Figure E5-2.1 Plot reciprocal of C_A versut t for a second-order reaction.

We see from the Excel anaysis and plot that the slope of the line is 0.12 dm³/mol/min.

$$k' = 0.12 \frac{dm^3}{mol \cdot min}$$

Calculating k,

$$k = \frac{k'}{C_{B0}} = \frac{0.12}{0.5} \frac{dm^3/mol/min}{mol/dm^3} = 0.24\left(\frac{dm^3}{mol}\right)^2/min$$

The rate law is

$$-r_A = \left[0.24\left(\frac{dm^3}{mol}\right)^2/min\right]C_A^2 C_B$$

We note the integral method tends to smooth the data.

Polymath

An alternate computer solution would be to regress $\frac{1}{C_A}$ versus t with a software package such as Polymath.

$$\frac{1}{C_A} = \frac{1}{C_{A0}} + k't \tag{E5-2.4}$$

Let CA inverse $= \frac{1}{C_A}$, $a_0 = \frac{1}{C_{A0}}$, and $a_1 = k'$ and then enter the data in Table E5-2.1.

Linear Regression Report

Model: CAinverse = a0 + a1*t

Variable	Value	95% confidence
a0	20.117525	0.225264
a1	0.124794	0.0012495

From the Polymath output, we obtain $k' = 0.125$ dm³/mol/min, which yields $k = 0.25$ dm³/mol/min. We shall discuss regression in Example 5-3.

By comparing the methods of analysis of the rate data presented in Example 5-2, we note that the differential method tends to accentuate the uncertainties in the data, while the integral method tends to smooth the data, thereby disguising the uncertainties in it. In most analyses, it is imperative that the engineer know the limits and uncertainties in the data. This prior knowledge is necessary to provide for a safety factor when scaling up a process from laboratory experiments to design either a pilot plant or full-scale industrial plant.

5.2.3 Nonlinear Regression

In nonlinear regression analysis, we search for those parameter values that minimize the sum of the squares of the differences between the measured values and the calculated values for all the data points.[2] Not only can nonlinear regression find the best estimates of parameter values, it can also be used to discriminate between different rate law models, such as the Langmuir–Hinshelwood models discussed in Chapter 10. Many software programs are available to find these parameter values so that all one has to do is enter the data. The Polymath software will be used to illustrate this technique. In order to carry out the search efficiently, in some cases one has to enter initial estimates of the parameter values close to the actual values. These estimates can be obtained using the linear-least-squares technique discussed on the CD-ROM Professional Reference Shelf.

We will now apply nonlinear least-squares analysis to reaction rate data to determine the rate law parameters. Here we make estimates of the parameter values (e.g., reaction order, specific rate constants) in order to calculate the rate of reaction, r_c. We then search for those values that will minimize the sum of the squared differences of the measured reaction rates, r_m, and the calculated reaction rates, r_c. That is, we want the sum of $(r_m - r_c)^2$ for all data points to be minimum. If we carried out N experiments, we would want to find the parameter values (e.g., E, activation energy, reaction orders) that would minimize the quantity

$$\sigma^2 = \frac{s^2}{N-K} = \sum_{i=1}^{N} \frac{(r_{im} - r_{ic})^2}{N-K} \qquad (5\text{-}34)$$

where

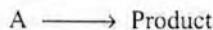$s^2 = \Sigma\, (r_{im} - r_{ie})^2$

$N = $ number of runs

$K = $ number of parameters to be determined

$r_{im} = $ measured reaction rate for run i (i.e., $-r_{Aim}$)

$r_{ic} = $ calculated reaction rate for run i (i.e., $-r_{Aic}$)

---

[2] See also R. Mezakiki and J. R. Kittrell, *AIChE J.*, *14*, 513 (1968), and J. R. Kittrell, *Ind. Eng. Chem.*, *61* (5), 76–78 (1969).

To illustrate this technique, let's consider the first-order reaction

$$A \longrightarrow Product$$

for which we want to learn the reaction order, α, and the specific reaction rate,

$$r = kC_A^\alpha$$

The reaction rate will be measured at a number of different concentrations. W now choose values of k and α and calculate the rate of reaction (r_{ic}) at eac concentration at which an experimental point was taken. We then subtract th calculated value (r_{ic}) from the measured value (r_{im}), square the result, and su: the squares for all the runs for the values of k and α we have chosen.

This procedure is continued by further varying α and k until we find the best values, that is, those values that minimize the sum of the squares. Mar well-known searching techniques are available to obtain the minimum valu σ_{min}^2.[3] Figure 5-7 shows a hypothetical plot of the sum of the squares as function of the parameters α and k:
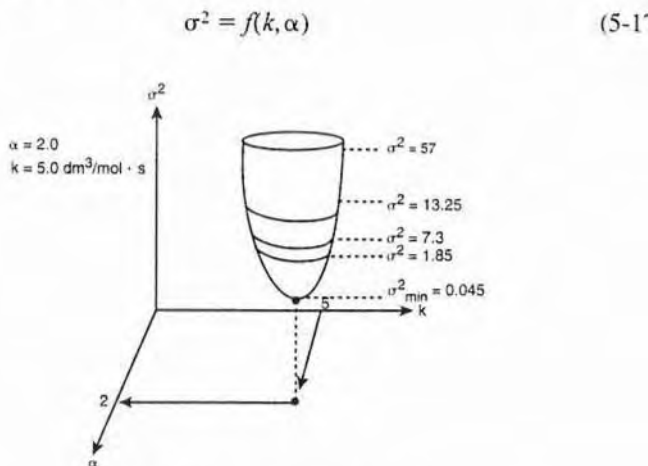
$$\sigma^2 = f(k, \alpha) \tag{5-1}$$

Figure 5-7   Minimum sum of squares.

In searching to find the parameter values that give the minimum of th sum of squares σ^2, one can use a number of optimization techniques or sof ware packages. The searching procedure begins by guessing parameter value and then calculating r_c and then σ^2 for these values. Next a few sets of param eters are chosen around the initial guess, and σ^2 is calculated for these sets a well. The search technique looks for the smallest value of σ^2 in the vicinity c

[3] (a) B. Carnahan and J. O. Wilkes, *Digital Computing and Numerical Methods* (Ne York: Wiley, 1973), p. 405. (b) D. J. Wilde and C. S. Beightler, *Foundations of Opt mization* 2nd ed. (Upper Saddle River, N.J.: Prentice Hall, 1979). (c) D. Miller an M. Frenklach, *Int. J. Chem. Kinet., 15,* 677 (1983).
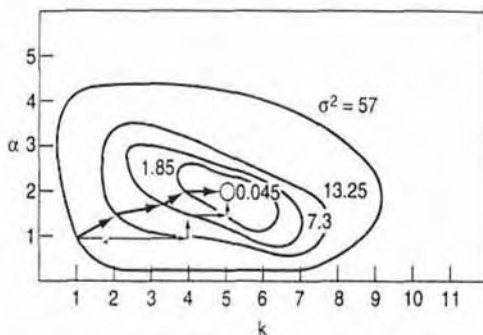
Figure 5-8 Trajectory to find the best values of k and α.

$\alpha = 2$
$k = 5 \ dm^3/mol \cdot s$

the initial guess and then proceeds along a trajectory in the direction of decreasing σ^2 to choose different parameter values and determine the corresponding σ^2. The trajectory is continually adjusted so as always to proceed in the direction of decreasing σ^2 until the minimum value of σ^2 is reached. A schematic of this procedure is shown in Figure 5-8, where the parameter values at the minimum are $\alpha = 2$ and $k = 5 \ s^{-1}$. If the equations are highly nonlinear, the initial guess is extremely important. In some cases it is useful to try different initial guesses of the parameter to make sure that the software program converges on the same minimum for the different initial guesses. The dark lines and heavy arrows represent a computer trajectory, and the light lines and arrows represent the hand calculations. In extreme cases, one can use *linear least squares* (see CD-ROM) to obtain initial estimates of the parameter values.

Vary the initial guesses of parameters to make sure you find the true minimum.

A number of software packages are available to carry out the procedure to determine the best estimates of the parameter values and the corresponding confidence limits. All one has to do is to type the experimental values in the computer, specify the model, enter the initial guesses of the parameters, and then push the computer button, and the best estimates of the parameter values along with 95% confidence limits appear. If the confidence limits for a given parameter are larger than the parameter itself, the parameter is probably not significant and should be dropped from the model. After the appropriate model parameters are eliminated, the software is run again to determine the best fit with the new model equation.

Reference Shelf

Concentration-Time Data.   We will now use nonlinear regression to determine the rate law parameters from concentration–time data obtained in batch experiments. We recall that the combined rate law-stoichiometry-mole balance for a constant-volume batch reactor is

$$\frac{dC_A}{dt} = -kC_A^\alpha \tag{5-6}$$

We now integrate Equation (5-6) to give

$$C_{A0}^{1-\alpha} - C_A^{1-\alpha} = (1-\alpha)kt$$

Rearranging to obtain the concentration as a function of time, we obtain

$$C_A = [C_{A0}^{1-\alpha} - (1-\alpha)kt]^{1/(1-\alpha)} \tag{5-18}$$

Now we could use Polymath or MATLAB to find the values of α and k that would minimize the sum of squares of the differences between the measured and calculated concentrations. That is, for N data points,

$$s^2 = \sum_{i=1}^{N} (C_{Ami} - C_{Aci})^2 = \sum_{i=1}^{N} \left[C_{Ami} - [C_{A0}^{1-\alpha} - (1-\alpha)kt_i]^{1/(1-\alpha)} \right]^2 \tag{5-19}$$

we want the values of α and k that will make s^2 a minimum.

If Polymath is used, one should use the absolute value for the term in brackets in Equation (5-19), that is,

$$s^2 = \sum_{i=1}^{n} \left[C_{Ami} - \{(abs[C_{A0}^{1-\alpha} - (1-\alpha)kt_i]\}^{1/(1-\alpha)} \right]^2 \tag{5-20}$$

Another way to solve for the parameter values is to use time rather than concentrations:

$$\boxed{t_c = \frac{C_{A0}^{1-\alpha} - C_A^{1-\alpha}}{k(1-\alpha)}} \tag{5-21}$$

That is, we find the values of k and α that minimize

$$s^2 = \sum_{i=1}^{N} (t_{mi} - t_{ci})^2 = \sum_{i=1}^{N} \left[t_{mi} - \frac{C_{A0}^{1-\alpha} - C_{Ai}^{1-\alpha}}{k(1-\alpha)} \right]^2 \tag{5-22}$$
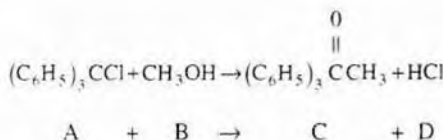
Finally, a discussion of *weighted least squares* as applied to a first-order reaction is provided in the *Professional Reference Shelf R5.2* on the CD-ROM.

Reference Shelf

Example 5–3 Use of Regression to Find the Rate Law Parameters

We shall use the reaction and data in Example 5-1 to illustrate how to use regression to find α and k'.

$$(C_6H_5)_3CCl + CH_3OH \rightarrow (C_6H_5)_3 \overset{\displaystyle O}{\overset{\displaystyle \|}{C}} CH_3 + HCl$$

$$A \quad + \quad B \quad \rightarrow \quad C \quad + \quad D$$

The Polymath regression program is included on the CD-ROM. Recalling Equation (E5-1.5)

$$-\frac{dC_A}{dt} = k'C_A^\alpha \tag{E5-1.5}$$

and integrating with the initial condition when $t = 0$ and $C_A = C_{A0}$ for $\alpha \ne 1.0$

$$t = \frac{1}{k'}\frac{C_{A0}^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1-\alpha)} \tag{E5-3.1}$$

Substituting for the initial concentration $C_{A0} = 0.05$ mol/dm³

$$t = \frac{1}{k'}\frac{(0.05)^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1-\alpha)} \tag{E5-3.2}$$

Let's do a few calculations by hand to illustrate regression. We will first assume a value of α and k and then calculate t for the concentrations of A given in Table E5-1.1. We will then calculate the sum of the squares of the difference between the measured times t_m and the calculated times (i.e., s^2). For N measurements,

$$s^2 = \sum_{i=1}^{N}(t_{mi} - t_{ci})^2 = \sum_{i=1}^{N}\left(t_{mi} - \frac{C_{A0}^{1-\alpha} - C_A^{1-\alpha}}{k'(1-\alpha)}\right)^2$$

Our first guess is going to be $\alpha = 3$ and $k' = 5$, with $C_{A0} = 0.05$. Equation (E5-3.2) becomes

$$t_c = \frac{1}{2k'}\left[\frac{1}{C_A^2} - \frac{1}{C_{A0}^2}\right] = \frac{1}{10}\left[\frac{1}{C_A^2} - 400\right] \tag{E5-3.3}$$

We now make the calculations for each measurement of concentration and fill in columns 3 and 4 of Table E5-3.1. For example, when $C_A = 0.038$ mol/dm³ then

$$t_{c1} = \frac{1}{10}\left[\frac{1}{(0.038)^2} - 400\right] = 29.2 \text{ min}$$

which is shown in Table E5-3.1 on line 2 for guess 1. We next calculate the squares of difference $(t_{m1} - t_{c1})^2 = (50 - 29.2)^2 = 433$. We continue in this manner for points 2, 3, and 4 to calculate the sum $s^2 = 2916$.

After calculating s^2 for $\alpha = 3$ and $k = 5$, we make a second guess for α and k'. For our second guess we choose $\alpha = 2$ and $k = 5$; Equation (E5-3.2) becomes

$$t_c = \frac{1}{k'}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right] = \frac{1}{5}\left[\frac{1}{C_A} - 20\right] \tag{E5-3.4}$$

We now proceed with our second guess to find the sum of $(t_m - t_c)^2$ to be $s^2 = 49.895$, which is far worse than our first guess. So we continue to make more guesses of α and k and find s^2. Let's stop and take a look at t_c for guesses 3 and 4.

We shall only use four points for this illustration.

TABLE E5-3.1.   REGRESSION OF DATA

			Guess 1 $\alpha = 3$ $k' = 5$		Guess 2 $\alpha = 2$ $k' = 5$		Guess 3 $\alpha = 2$ $k' = 0.2$		Guess 4 $\alpha = 2$ $k' = 0.1$	
	Original Data									
	t (min)	$C_A \times 10^3$ (mol/dm³)	t_C	$(t_m - t_C)^2$	t_C	$(t_m - t_C)^2$	t_C	$(t_m - t_C)^2$	t_C	$(t_m - t_C)^2$
1	0	50	0	0	0	0	0	0	0	0
2	50	38	29.2	433	1.26	2,375	31.6	339	63.2	174
3	100	30.6	66.7	1,109	2.5	9,499	63.4	1,340	126.8	718
4	200	22.2	163	1,375	5.0	38,622	125.2	5,591	250	2,540
				$s^2 = 2916$		$s^2 = 49,895$		$s^2 = 7270$		$s^2 = 3432$

We see that ($k' = 0.2$ dm³/mol · min) underpredicts the time (e.g., 31.6 min vers 50 minutes), while ($k' = 0.1$ dm³/mol · min) overpredicts the time (e.g., 63 min vε sus 50 minutes). We could continue in this manner by choosing k' between $0.1 <$ < 0.2, but why bother to go to all the trouble? Nobody has that much time on th hands. Why don't we just let the Polymath regression program find the values of and α that will minimize s^2?

The Polymath tutorial on the CD-ROM shows screen shots of how to en the raw data in Table E5-1.1 and to carry out a nonlinear regression on Equati (E5-3.1). For $C_{A0} = 0.05$ mol/dm³, that is, Equation (E5-3.1) becomes

A Polymath tutorial on regression is given on the CD-ROM.

$$t_c = \frac{1}{k'} \frac{(0.05)^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1 - \alpha)}$$

We want to minimize the sum to give α and k'

$$s^2 = \sum_{i=1}^{N} (t_{mi} - t_{ci})^2 = \sum_{i=1}^{N} \left[t_{mi} - \frac{0.05^{1-\alpha} - C_{Ai}^{1-\alpha}}{k(1-\alpha)} \right]^2 \qquad (5-2$$

TABLE E5-3.2.   RESULTS OF 1ST REGRESSION

POLYMATH Results
Example 5-3 Use of Regression to Find Rate Law Parameters 08-05-2004

Nonlinear regression (L-M)

Model: t = (.05^(1-a)-Ca^(1-a))/(k'(1-a))

Variable	Ini guess	Value	95% confidence
a	3	2.04472	0.0317031
k	0.1	0.1467193	0.0164118

Nonlinear regression settings
Max # iterations = 64

Precision
R^2   = 0.9999717
R^2adj = 0.999966
Rmsd   = 0.2011604
Variance = 0.3965818

TABLE E5-3.3.   RESULTS OF 2ND REGRESSION

POLYMATH Results
Example 5-3 Use of Regression to Find Rate Law Parameters 08-05-2004

Nonlinear regression (L-M)

Model: t = (.05^(1-2)-Ca^(1-2))/(k'(1-2))

Variable	Ini guess	Value	95% confiden
k	0.1	0.1253404	7.022E-04

Nonlinear regression settings
Max # iterations = 64

Precision
R^2   = 0.9998978
R^2adj = 0.9998978
Rmsd   = 0.3821581
Variance = 1.1926993

The results shown are

$$\boxed{\begin{array}{l} \alpha = 2.04 \\ k' = 0.147 \ \text{dm}^3/\text{mol}\cdot\text{min} \end{array}} \qquad \boxed{\begin{array}{l} \alpha = 2.0 \\ k' = 0.125 \ \text{dm}^3/\text{mol}\cdot\text{min} \end{array}}$$

We shall round off α to make the reaction second order, (i.e., $\alpha = 2.00$). Now having fixed α at 2.0, we must do another regression [cf. Table E5-3.3] on k' because the k' given in Table E.5-3.1 is for $\alpha = 2.0447$. We now regress the equation

$$t = \frac{1}{k'}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right]$$

and find $k' = 0.125$ dm³/mol · min.

$$k = \frac{k'}{C_{A0}} = 0.25 \left(\frac{\text{dm}^3}{\text{mol}}\right)^2/\text{min}$$

We note that the reaction order is the same as that in Examples 5-1 and 5-2; however, the value of k is about 8% larger.

Model Discrimination.   One can also determine which model or equation best fits the experimental data by comparing the sums of the squares for each model and then choosing the equation with a smaller sum of squares and/or carrying out an F-test. Alternatively, we can compare the residual plots for each model. These plots show the error associated with each data point, and one looks to see if the error is randomly distributed or if there is a trend in the error. When the error is randomly distributed, this is an additional indication that the correct rate law has been chosen. An example of model discrimination using nonlinear regression is given on the CD-ROM in Chapter 10 of the *Summary Notes*.

5.3 Method of Initial Rates

The use of the differential method of data analysis to determine reaction orders and specific reaction rates is clearly one of the easiest, since it requires only one experiment. However, other effects, such as the presence of a significant *reverse* reaction, could render the differential method ineffective. In these cases, the method of initial rates could be used to determine the reaction order and the specific rate constant. Here, a series of experiments is carried out at different initial concentrations, C_{A0}, and the initial rate of reaction, $-r_{A0}$, is determined for each run. The initial rate, $-r_{A0}$, can be found by differentiating the data and extrapolating to zero time. For example, in the Trityl–Methanol reaction shown in Example 5-1, the initial rate was found to be 0.00028 mol/dm³ · min. By various plotting or numerical analysis techniques relating $-r_{A0}$ to C_{A0}, we can obtain the appropriate rate law. If the rate law is in the form

$$-r_{A0} = kC_{A0}^{\alpha}$$

the slope of the plot of $\ln(-r_{A0})$ versus $\ln C_{A0}$ will give the reaction order α.
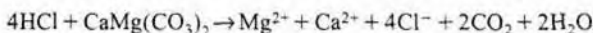
Links

Used when reactions are reversible

OIL
WELL

ACID

Example 5–4 Method of Initial Rates in Solid–Liquid Dissolution Kinetics

The dissolution of dolomite, calcium magnesium carbonate, in hydrochloric acid is a reaction of particular importance in the acid stimulation of dolomite oil reservoirs.[4] The oil is contained in pore space of the carbonate material and must flow through the small pores to reach the well bore. In matrix stimulation, HCl is injected into a well bore to dissolve the porous carbonate matrix. By dissolving the solid carbonate, the pores will increase in size, and the oil and gas will be able to flow out at faster rates, thereby increasing the productivity of the well.[5] The dissolution reaction is

An important
reaction for
enhancement of oil
flow in carbonate
reservoirs

$$4HCl + CaMg(CO_3)_2 \rightarrow Mg^{2+} + Ca^{2+} + 4Cl^- + 2CO_2 + 2H_2O$$

The concentration of HCl at various times was determined from atomic absorption spectrophotometer measurements of the calcium and magnesium ions.

Determine the reaction order with respect to HCl from the data presented in Figure E5-4.1 for this batch reaction. Assume that the rate law is in the form given by Equation (5-1) and that the combined rate law and mole balance for HCl can be given by Equation (5-6).
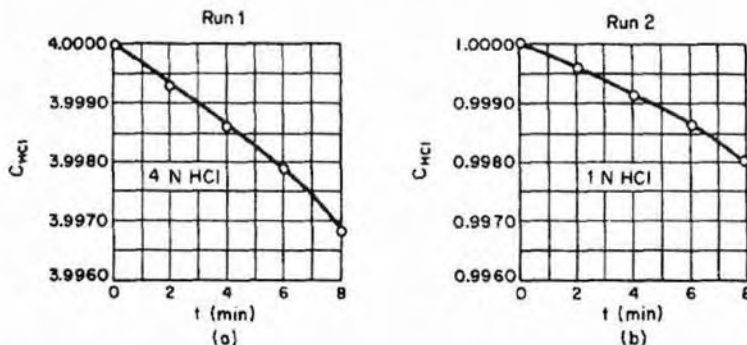

Wormholes etched
by acid

Figure E5-4.1   Concentration–time data.

Solution

Evaluating the mole balance on a constant-volume batch reactor at time $t = 0$ gives

$$\left(-\frac{dC_{HCl}}{dt}\right)_0 = -(r_{HCl})_0 = kC_{HCl,0}^\alpha \qquad (E5\text{-}4.1)$$

Taking the log of both sides of Equation (E5-4.1), we have

$$\ln\left(-\frac{dC_{HCl}}{dt}\right)_0 = \ln k + \alpha \ln C_{HCl,0} \qquad (E5\text{-}4.2)$$

[4] K. Lund, H. S. Fogler, and C. C. McCune, *Chem. Eng. Sci.*, 28, 691 (1973).

[5] M. Hoefner and H. S. Fogler, *AIChE Journal*, 34(1), 45 (1988).

The derivative at time $t = 0$ can be found from the slope of the plot of concentration versus time evaluated at $t = 0$. Figure E5-4.1(a) and (b) give

4 N HCl solution	1 N HCl solution
$-r_{HCl,0} = -\dfrac{3.9982 - 4.0000}{5 - 0}$	$-r_{HCl,0} = -\dfrac{0.9987 - 1.0000}{6 - 0}$
$-r_{HCl,0} = 3.6 \times 10^{-4}$ mol/dm$^3 \cdot$ min	$-r_{HCl,0} = 2.2 \times 10^{-4}$ mol/dm$^3 \cdot$ min

Converting to a rate per unit area, $-r_A''$, and to seconds (30 cm^2 of solid per liter of solution), the rates at 1 N and 4 N become 1.2×10^{-7} mol/cm$^2 \cdot$ s and 2.0×10^{-7} mol/cm$^2 \cdot$ s, respectively. We also could have used either Polymath or the differentiation formulas to find the derivative at $t = 0$.

If we were to continue in this manner, we would generate the following data set in Table E5-4.1.[6]

TABLE E5-4.1.

$C_{HCl,0}$ (mol/dm^3)	1.0	4.0	2.0	0.1	0.5
$-r_{HCl,0}''$ (mol/cm$^2 \cdot$ s) $\times 10^7$	1.2	2.0	1.36	0.36	0.74

These data are plotted on Figure E5-4.2. The slope of this ln-ln plot of $-r_{HCl,0}''$ versus $C_{HCl,0}$ shown in Figure E5-4.2 gives a reaction order of 0.44. The rate law is

$$-r_{HCl,0}'' = kC_{HCl}^{0.44} \tag{E5-4.3}$$

For this dissolution of dolomite in HCl, the reaction order was also found to vary with temperature.

$\alpha = \dfrac{\Delta Y}{\Delta X} = \dfrac{0.88}{2} = 0.44$
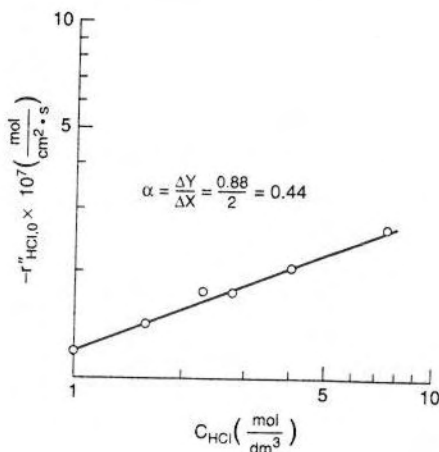
Figure E5-4.2   Initial rate as a function of initial HCl concentration.

[6] K. Lund, H. S. Fogler, and C. C. McCune, *Chem. Eng. Sci.*, 28, 691 (1973). C. Fredd and H. S. Fogler, *AIChE J.*, 44, p1933 (1998).

5.4 Method of Half-Lives

The half-life of a reaction, $t_{1/2}$, is defined as the time it takes for the conce tration of the reactant to fall to half of its initial value. By determining half-life of a reaction as a function of the initial concentration, the reacti order and specific reaction rate can be determined. If two reactants involved in the chemical reaction, the experimenter will use the method excess in conjunction with the method of half-lives to arrange the rate law the form

$$-r_A = kC_A^\alpha \qquad (5$$

For the irreversible reaction

$$A \longrightarrow \text{Products}$$
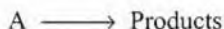
The concept of a
half life, $t_{1/2}$, is
very important in
drug medication.
a mole balance on species A in a constant-volume batch reaction system co bined with the rate law results in the following expression:

$$-\frac{dC_A}{dt} = -r_A = kC_A^\alpha \qquad (5$$

Integrating with the initial condition $C_A = C_{A0}$ when $t = 0$, we find that

$$t = \frac{1}{k(\alpha - 1)}\left(\frac{1}{C_A^{\alpha-1}} - \frac{1}{C_{A0}^{\alpha-1}}\right)$$

$$= \frac{1}{kC_{A0}^{\alpha-1}(\alpha - 1)}\left[\left(\frac{C_{A0}}{C_A}\right)^{\alpha-1} - 1\right] \qquad (5\text{-}$$

The half-life is defined as the time required for the concentration to drop half of its initial value; that is,

$$t = t_{1/2} \quad \text{when} \quad C_A = \tfrac{1}{2}C_{A0}$$

Substituting for C_A in Equation (5-23) gives us

$$t_{1/2} = \frac{2^{\alpha-1} - 1}{k(\alpha - 1)}\left(\frac{1}{C_{A0}^{\alpha-1}}\right) \qquad (5\text{-}$$

There is nothing special about using the time required for the concent tion to drop to one-half of its initial value. We could just as well use the ti required for the concentration to fall to $1/n$ of the initial value, in which ca

$$t_{1/n} = \frac{n^{\alpha-1} - 1}{k(\alpha - 1)}\left(\frac{1}{C_{A0}^{\alpha-1}}\right) \qquad (5\text{-}$$

For the method of half-lives, taking the natural log of both sides of Equation (5-24),

$$\ln t_{1/2} = \ln \frac{2^{\alpha-1}-1}{(\alpha-1)k} + (1-\alpha)\ln C_{A0}$$

we see that the slope of the plot of $\ln t_{1/2}$ as a function of $\ln C_{A0}$ is equal to 1 minus the reaction order [i.e., slope = $(1-\alpha)$]:
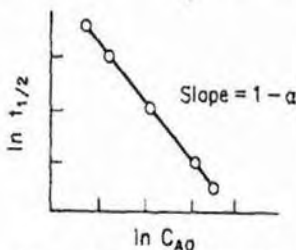

Rearranging:

$\alpha = 1 - \text{slope}$

For the plot shown in Figure 5-9, the slope is -1:

$\alpha = 1 - (-1) = 2$

The corresponding rate law is

$-r_A = kC_A^2$

Figure 5-9   Method of half-lives.

Note: We also could have used nonlinear regression on the half-life data. However, by plotting the data, one often gets a "better feel" for the accuracy and precision of the data.

5.5 Differential Reactors

Data acquisition using the method of initial rates and a differential reactor are similar in that the rate of reaction is determined for a specified number of predetermined initial or entering reactant concentrations. A differential reactor is normally used to determine the rate of reaction as a function of either concentration or partial pressure. It consists of a tube containing a very small amount of catalyst usually arranged in the form of a thin wafer or disk. A typical arrangement is shown schematically in Figure 5-10. The criterion for a reactor being differential is that the conversion of the reactants in the bed is extremely small, as is the change in temperature and reactant concentration through the bed. As a result, the reactant concentration through the reactor is essentially constant and approximately equal to the inlet concentration. That is, the reactor is considered to be gradientless,[7] and the reaction rate is considered spatially uniform within the bed.

> Most commonly used catalytic reactor to obtain experimental data

The differential reactor is relatively easy to construct at a low cost. Owing to the low conversion achieved in this reactor, the heat release per unit volume will be small (or can be made small by diluting the bed with inert solids) so that the reactor operates essentially in an isothermal manner. When operating this reactor, precautions must be taken so that the reactant gas or liquid does not bypass or channel through the packed catalyst, but instead flows uniformly across the catalyst. If the catalyst under investigation decays rapidly, the differential reactor is not a good choice because the reaction rate parameters at the

> Limitations of the differential reactor

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[7] B. Anderson, ed., *Experimental Methods in Catalytic Research* (San Diego, Calif.: Academic Press, 1976).

start of a run will be different from those at the end of the run. In some cases sampling and analysis of the product stream may be difficult for small conversions in multicomponent systems.
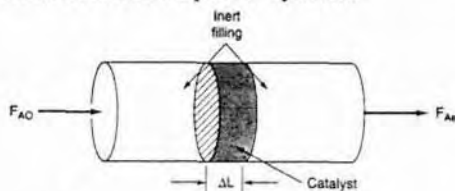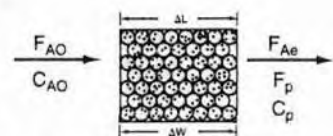

Figure 5-10 Differential reactor.

Figure 5-11 Differential catalyst bed.

$$A \rightarrow P$$

The volumetric flow rate through the catalyst bed is monitored, as are the entering and exiting concentrations (Figure 5-11). Therefore, if the weight of catalyst, ΔW, is known, the rate of reaction per unit mass of catalyst, $-r'_A$, can be calculated. Since the differential reactor is assumed to be *gradientless*, the design equation will be similar to the CSTR design equation. A steady-state mole balance on reactant A gives

$$\begin{bmatrix} \text{Flow} \\ \text{rate} \\ \text{in} \end{bmatrix} - \begin{bmatrix} \text{Flow} \\ \text{rate} \\ \text{out} \end{bmatrix} + \begin{bmatrix} \text{Rate of} \\ \text{generation} \end{bmatrix} = \begin{bmatrix} \text{Rate of} \\ \text{accumulation} \end{bmatrix}$$

$$[F_{A0}] - [F_{Ae}] + \left[\left(\frac{\text{Rate of reaction}}{\text{Mass of cat}} \right) (\text{Mass of cat}) \right] = 0$$

$$F_{A0} - F_{Ae} + (r'_A)(\Delta W) = 0$$

The subscript e refers to the exit of the reactor. Solving for $-r'_A$, we have

$$-r'_A = \frac{F_{A0} - F_{Ae}}{\Delta W} \tag{5-26}$$

The mole balance equation can also be written in terms of the concentration

Differential reactor
design equation

$$\boxed{-r'_A = \frac{v_0 C_{A0} - v C_{Ae}}{\Delta W}} \tag{5-27}$$

or in terms of the conversion or product flow rate F_P:

$$\boxed{-r'_A = \frac{F_{A0} X}{\Delta W} = \frac{F_P}{\Delta W}} \tag{5-28}$$

The term $F_{A0}X$ gives the rate of formation of the product, F_P, when the stoichiometric coefficients of A and of P are identical.

For constant volumetric flow, Equation (5-27) reduces to

$$-r_A' = \frac{v_0(C_{A0} - C_{Ae})}{\Delta W} = \frac{v_0 C_P}{\Delta W} \tag{5-29}$$

Consequently, we see that the reaction rate, $-r_A'$, can be determined by measuring the product concentration, C_P.

By using very little catalyst and large volumetric flow rates, the concentration difference, $(C_{A0} - C_{Ae})$, can be made quite small. The rate of reaction determined from Equation (5-29) can be obtained as a function of the reactant concentration in the catalyst bed, C_{Ab}:

$$-r_A' = -r_A'(C_{Ab}) \tag{5-30}$$

by varying the inlet concentration. One approximation of the concentration of A within the bed, C_{Ab}, would be the arithmetic mean of the inlet and outlet concentrations:

$$C_{Ab} = \frac{C_{A0} + C_{Ae}}{2} \tag{5-31}$$

However, since very little reaction takes place within the bed, the bed concentration is essentially equal to the inlet concentration,

$$C_{Ab} \approx C_{A0}$$

so $-r_A'$ is a function of C_{A0}:

$$-r_A' = -r_A'(C_{A0}) \tag{5-32}$$

As with the method of initial rates, various numerical and graphical techniques can be used to determine the appropriate algebraic equation for the rate law. When collecting data for fluid-solid reacting systems, care must be taken that we use high flow rates through the differential reactor and small catalyst particle sizes in order to avoid mass transfer limitations. If data show the reaction to be first order with a low activation energy, say 8 kcal/moles, one should suspect the data is being collected in the mass transfer limited regime. We will expand on mass transfer limitations and how to avoid them in Chapters 10, 11, and 12.

CAUTION

Example 5–5 Differential Reactor

The formation of methane from carbon monoxide and hydrogen using a nickel alyst was studied by Pursley.[8] The reaction

$$3H_2 + CO \rightarrow CH_4 + 2H_2O$$
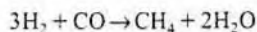
was carried out at 500°F in a differential reactor where the effluent concentration methane was measured.

(a) Relate the rate of reaction to the exit methane concentration.

(b) The reaction rate law is assumed to be the product of a function of the par pressure of CO, $f(CO)$, and a function of the partial pressure of H_2, $g(H_2)$

$$r'_{CH_4} = f(CO) \cdot g(H_2) \tag{E5-}$$

Determine the reaction order with respect to carbon monoxide, using the data Table E5-5.1. Assume that the functional dependence of r'_{CH_4} on P_{CO} is of the f

$$r'_{CH_4} \sim P_{CO}^{\alpha} \tag{E5-}$$

TABLE E5-5.1.   RAW DATA

Run	P_{CO} (atm)	P_{H_2} (atm)	C_{CH_4} (mol/dm³)
1	1	1.0	1.73×10^{-4}
2	1.8	1.0	4.40×10^{-4}
3	4.08	1.0	10.0×10^{-4}
4	1.0	0.1	1.65×10^{-4}
5	1.0	0.5	2.47×10^{-4}
6	1.0	4.0	1.75×10^{-4}

P_{H_2} is constant in
Runs 1, 2, 3
P_{CO} is constant in
Runs 4, 5, 6

The exit volumetric flow rate from a differential packed bed containing 10 g of alyst was maintained at 300 dm³/min for each run. The partial pressures of H_2 CO were determined at the entrance to the reactor, and the methane concentra was measured at the reactor exit.

Solution

(a) In this example the product composition, rather than the reactant concentrat is being monitored. $-r'_{CO}$ can be written in terms of the flow rate of methane fr the reaction,

$$-r'_{CO} = r'_{CH_4} = \frac{F_{CH_4}}{\Delta W}$$

[8] J. A. Pursley, An Investigation of the Reaction between Carbon Monoxide and Hyc gen on a Nickel Catalyst above One Atmosphere, Ph.D. thesis, University of Michig

Substituting for F_{CH_4} in terms of the volumetric flow rate and the concentration of methane gives

$$-r'_{CO} = \frac{v_0 C_{CH_4}}{\Delta W} \qquad (E5\text{-}5.3)$$

Since v_0, C_{CH_4}, and ΔW are known for each run, we can calculate the rate of reaction. For run 1:

$$-r'_{CO} = \left(\frac{300 \text{ dm}^3}{\text{min}}\right) \frac{1.73 \times 10^{-4}}{10 \text{ g cat}} \text{ mol/dm}^3 = 5.2 \times 10^{-3} \frac{\text{mol CH}_4}{\text{g cat} \times \text{min}}$$

The rate for runs 2 through 6 can be calculated in a similar manner (Table E5-5.2).

<div align="center">TABLE E5-5.2.   RAW AND CALCULATED DATA</div>

Run	P_{CO} (atm)	P_{H_2} (atm)	C_{CH_4} (mol/dm^3)	$r'_{CH_4} \left(\dfrac{\text{mol CH}_4}{\text{cat} \times \text{min}}\right)$
1	1.0	1.0	1.73×10^{-4}	5.2×10^{-3}
2	1.8	1.0	4.40×10^{-4}	13.2×10^{-3}
3	4.08	1.0	10.0×10^{-4}	30.0×10^{-3}
4	1.0	0.1	1.65×10^{-4}	4.95×10^{-3}
5	1.0	0.5	2.47×10^{-4}	7.42×10^{-3}
6	1.0	4.0	1.75×10^{-4}	5.25×10^{-3}

Determining the Rate Law Dependence in CO

For constant hydrogen concentration, the rate law

$$r'_{CH_4} = k P_{CO}^{\alpha} \cdot g(P_{H_2})$$

can be written as

$$r'_{CH_4} = k' P_{CO}^{\alpha} \qquad (E5\text{-}5.4)$$

Taking the log of Equation (E5-5.4) gives us

$$\ln(r'_{CH_4}) = \ln k' + \alpha \ln P_{CO}$$

We now plot $\ln(r'_{CH_4})$ versus $\ln P_{CO}$ for runs 1, 2, and 3.

(b) Runs 1, 2, and 3, for which the H_2 concentration is constant, are plotted in Figure E5-5.1. We see from the Excel plot that $\alpha = 1.22$. Had we included more points we would have found that the reaction is essentially first order with $\alpha = 1$, that is,

$$-r'_{CO} = k' P_{CO} \qquad (E5\text{-}5.5)$$

From the first three data points where the partial pressure of H_2 is constant, we see the rate is linear in partial pressure of CO.
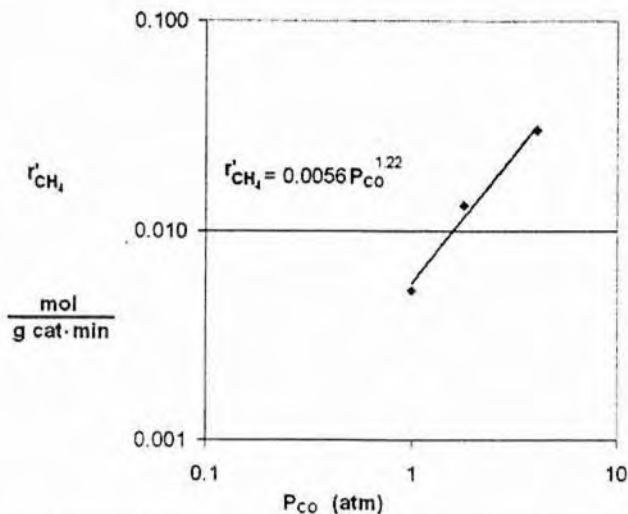
$$r'_{CH_4} = k'' P_{CO} f(P_{H_2})$$

Figure E5-5.1 Reaction rate as a function of concentration.

Now let's look at the hydrogen dependence.

Determining the Rate Law Dependence on H_2

From Table E5-5.2 it appears that the dependence of r'_{CH_4} on P_{H_2} cannot be represented by a power law. Comparing run 4 with run 5 and run 1 with run 6, we see that the reaction rate first increases with increasing partial pressure of hydrogen, and subsequently decreases with increasing P_{H_2}. That is, there appears to be a concentration of hydrogen at which the rate is maximum. One set of rate laws that is consistent with these observations is:

1. At low H_2 concentrations where r'_{CH_4} increases as P_{H_2} increases, the rate law may be of the form

$$r'_{CH_4} \sim P_{H_2}^{\beta_1} \tag{E5-5.6}$$

2. At high H_2 concentrations where r'_{CH_4} decreases as P_{H_2} increases,

$$r'_{CH_4} \sim \frac{1}{P_{H_2}^{\beta_2}} \tag{E5-5.7}$$

We would like to find one rate law that is consistent with reaction rate data at both high and low hydrogen concentrations. Application of Chapter 10 material suggests Equations (E5-5.6) and (E5-5.7) can be combined into the form

$$r'_{CH_4} \sim \frac{P_{H_2}^{\beta_1}}{1 + b P_{H_2}^{\beta_2}} \tag{E5-5.8}$$