that 30% of the benzoyl chloride is converted after 30 minutes. How long will it take for 95% of the benzoyl chloride to be converted?

### Solution

Note that  $C_A \gg C_B$ . Therefore, equation 3.77 applies. Rearranging equation 3.77 yields

$$\frac{1}{k_1} \ln \left( \frac{C_B^0}{C_B} \right) = \tau \quad (3.I.1)$$

with  $k_1 = k_B C_A^0$ . Rearranging yields

$$k_1 = \frac{1}{\tau} \ln \left( \frac{C_B^0}{C_B} \right) = \frac{1}{30 \text{ minutes}} \ln \left( \frac{1}{1-0.3} \right) = 1.1 \times 10^{-2} / \text{minute} \quad (3.I.2)$$

when  $X_B = 0.95$ ,  $C_B = (1 - X_B) 1 \text{ mol/liter}$ . Substituting into equation (3.I.1) yields

$$\tau = \frac{1}{k} \ln \left( \frac{1}{1-0.95} \right) = 250 \text{ minutes} \quad (3.I.3)$$

**Example 3.J Multiple Reactants** In Section 3.I.3, we did a problem on the Diels-Alder reaction of benzoquinone (B) and cyclopentadiene (C) to yield an adduct. Assume that you now want to use dimethyl cyclopentadiene (C') for the reaction. Adding the methyl groups increases  $k$ . Assume a 20% increase ( $I$  made up a number).

First, 0.1 mol/liter of C and 0.08 mol/liter of B are loaded into a well-stirred batch reactor.

- (a) Determine the residence time needed to convert 95% of the benzoquinone to adduct.  
 (b) Reminder, the reaction took 2.2 hours with cyclopentadiene.

**Solution** From equation (3.79)

$$\tau = \frac{1}{k_B} \left( \int_{C_B^0}^{C_B} \frac{dC_B}{C_B C_C} \right)$$

The term in brackets is constant. If  $k_B$  goes up 20%,  $\tau$  goes down by 20%:

$$\tau = \frac{2.2 \text{ hours}}{1.2} = 1.8 \text{ hours}$$

**Example 3.K Van't Hoff Plots for More Complex Reactions** Bodenstein and Lund (1904) examined the rate of the reaction:



in a batch reactor. They did runs where they mixed known amounts of  $H_2$  and  $Br_2$ , and measured the HBr concentration as a function of time. The data listed in Table 3.K.1 were obtained at 301.3°C.

How well do the data in Table 3.K.1 fit the rate equations

$$r_{HBr} = k_2[H_2][Br_2] \quad (3.K.2)$$

$$r_{HBr} = k_{1.5}[H_2][Br_2]^{1/2} \quad (3.K.3)$$

**Solution** I will use equation (3.30) to solve this problem.

$$\int_{C_A^0}^{C_A} \frac{-dC_A}{-r_A} = \tau \quad (3.30)$$

I am going to work in terms of the HBr concentration. According to equation (3.30)

$$\tau = \int_{C_{HBr}^0}^{C_{HBr}^F} \frac{d[HBr]}{(-r_{HBr})} \quad (3.K.4)$$

Inverting the limits yields

$$\tau = \int_{C_{HBr}^0}^{C_{HBr}^F} \frac{d[HBr]}{(r_{HBr})} \quad (3.K.5)$$

Next, I need an expression for  $r_{HBr}$ . Equations (3.K.2) and (3.K.3) give me expressions for  $r_{HBr}$  in terms of the concentrations  $[H_2]$ ,  $[Br_2]$  in the reactor. In order to use the equations, I will need to know how  $[H_2]$  and  $[Br_2]$  are changing as the reaction proceeds.

Next, I will use the stoichiometric table (Table 3.K.2) to develop an expression for  $[H_2]$  and  $[Br_2]$  in terms of the initial concentration in the reactor and  $[HBr]$ .

If we call  $[HBr]$  the amount of HBr that forms, then the change in the  $Br_2$  concentration is

$$\Delta[Br_2] = \frac{(-1)}{(2)} [HBr] \quad (3.K.6)$$

**Table 3.K.2** Stoichiometric table for Example 3.K

Species	Initial Concentration	Change	Final Calculation
HBr	0	$[HBr]$	$[HBr]$
$Br_2$	$[Br_2]^0$	$+\frac{(-1)}{(2)}[HBr]$	$[Br_2]^0 - \frac{1}{2}[HBr]$
$H_2$	$[H_2]^0$	$+\frac{(-1)}{(2)}[HBr]$	$[H_2]^0 - \frac{1}{2}[HBr]$

where  $(-1)$  is the stoichiometric coefficient of  $Br_2$  and  $(2)$  is the stoichiometric coefficient of HBr. The rest of the stoichiometric table is given above.  
From the stoichiometric table

$$[Br_2] = [Br_2]^0 - 0.5[HBr] \quad (3.K.7)$$

$$[H_2] = [H_2]^0 - 0.5[HBr] \quad (3.K.8)$$

where  $[H_2]^0$  and  $[Br_2]^0$  are the initial concentrations of  $H_2$  and  $Br_2$ , respectively. If equation (3.K.2) works, then

$$r_{HBr} = k_2([H_2]^0 - 0.5[HBr])([Br_2]^0 - 0.5[HBr]) \quad (3.K.9)$$

According to equation (3.K.5)

$$\tau = \int_{C_{HBr}^0}^{C_{HBr}^F} \frac{d[HBr]}{(r_{HBr})} \quad (3.K.10)$$

Substituting equation (3.K.9) into equation (3.K.10) and looking up the integral in an integral table yields

$$\tau = \frac{2}{k_2([H_2]^0 - [Br_2]^0)} \ln \left( \frac{[Br_2]^0([H_2]^0 - 0.5[HBr])}{[H_2]^0([Br_2]^0 - 0.5[HBr])} \right) \quad (3.K.11)$$

Solving for  $k_2$  yields

$$k_2 = \frac{2}{\tau([H_2]^0 - [Br_2]^0)} \ln \left( \frac{[Br_2]^0([H_2]^0 - 0.5[HBr])}{[H_2]^0([Br_2]^0 - 0.5[HBr])} \right) \quad (3.K.12)$$

Here is an Excel spreadsheet to do the calculations. Column A is the initial hydrogen concentration, column B is the initial bromine concentration, column C is the final HBr

**Table 3.K.1** Bodenstein and Lund's [1904, 1907] data for HBr production in a batch reactor

Run 1		Run 2		Run 3	
$[H_2]^0 = 0.5637$	$[Br_2]^0 = 0.2947$	$[H_2]^0 = 0.2281$	$[Br_2]^0 = 0.1517$	$[H_2]^0 = 0.3103$	$[Br_2]^0 = 0.5069$
Time, minutes	$[HBr]$	Time, minutes	$[HBr]$	Time, minutes	$[HBr]$
0	0	0	0	0	0
14.5	0.0669	19.5	0.0322	15	0.0492
24.5	0.0985	34.5	0.0527	35	0.1031
34.5	0.1262	54.5	0.0713	55	0.1406
49.5	0.1644	79.5	0.0912	80	0.1752
79.5	0.2093	99.5	0.1040	102	0.1963
99.5	0.2306	124.5	0.1142	125	0.2179
124.5	0.2502	149.5	0.1217	155	0.2360
149.5	0.2619	174.5	0.1295	196	0.2533

concentration, column D is  $\tau$ , and column E is  $k_2$  calculated from equation (3.K.11).

A	B	C	D	E
3	$[H_2]^\circ$	$[HBr]$	$\tau$	$k_2$
4	0.5637	0.2947	14.5	$=2/D_4/(A_4-B_4) \cdot \ln(B_4/A_4) / (A_4-0.5 \cdot C_4) / (B_4-0.5 \cdot C_4)$
5	0.5637	0.2947	24.5	$=2/D_5/(A_5-B_5) \cdot \ln(B_5/A_5) / (A_5-0.5 \cdot C_5) / (B_5-0.5 \cdot C_5)$
6	0.5637	0.2947	34.5	$=2/D_6/(A_6-B_6) \cdot \ln(B_6/A_6) / (A_6-0.5 \cdot C_6) / (B_6-0.5 \cdot C_6)$
7	0.5637	0.2947	49.5	$=2/D_7/(A_7-B_7) \cdot \ln(B_7/A_7) / (A_7-0.5 \cdot C_7) / (B_7-0.5 \cdot C_7)$
8	0.5637	0.2947	79.5	$=2/D_8/(A_8-B_8) \cdot \ln(B_8/A_8) / (A_8-0.5 \cdot C_8) / (B_8-0.5 \cdot C_8)$
9	0.5637	0.2947	99.5	$=2/D_9/(A_9-B_9) \cdot \ln(B_9/A_9) / (A_9-0.5 \cdot C_9) / (B_9-0.5 \cdot C_9)$
10	0.5637	0.2947	124.5	$=2/D_{10}/(A_{10}-B_{10}) \cdot \ln(B_{10}/A_{10}) / (A_{10}-0.5 \cdot C_{10}) / (B_{10}-0.5 \cdot C_{10})$
11	0.5637	0.2947	149.5	$=2/D_{11}/(A_{11}-B_{11}) \cdot \ln(B_{11}/A_{11}) / (A_{11}-0.5 \cdot C_{11}) / (B_{11}-0.5 \cdot C_{11})$
12				
13	0.2281	0.1517	19.5	$=2/D_{13}/(A_{13}-B_{13}) \cdot \ln(B_{13}/A_{13}) / (A_{13}-0.5 \cdot C_{13}) / (B_{13}-0.5 \cdot C_{13})$
14	0.2281	0.1517	34.5	$=2/D_{14}/(A_{14}-B_{14}) \cdot \ln(B_{14}/A_{14}) / (A_{14}-0.5 \cdot C_{14}) / (B_{14}-0.5 \cdot C_{14})$
15	0.2281	0.1517	54.5	$=2/D_{15}/(A_{15}-B_{15}) \cdot \ln(B_{15}/A_{15}) / (A_{15}-0.5 \cdot C_{15}) / (B_{15}-0.5 \cdot C_{15})$
16	0.2281	0.1517	79.5	$=2/D_{16}/(A_{16}-B_{16}) \cdot \ln(B_{16}/A_{16}) / (A_{16}-0.5 \cdot C_{16}) / (B_{16}-0.5 \cdot C_{16})$
17	0.2281	0.1517	99.5	$=2/D_{17}/(A_{17}-B_{17}) \cdot \ln(B_{17}/A_{17}) / (A_{17}-0.5 \cdot C_{17}) / (B_{17}-0.5 \cdot C_{17})$
18	0.2281	0.1517	124.5	$=2/D_{18}/(A_{18}-B_{18}) \cdot \ln(B_{18}/A_{18}) / (A_{18}-0.5 \cdot C_{18}) / (B_{18}-0.5 \cdot C_{18})$
19	0.2281	0.1517	149.5	$=2/D_{19}/(A_{19}-B_{19}) \cdot \ln(B_{19}/A_{19}) / (A_{19}-0.5 \cdot C_{19}) / (B_{19}-0.5 \cdot C_{19})$
20	0.2281	0.1517	174.5	$=2/D_{20}/(A_{20}-B_{20}) \cdot \ln(B_{20}/A_{20}) / (A_{20}-0.5 \cdot C_{20}) / (B_{20}-0.5 \cdot C_{20})$
21				
22	0.3103	0.5069	15	$=2/D_{22}/(A_{22}-B_{22}) \cdot \ln(B_{22}/A_{22}) / (A_{22}-0.5 \cdot C_{22}) / (B_{22}-0.5 \cdot C_{22})$
23	0.3103	0.5069	35	$=2/D_{23}/(A_{23}-B_{23}) \cdot \ln(B_{23}/A_{23}) / (A_{23}-0.5 \cdot C_{23}) / (B_{23}-0.5 \cdot C_{23})$

(continued overleaf)

	A	B	C	D	E
24	0.3103	0.5069	0.1406	55	$=2/D_{24}/(A_{24}-B_{24}) \cdot \ln(B_{24}/A_{24}) / (A_{24}-0.5 \cdot C_{24}) / (B_{24}-0.5 \cdot C_{24})$
25	0.3103	0.5069	0.1752	80	$=2/D_{25}/(A_{25}-B_{25}) \cdot \ln(B_{25}/A_{25}) / (A_{25}-0.5 \cdot C_{25}) / (B_{25}-0.5 \cdot C_{25})$
26	0.3103	0.5069	0.1963	102	$=2/D_{26}/(A_{26}-B_{26}) \cdot \ln(B_{26}/A_{26}) / (A_{26}-0.5 \cdot C_{26}) / (B_{26}-0.5 \cdot C_{26})$
27	0.3103	0.5069	0.2179	125	$=2/D_{27}/(A_{27}-B_{27}) \cdot \ln(B_{27}/A_{27}) / (A_{27}-0.5 \cdot C_{27}) / (B_{27}-0.5 \cdot C_{27})$
28	0.3103	0.5069	0.236	155	$=2/D_{28}/(A_{28}-B_{28}) \cdot \ln(B_{28}/A_{28}) / (A_{28}-0.5 \cdot C_{28}) / (B_{28}-0.5 \cdot C_{28})$
29	0.3103	0.5069	0.2533	196	$=2/D_{29}/(A_{29}-B_{29}) \cdot \ln(B_{29}/A_{29}) / (A_{29}-0.5 \cdot C_{29}) / (B_{29}-0.5 \cdot C_{29})$

Here are the results:

	A	B	C	D	E
3	$[H_2]^\circ$	$[Br_2]^\circ$	$[HBr]$	$\tau$	$k_2$
4	0.5637	0.2947	0.0699	14.5	0.03191
5	0.5637	0.2947	0.0985	24.5	0.027749
6	0.5637	0.2947	0.1262	34.5	0.026342
7	0.5637	0.2947	0.1644	49.5	0.025444
8	0.5637	0.2947	0.2093	79.5	0.021819
9	0.5637	0.2947	0.2306	99.5	0.019989
10	0.5637	0.2947	0.2502	124.5	0.01801
11	0.5637	0.2947	0.2619	149.5	0.016076
12					
13	0.2281	0.1517	0.0322	19.5	0.052353
14	0.2281	0.1517	0.0527	34.5	0.051628
15	0.2281	0.1517	0.0713	54.5	0.047042
16	0.2281	0.1517	0.0912	79.5	0.044285
17	0.2281	0.1517	0.104	99.5	0.04236
18	0.2281	0.1517	0.1142	124.5	0.038715
19	0.2281	0.1517	0.1217	149.5	0.035441
20	0.2281	0.1517	0.1295	174.5	0.033406
21					
22	0.3103	0.5069	0.0492	15	0.022279
23	0.3103	0.5069	0.1031	35	0.021633
24	0.3103	0.5069	0.1406	55	0.019903
25	0.3103	0.5069	0.1752	80	0.018055
26	0.3103	0.5069	0.1963	102	0.01646
27	0.3103	0.5069	0.2179	125	0.015504
28	0.3103	0.5069	0.236	155	0.014012
29	0.3103	0.5069	0.2533	196	0.012302

Similarly, let's assume that  $\tau_{\text{HBr}}$  is given by

$$\tau_{\text{HBr}} = k_{1.5}[\text{H}_2][\text{Br}_2]^{1/2} \quad (3.K.13)$$

Substituting equations (3.K.7) and (3.K.8) into (3.K.13) yields

$$\tau_{\text{HBr}} = k_{1.5}([\text{H}_2]^0 - 0.5[\text{HBr}])([\text{Br}_2]^0 - 0.5[\text{HBr}])^{1/2} \quad (3.K.14)$$

Substituting equation (3.K.14) into (3.K.10), looking up the integral in Gradsteyn and Ryzhik or Mathematica, and rearranging yields for  $[\text{H}_2]^0 = [\text{Br}_2]^0$ :

$$k_{1.5} = \frac{4}{\tau} \left( \frac{1}{([\text{Br}_2]^0 - 0.5[\text{HBr}])^{0.5}} - \frac{1}{([\text{Br}_2]^0)^{0.5}} \right) \quad (3.K.15)$$

for  $[\text{H}_2]^0 > [\text{Br}_2]^0$ :

$$k_{1.5} = \frac{4}{\tau \sqrt{[\text{H}_2]^0 - [\text{Br}_2]^0}} \times \left( \arctan \left( \frac{\sqrt{[\text{Br}_2]^0}}{\sqrt{[\text{H}_2]^0 - [\text{Br}_2]^0}} \right) - \arctan \left( \frac{\sqrt{[\text{Br}_2]^0 - 0.5[\text{HBr}]} }{\sqrt{[\text{H}_2]^0 - [\text{Br}_2]^0}} \right) \right) \quad (3.K.16)$$

for  $[\text{Br}_2]^0 > [\text{H}_2]^0$ :

$$k_{1.5} = \frac{2}{\tau \sqrt{([\text{Br}_2]^0 - [\text{H}_2]^0)^{0.5}}}$$

**Table 3.K.3 The Excel module used to calculate  $k_{1.5}$**

Public Function kk(h20, br20, hbr, tau) As Variant

If (br20 = h20) Then

kk = 4#/tau\*(1#/Sqr(br20 - 0.5\*hbr) - 1#/Sqr(br20))

Exit Function

End If

If (h20 > br20) Then

kk = Atn(Sqr(br20)/Sqr(h20-br20))

kk = kk - Atn(Sqr(br20 - 0.5\*hbr)/Sqr(h20 - br20))

kk = kk\*4#/tau/Sqr(h20 - br20)

Exit Function

End If

x1 = Sqr(br20 - 0.5\*hbr) + Sqr(br20 - h20)

x2 = Sqr(br20) - Sqr(br20 - h20)

x3 = Sqr(br20 - 0.5\*hbr) - Sqr(br20 - h20)

x4 = Sqr(br20) + Sqr(br20 - h20)

kk = 2/tau/Sqr(br20 - h20)\*Log((x1\*x2)/(x3\*x4))

End Function

Again, I used a spreadsheet to do the calculations:

This function is so complicated that I found it easier to write an Excel module to calculate  $k_{1.5}$ . Table 3.K.3 is a printout of my module.

Table 3.K.4 is the spreadsheet using the Excel module. I listed the values of  $[\text{H}_2]^0$  in column A,  $[\text{Br}_2]^0$  in column B,  $[\text{HBr}]$  in column C, and  $\tau$  in column D. I then used my function to calculate the values of  $k_{1.5}$  in column E.

Next, I show a spreadsheet that calculates the formulas by hand.

**Table 3.K.4 The formulas in the spreadsheet used to calculate  $k_{1.5}$**

A	B	C	D	E
$[\text{H}_2]^0$	$\text{Br}_2^0$	$[\text{HBr}]$	tau	$k_{1.5}$
40.5637	0.2947	0.0699	14.5	=KK(A4,B4,C4,D4)
60.5637	0.2947	0.0985	24.5	=KK(A5,B5,C5,D5)
60.5637	0.2947	0.1262	34.5	=KK(A6,B6,C6,D6)
70.5637	0.2947	0.1644	49.5	=KK(A7,B7,C7,D7)
80.5637	0.2947	0.2093	79.5	=KK(A8,B8,C8,D8)
90.5637	0.2947	0.2306	99.5	=KK(A9,B9,C9,D9)
100.5637	0.2947	0.2502	124.5	=KK(A10,B10,C10,D10)
110.5637	0.2947	0.2619	149.5	=KK(A11,B11,C11,D11)
120.2281	0.1517	0.0322	19.5	=KK(A13,B13,C13,D13)
140.2281	0.1517	0.0527	34.5	=KK(A14,B14,C14,D14)
160.2281	0.1517	0.0713	54.5	=KK(A15,B15,C15,D15)
160.2281	0.1517	0.0912	79.5	=KK(A16,B16,C16,D16)
170.2281	0.1517	0.104	99.5	=KK(A17,B17,C17,D17)
180.2281	0.1517	0.1142	124.5	=KK(A18,B18,C18,D18)
190.2281	0.1517	0.1217	149.5	=KK(A19,B19,C19,D19)
200.2281	0.1517	0.1295	174.5	=KK(A20,B20,C20,D20)
220.3103	0.5069	0.0492	15	=KK(A22,B22,C22,D22)
240.3103	0.5069	0.1031	35	=KK(A23,B23,C23,D23)
240.3103	0.5069	0.1406	55	=KK(A24,B24,C24,D24)
260.3103	0.5069	0.1752	80	=KK(A25,B25,C25,D25)
260.3103	0.5069	0.1963	102	=KK(A26,B26,C26,D26)
270.3103	0.5069	0.2179	125	=KK(A27,B27,C27,D27)
280.3103	0.5069	0.236	155	=KK(A28,B28,C28,D28)
290.3103	0.5069	0.2533	196	=KK(A29,B29,C29,D29)

$$\times \ln \left( \frac{([\text{Br}_2]^0 - 0.5[\text{HBr}])^{0.5} + ([\text{Br}_2]^0 - [\text{H}_2]^0)^{0.5}}{([\text{Br}_2]^0)^{0.5} - ([\text{Br}_2]^0 - [\text{H}_2]^0)^{0.5}} \right) \quad (3.K.17)$$



A	B	C	D	E
13	19.5	0.2281	0.1517	$=4/D13/SQRT(A13-B13)*(ATAN(SQRT(B13)/SQRT(A13-B13)))-ATAN(SQRT(B13-0.5*C13)/SQRT(A13-B13))$
14	34.5	0.2281	0.1517	$=4/D14/SQRT(A14-B14)*(ATAN(SQRT(B14)/SQRT(A14-B14)))-ATAN(SQRT(B14-0.5*C14)/SQRT(A14-B14))$
15	54.5	0.2281	0.1517	$=4/D15/SQRT(A15-B15)*(ATAN(SQRT(B15)/SQRT(A15-B15)))-ATAN(SQRT(B15-0.5*C15)/SQRT(A15-B15))$
16	79.5	0.2281	0.1517	$=4/D16/SQRT(A16-B16)*(ATAN(SQRT(B16)/SQRT(A16-B16)))-ATAN(SQRT(B16-0.5*C16)/SQRT(A16-B16))$
17	99.5	0.2281	0.1517	$=4/D17/SQRT(A17-B17)*(ATAN(SQRT(B17)/SQRT(A17-B17)))-ATAN(SQRT(B17-0.5*C17)/SQRT(A17-B17))$
18	124.5	0.2281	0.1517	$=4/D18/SQRT(A18-B18)*(ATAN(SQRT(B18)/SQRT(A18-B18)))-ATAN(SQRT(B18-0.5*C18)/SQRT(A18-B18))$
19	149.5	0.2281	0.1517	$=4/D19/SQRT(A19-B19)*(ATAN(SQRT(B19)/SQRT(A19-B19)))-ATAN(SQRT(B19-0.5*C19)/SQRT(A19-B19))$
20	174.5	0.2281	0.1517	$=4/D20/SQRT(A20-B20)*(ATAN(SQRT(B20)/SQRT(A20-B20)))-ATAN(SQRT(B20-0.5*C20)/SQRT(A20-B20))$
21				
22	15	0.3103	0.5069	$=2/D22/SQRT(B22-A22)*LN((SQRT(B22-0.5*C22)+SQRT(B22-A22))*(SQRT(B22)-SQRT(B22-A22))/(SQRT(B22-0.5*C22)-SQRT(B22-A22)))/(SQRT(B22)+SQRT(B22-A22))$

A	B	C	D	E
3	tau	[Br <sub>2</sub> ] <sup>o</sup>	[HBr]	k <sub>1.5</sub>
4	14.5	0.5637	0.2947	$=4/D4/SQRT(A4-B4)*(ATAN(SQRT(B4)/SQRT(A4-B4)))-ATAN(SQRT(B4-0.5*C4)/SQRT(A4-B4))$
5	24.5	0.5637	0.2947	$=4/D5/SQRT(A5-B5)*(ATAN(SQRT(B5)/SQRT(A5-B5)))-ATAN(SQRT(B5-0.5*C5)/SQRT(A5-B5))$
6	34.5	0.5637	0.2947	$=4/D6/SQRT(A6-B6)*(ATAN(SQRT(B6)/SQRT(A6-B6)))-ATAN(SQRT(B6-0.5*C6)/SQRT(A6-B6))$
7	49.5	0.5637	0.2947	$=4/D7/SQRT(A7-B7)*(ATAN(SQRT(B7)/SQRT(A7-B7)))-ATAN(SQRT(B7-0.5*C7)/SQRT(A7-B7))$
8	79.5	0.5637	0.2947	$=4/D8/SQRT(A8-B8)*(ATAN(SQRT(B8)/SQRT(A8-B8)))-ATAN(SQRT(B8-0.5*C8)/SQRT(A8-B8))$
9	99.5	0.5637	0.2947	$=4/D9/SQRT(A9-B9)*(ATAN(SQRT(B9)/SQRT(A9-B9)))-ATAN(SQRT(B9-0.5*C9)/SQRT(A9-B9))$
10	124.5	0.5637	0.2947	$=4/D10/SQRT(A10-B10)*(ATAN(SQRT(B10)/SQRT(A10-B10)))-ATAN(SQRT(B10-0.5*C10)/SQRT(A10-B10))$
11	149.5	0.5637	0.2947	$=4/D11/SQRT(A11-B11)*(ATAN(SQRT(B11)/SQRT(A11-B11)))-ATAN(SQRT(B11-0.5*C11)/SQRT(A11-B11))$
12				

Here are the results:

A	B	C	D	E
$[H_2]^0$	$[Br_2]^0$	[HBr]	tau	$k_{1.5}$
0 0.5637	0.2947	0.0699	14.5	0.016782
4 0.5637	0.2947	0.0985	24.5	0.014386
8 0.5637	0.2947	0.1262	34.5	0.013456
12 0.5637	0.2947	0.1644	49.5	0.012715
16 0.5637	0.2947	0.2093	79.5	0.010596
20 0.5637	0.2947	0.2306	99.5	0.009564
24 0.5637	0.2947	0.2502	124.5	0.008494
28 0.5637	0.2947	0.2619	149.5	0.007513
32 0.2281	0.1517	0.0322	19.5	0.019823
36 0.2281	0.1517	0.0527	34.5	0.01916
40 0.2281	0.1517	0.0713	54.5	0.017116
44 0.2281	0.1517	0.0912	79.5	0.015742
48 0.2281	0.1517	0.104	99.5	0.014815
52 0.2281	0.1517	0.1142	124.5	0.013355
56 0.2281	0.1517	0.1217	149.5	0.012096
60 0.2281	0.1517	0.1295	174.5	0.01127
64 0.3103	0.5069	0.0492	15	0.015663
68 0.3103	0.5069	0.1031	35	0.014984
72 0.3103	0.5069	0.1406	55	0.013632
76 0.3103	0.5069	0.1752	80	0.012232
80 0.3103	0.5069	0.1963	102	0.011073
84 0.3103	0.5069	0.2179	125	0.010352
88 0.3103	0.5069	0.236	155	0.009294
92 0.3103	0.5069	0.2533	196	0.008107

Neither fit perfectly, but equation (3.K.3) fits better. One does need to do an analysis of variance (ANOVA) to see if the difference is statistically significant.

### 3.18 SUGGESTIONS FOR FURTHER READING

Techniques for analysis of kinetic data are discussed in:

J. H. Van' Hoff, *Studies in Chemical Dynamics*, Edward Arnold, London, 1896.  
 K. J. Laidler, *Chemical Kinetics*, Harper & Row, New York, 1987.  
 J. I. Steinfeld, J. S. Francisco, and W. L. Hase, *Chemical Kinetics and Dynamics*, 2nd ed., Prentice Hall, Upper Saddle River, ND, 1998.  
 B. Fogler, *Elements of Chemical Reaction Engineering*, 3rd ed., Prentice-Hall, Upper Saddle River ND, 1998.

A	B	C	D	E
23	0.3103	0.5069	0.1031	$=2/D23/SQRT(B23-A23)*LN((SQRT(B23-0.5*C23)+SQRT(B23-A23))/(SQRT(B23)+SQRT(B23-A23)))$
24	0.3103	0.5069	0.1406	$=2/D24/SQRT(B24-A24)*LN((SQRT(B24-0.5*C24)+SQRT(B24-A24))/(SQRT(B24)+SQRT(B24-A24)))$
25	0.3103	0.5069	0.1752	$=2/D25/SQRT(B25-A25)*LN((SQRT(B25-0.5*C25)+SQRT(B25-A25))/(SQRT(B25)+SQRT(B25-A25)))$
26	0.3103	0.5069	0.1963	$=2/D26/SQRT(B26-A26)*LN((SQRT(B26-0.5*C26)+SQRT(B26-A26))/(SQRT(B26)+SQRT(B26-A26)))$
27	0.3103	0.5069	0.2179	$=2/D27/SQRT(B27-A27)*LN((SQRT(B27-0.5*C27)+SQRT(B27-A27))/(SQRT(B27)+SQRT(B27-A27)))$
28	0.3103	0.5069	0.236	$=2/D28/SQRT(B28-A28)*LN((SQRT(B28-0.5*C28)+SQRT(B28-A28))/(SQRT(B28)+SQRT(B28-A28)))$
29	0.3103	0.5069	0.2533	$=2/D29/SQRT(B29-A29)*LN((SQRT(B29-0.5*C29)+SQRT(B29-A29))/(SQRT(B29)+SQRT(B29-A29)))$