Collection and Analysis of Rate Data

5

You can observe a lot just by watching.

Yogi Berra, New York Yankees

Overview. In Chapter 4 we have shown that once the rate law is known, it can be substituted into the appropriate design equation, and through the use of the appropriate stoichiometric relationships, we can apply the **CRE** algorithm to size any isothermal reaction system. In this chapter we focus on ways of obtaining and analyzing reaction rate data to obtain the rate law for a specific reaction. In particular, we discuss two common types of reactors for obtaining rate data: the batch reactor, which is used primarily for homogeneous reactions, and the differential reactor, which is used for solid–fluid heterogeneous reactions. In batch reactor experiments, concentration, pressure, and/or volume are usually measured and recorded at different times during the course of the reaction. Data are collected from the batch reactor during transient operation, whereas measurements on the differential reactor are made during steady-state operation. In experiments with a differential reactor, the product concentration is usually monitored for different sets of feed conditions.

Two techniques of data acquisition are presented: concentration-time measurements in a batch reactor and concentration measurements in a differential reactor. Six different methods of analyzing the data collected are used: the differential method, the integral method, the method of half-lives, method of initial rates, and linear and nonlinear regression (least-squares analysis). The differential and integral methods are used primarily in analyzing batch reactor data. Because a number of software packages (e.g., Polymath, MATLAB) are now available to analyze data, a rather extensive discussion of nonlinear regression is included. We close the chapter with a discussion of experimental planning and of laboratory reactors (CD-ROM).

5.1 The Algorithm for Data Analysis

For batch systems, the usual procedure is to collect concentration time data, which we then use to determine the rate law. Table 5-1 gives the procedure we will emphasize in analyzing reaction engineering data.

Data for homogeneous reactions is most often obtained in a batch reactor. After postulating a rate law and combining it with a mole balance, we next use any or all of the methods in Step 5 to process the data and arrive at the reaction orders and specific reaction rate constants.

Analysis of heterogeneous reactions is shown in Step 6. For gas–solid heterogeneous reactions, we need to have an understanding of the reaction and possible mechanisms in order to postulate the rate law in Step 6B. After studying Chapter 10 on heterogeneous reactions, one will be able to postulate different rate laws and then use Polymath nonlinear regression to choose the "best" rate law and reaction rate parameters.

The procedure we should use to delineate the rate law and rate law parameter is given in Table 5-1.

TABLE 5-1.   STEPS IN ANALYZING RATE DATA

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1. **Postulate a rate law.**
   A.   Power law models for homogeneous reactions

   $$-r_A = kC_A^\alpha, \quad -r_A = kC_A^\alpha C_B^\beta$$

   B.   Langmuir-Hinshelwood models for heterogeneous reactions

   $$-r_A' = \frac{kP_A}{1 + K_A P_A}, \quad -r_A' = \frac{kP_A P_B}{(1 + K_A P_A + P_B)^2}$$

2. **Select reactor type and corresponding mole balance.**
   A.   If batch reactor (Section 5.2), use mole balance on Reactant A

   $$-r_A = -\frac{dC_A}{dt} \qquad \text{(TE5-1.1)}$$

   B.   If differential PBR (Section 5.5), use mole balance on Product P (A → P)

   $$-r_A' = \frac{F_P}{\Delta W} = C_p v_0 / \Delta W \qquad \text{(TE5-1.2)}$$

3. **Process your data in terms of measured variable** (e.g., N_A, C_A, or P_A). If necessary, rewrite your mole balance in terms of the measured variable (e.g., P_A).
4. **Look for simplifications.** For example, if one of the reactants in excess, assume its concentration is constant. If the gas phase mole fraction of reactant is small, set $\varepsilon \approx 0$.
5. **For a batch reactor, calculate $-r_A$ as a function of concentration C_A to determine reaction order.**
   A.   Differential analysis
        Combine the mole balance (TE5-1.1) and power law model (TE5-1.3).

   $$-r_A = kC_A^\alpha \qquad \text{(TE5-1.3)}$$

TABLE 5-1.   STEPS IN ANALYZING RATE DATA (CONTINUED)

$$-\frac{dC_A}{dt} = kC_A^\alpha \qquad\qquad \text{(TE5-1.4)}$$

and then take the natural log.

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln(-r_A) = \ln k + \alpha \ln C_A \qquad \text{(TE5-1.5)}$$

(1) Find $-\dfrac{dC_A}{dt}$ from C_A versus t data by

    (a) Graphical method
    (b) Finite differential method
    (c) Polynominal

(2) Plot $\ln -\dfrac{dC_A}{dt}$ versus $\ln C_A$ and find reaction order α, which is the slope of

the line fit to the data.
(3) Find k.

B.   Integral method
For $-r_A = kC_A^\alpha$, the combined mole balance and rate law is

$$-\frac{dC_A}{dt} = kC_A^\alpha \qquad\qquad \text{(TE5-1.4)}$$

(1) Guess α and integrate Equation (TE5-1.6). Rearrange your equation to obtain the appropriate function of C_A, which when plotted as a function of time should be linear. If it is linear, then the guessed value of α is correct and the slope is specific reaction rate, k. If it is not linear, guess again for α. If you guess $\alpha = 0$, 1, and 2 and none of theses orders fit the data, proceed to nonlinear reression.

(2) Nonlinear regression (Polymath)
Integrate Equation (TE5-1.4) to obtain

$$t = \frac{1}{k}\left[\frac{C_{A0}^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1-\alpha)} \right] \text{ for } \alpha \neq 1 \qquad \text{(TE5-1.6)}$$

Use Polymath regression to find α and k. A Polymath tutorial on regression with screen shots is shown in the Chapter 5 *Summary Notes* on the CD-ROM and web.

6. **For differential PBR calculate $-r_A'$ as a function of C_A or P_A**

A.   Calculate $-r_A' = \dfrac{v_0 C_P}{\Delta W}$ as a function of reactant concentration, C_A.

B.   Choose model (see Chapter 10), e.g.,

$$-r_A' = \frac{kP_A}{1 + K_A P_A}$$

C.   Use nonlinear regression to find the best model and model parameters. See example on the CD-ROM *Summary Notes* using data form heterogeneous catalysis, Chapter 10.

7. **Analyze your rate law model for "goodness of fit."** Calculate a correlation coefficient.

Summary Notes

5.2 Batch Reactor Data

Batch reactors are used primarily to determine rate law parameters for hom
geneous reactions. This determination is usually achieved by measuring co
centration as a function of time and then using either the differential, integr
or nonlinear regression method of data analysis to determine the reacti
order, α, and specific reaction rate constant, k. If some reaction parame

*Process data in
terms of the
measured
variable*

other than concentration is monitored, such as pressure, the mole balance m
be rewritten in terms of the measured variable (e.g., pressure as shown in t
example in *Solved Problems* on the CD).

When a reaction is *irreversible*, it is possible in many cases to determi
the reaction order α and the specific rate constant by either nonlinear regre
sion or by numerically differentiating *concentration versus time data*. This l
ter method is most applicable when reaction conditions are such that the r
is essentially a function of the concentration of only one reactant; for examp
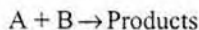if, for the decomposition reaction,

*Assume that the
rate law is of the
form
$-r_A = k_A C_A^\alpha$*

$$A \rightarrow \text{Products}$$
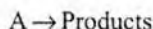
$$-r_A = k_A C_A^\alpha \tag{5-}$$

then the differential method may be used.

However, by utilizing the method of excess, it is also possible to dete
mine the relationship between $-r_A$ and the concentration of other reactan
That is, for the irreversible reaction

$$A + B \rightarrow \text{Products}$$

with the rate law

$$-r_A = k_A C_A^\alpha C_B^\beta \tag{5-}$$

where α and β are both unknown, the reaction could first be run in an exce
of B so that C_B remains essentially unchanged during the course of the rea
tion and

$$-r_A = k' C_A^\alpha \tag{5-}$$

where

Method of excess

$$k' = k_A C_B^\beta \approx k_A C_{B0}^\beta$$

After determining α, the reaction is carried out in an excess of A, f
which the rate law is approximated as

$$-r_A = k'' C_B^\beta \tag{5-}$$

where $k'' = k_A C_A^\alpha \approx k_A C_{A0}^\alpha$

Once α and β are determined. k_A can be calculated from the measurement of $-r_A$ at known concentrations of A and B:

$$k_A = \frac{-r_A}{C_A^\alpha C_B^\beta} = (dm^3/mol)^{\alpha+\beta-1}/s \tag{5-5}$$

Both α and β can be determined by using the method of excess, coupled with a differential analysis of data for batch systems.

5.2.1 Differential Method of Analysis

To outline the procedure used in the differential method of analysis, we consider a reaction carried out isothermally in a constant-volume batch reactor and the concentration recorded as a function of time. *By combining the mole balance with the rate law given by Equation* (5-1), we obtain

Constant-volume batch reactor

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

After taking the natural logarithm of both sides of Equation (5-6),

$$\boxed{\ln\left(-\frac{dC_A}{dt}\right) = \ln k_A + \alpha \ln C_A} \tag{5-7}$$

observe that the slope of a plot of $\ln(-dC_A/dt)$ as a function of $(\ln C_A)$ is the reaction order, α (Figure 5-1).

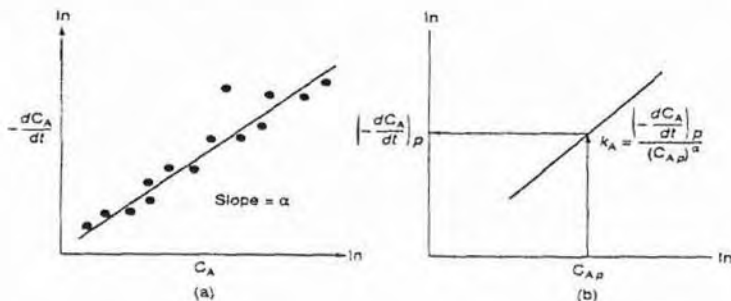**Plot $\ln\left(-\dfrac{dC_A}{dt}\right)$ versus $\ln C_A$ to find α and k_A**

Figure 5-1 Differential method to determine reaction order.

Figure 5-1(a) shows a plot of $[-(dC_A/dt)]$ versus $[C_A]$ on log-log paper (or use Excel to make the plot) where the slope is equal to the reaction order α. The specific reaction rate, k_A, can be found by first choosing a concentration

in the plot, say C_{Ap}, and then finding the corresponding value of $[-(dC_A/dt)]$ as shown in Figure 5-1(b). After raising C_{Ap} to the α power, we divide it into $[-(dC_A/dt)_p]$ to determine k_A:

$$k_A = \frac{-(dC_A/dt)_p}{(C_{Ap})^\alpha}$$

To obtain the derivative $-dC_A/dt$ used in this plot, we must differentiate the concentration-time data either numerically or graphically. We describe three methods to determine the derivative from data giving the concentration as a function of time. These methods are:

Methods for finding $-\dfrac{dC_A}{dt}$ from concentration-time data

- Graphical differentiation
- Numerical differentiation formulas
- Differentiation of a polynomial fit to the data
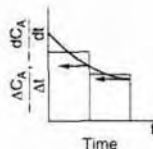
5.2.1A Graphical Method

With this method, disparities in the data are easily seen. Consequently, it is advantageous to use this technique to analyze the data before planning the next set of experiments. As explained in Appendix A.2, the graphical method involves plotting $-\Delta C_A/\Delta t$ as a function of t and then using equal-area differentiation to obtain $-dC_A/dt$. An illustrative example is also given in Appendix A.2.

See Appendix A.2.

In addition to the graphical technique used to differentiate the data, two other methods are commonly used: differentiation formulas and polynomial fitting.

5.2.1B Numerical Method

Numerical differentiation formulas can be used when the data points in the independent variable are *equally spaced*, such as $t_1 - t_0 = t_2 - t_1 = \Delta t$:

Time (min)	t_0	t_1	t_2	t_3	t_4	t_5
Concentration (mol/dm³)	C_{A0}	C_{A1}	C_{A2}	C_{A3}	C_{A4}	C_{A5}

The three-point differentiation formulas[1]

Initial point:
$$\left(\frac{dC_A}{dt}\right)_{t_0} = \frac{-3C_{A0} + 4C_{A1} - C_{A2}}{2\Delta t} \tag{5-8}$$

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[1] B. Carnahan, H. A. Luther, and J. O. Wilkes, *Applied Numerical Methods* (New York: Wiley, 1969), p. 129.

Interior points:
$$\left(\frac{dC_A}{dt}\right)_{t_i} = \frac{1}{2\Delta t}[(C_{A(i+1)} - C_{A(i-1)})] \tag{5-9}$$

$$\left[\text{e.g.,} \left(\frac{dC_A}{dt}\right)_{t_3} = \frac{1}{2\Delta t}[C_{A4} - C_{A2}] \right]$$

Last point:
$$\left(\frac{dC_A}{dt}\right)_{t_5} = \frac{1}{2\Delta t}[C_{A3} - 4C_{A4} + 3C_{A5}] \tag{5-10}$$

can be used to calculate dC_A/dt. Equations (5-8) and (5-10) are used for the first and last data points, respectively, while Equation (5-9) is used for all intermediate data points.

5.2.1C Polynomial Fit

Another technique to differentiate the data is to first fit the concentration-time data to an nth-order polynomial:

$$C_A = a_0 + a_1 t + a_2 t^2 + \cdots + a_n t^n \tag{5-11}$$

Many personal computer software packages contain programs that will calculate the best values for the constants a_i. One has only to enter the concentration-time data and choose the order of the polynomial. After determining the constants, a_i, one has only to differentiate Equation (5-11) with respect to time:

$$\frac{dC_A}{dt} = a_1 + 2a_2 t + 3a_3 t^2 + \cdots + na_n t^{n-1} \tag{5-12}$$

Thus concentration and the time rate of change of concentration are both known at any time t.

Care must be taken in choosing the order of the polynomial. If the order is too low, the polynomial fit will not capture the trends in the data and not go through many of the points. If too large an order is chosen, the fitted curve can have peaks and valleys as it goes through most all of the data points, thereby producing significant errors when the derivatives, dC_A/dt, are generated at the various points. An example of this higher order fit is shown in Figure 5-2, where the same concentration–time data fit to a third-order polynomial (a) and to a fifth-order polynomial (b). Observe how the derivative for the fifth order changes from a positive value at 15 minutes to a negative value at 20 minutes.
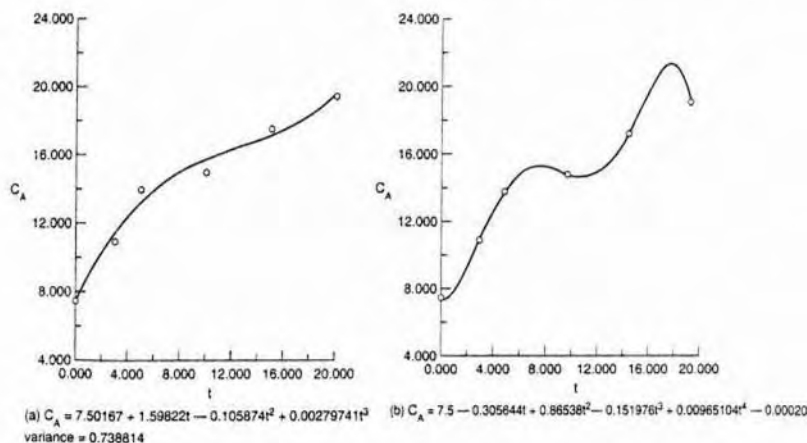
CAUTION

(a) $C_A = 7.50167 + 1.59822t - 0.105874t^2 + 0.00279741t^3$
variance = 0.738814

(b) $C_A = 7.5 - 0.305644t + 0.86538t^2 - 0.151976t^3 + 0.00965104t^4 - 0.00002$

Figure 5-2   Polynomial fit of concentration–time data.

5.2.1D Finding the Rate Law Parameters

Now, using either the graphical method, differentiation formulas, or the pol nomial derivative, the following table can be set up:

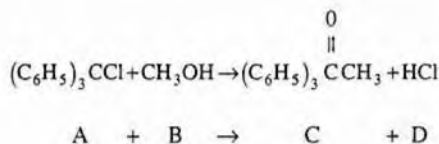| Time	t_0	t_1	t_2	t_3
Concentration	C_{A0}	C_{A1}	C_{A2}	C_{A3}
Derivative	$\left(-\dfrac{dC_A}{dt}\right)_0$	$\left(-\dfrac{dC_A}{dt}\right)_1$	$\left(-\dfrac{dC_A}{dt}\right)_2$	$\left(-\dfrac{dC_A}{dt}\right)_3$

The reaction order can now be found from a plot of $\ln(-dC_A/dt)$ as function of $\ln C_A$, as shown in Figure 5-1(a), since

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k_A + \alpha \ln C_A \qquad (5-$$

Before solving an example problem review the steps to determine the reacti rate law from a set of data points (Table 5-1).

Example 5–1   Determining the Rate Law

The reaction of triphenyl methyl chloride (trityl) (A) and methanol (B)

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

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

was carried out in a solution of benzene and pyridine at 25°C. Pyridine reacts with HCl that then precipitates as pyridine hydrochloride thereby making the reaction irreversible.

The concentration-time data in Table E5-1.1 was obtained in a batch reactor

<center>TABLE E5-1.1.   RAW DATA</center>

Time (min)	0	50	100	150	200	250	300
Concentration of A (mol/dm^3) $\times 10^3$	50	38	30.6	25.6	22.2	19.5	17.4

(At $t = 0$, $C_A = 0.05\ M$)

The initial concentration of methanol was 0.5 mol/dm^3.

Part (1)   Determine the reaction order with respect to triphenyl methyl chloride.

Part (2)   In a separate set of experiments, the reaction order wrt methanol was found to be first order. Determine the specific reaction rate constant.

Solution

Part (1)   Find reaction order wrt trityl.

Step 1   Postulate a rate law.

$$-r_A = kC_A^\alpha C_B^\beta \qquad (E5\text{-}1.1)$$

Step 2   Process your data in terms of the measured variable, which in this case is C_A.

Step 3   Look for simplifications. Because concentration of methanol is 10 times the initial concentration of triphenyl methyl chloride, its concentration is essentially constant

$$C_B = C_{B0} \qquad (E5\text{-}1.2)$$

Substituting for C_B in Equation (E5-1.1)

$$-r_A = \underbrace{kC_{B0}^\beta}_{k'}\, C_A^\alpha$$

$$-r_A = k' C_A^\alpha \qquad (E5\text{-}1.3)$$

Step 4   Apply the CRE algorithm
Mole Balance

$$\frac{dN_A}{dt} = r_A V \qquad (E5\text{-}1.4)$$

Rate Law

$$-r_A = k' C_A^\alpha \qquad (E5\text{-}1.3)$$

Stoichiometry: Liquid

$$V = V_0 \qquad (E5\text{-}1.4)$$

$$C_A = \frac{N_A}{V_0}$$

Following the Algorithm

Combine: Mole balance, rate law, and stoichiometry

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

Taking the natural log of both sides of Equation (E5-1.5)

$$\ln\left[-\frac{dC_A}{dt}\right] = \ln k' + \alpha \ln C_A \tag{E5-1.6}$$

The slope of a plot of $\ln\left[-\frac{dC_A}{dt}\right]$ versus $\ln C_A$ will yield the reaction order α with respect to triphenyl methyl chloride (A).

Step 5   Find $\left[-\frac{dC_A}{dt}\right]$ as a function of C_A from concentration-time data.

We will find $\left(-\frac{dC_A}{dt}\right)$ by each of the three methods just discussed, the graphical, finite difference, and polynomial methods.

Step 5A.1a *Graphical Method.* We now construct Table E5-1.2.

TABLE E5–1.2 PROCESSED DATA

t (min)	$C_A \times 10^3$ (mol/dm³)	$-\dfrac{\Delta C_A}{\Delta t} \times 10^4$ (mol/dm³ · min)	$-\dfrac{dC_A}{dt} \times 10^4$ (mol/dm³ · min)
0	50		3.0
		2.40[a]	
50	38		1.86
		1.48	
100	30.6		1.2
		1.00	
150	25.6		0.8
		0.68	
200	22.2		0.5
		0.54	
250	19.5		0.47
		0.42	
300	17.4		

[a]
$$-\frac{\Delta C_A}{\Delta t} = -\frac{C_{A2}-C_{A1}}{t_2-t_1} = -\left(\frac{38-50}{50-0}\right) \times 10^{-3} = 0.24 \times 10^{-3} = 2.4 \times 10^{-4} (\text{mol/dm}^3 \cdot \text{min})$$

The derivative $-dC_A/dt$ is determined by calculating and plotting $(-\Delta C_A/\Delta t)$ as a function of time, t, and then using the equal-area differentiation technique (Appendix A.2) to determine $(-dC_A/dt)$ as a function of C_A. First, we calculate the ratio $(-\Delta C_A/\Delta t)$ from the first two columns of Table E5-1.2; the result is written in the third column. Next we use Table E5-1.2 to plot the third column as a function of the

first column in Figure E5-1.1 [i.e., $(-\Delta C_A/\Delta t)$ versus t]. Using equal-area differentiation, the value of $(-dC_A/dt)$ is read off the figure (represented by the arrows); then it is used to complete the fourth column of Table E5-1.2.
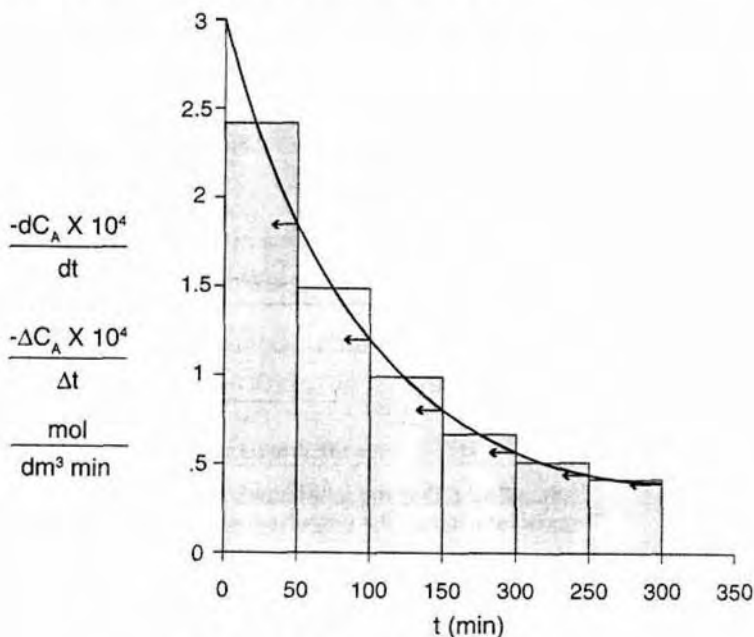

Figure E5-1.1   Graphical differentiation.

Step 5A.1b Finite Difference Method. We now calculate (dC_A/dt) using the finite difference formulas [i.e., Equations (5-8) through (5-10)].

$t = 0$ $\left(\dfrac{dC_A}{dt}\right)_{t=0} = \dfrac{-3C_{A0} + 4C_{A1} - C_{A2}}{2\Delta t}$

$$= \frac{[-3(50) + 4(38) - 30.6] \times 10^{-3}}{100}$$

$$= -2.86 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min}$$

$$-\frac{dC_A}{dt} \times 10^4 = 2.86 \text{ mol/dm}^3 / \text{min}$$

$t = 50$ $\left(\dfrac{dC_A}{dt}\right)_1 = \dfrac{C_{A2} - C_{A0}}{2\Delta t} = \dfrac{(30.6 - 50) \times 10^{-3}}{100}$

$$= -1.94 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min}$$

$$t = 100 \quad \left(\frac{dC_A}{dt}\right)_2 = \frac{C_{A3} - C_{A1}}{2\Delta t} = \frac{(25.6 - 38) \times 10^{-3}}{100}$$

$$= -1.24 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min}$$

$$t = 150 \quad \left(\frac{dC_A}{dt}\right)_3 = \frac{C_{A4} - C_{A2}}{2\Delta t} = \frac{(22.2 - 30.6) \times 10^{-3}}{100}$$

$$= -0.84 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min}$$

$$t = 200 \quad \left(\frac{dC_A}{dt}\right)_4 = \frac{C_{A5} - C_{A3}}{2\Delta t} = \frac{(19.5 - 25.6) \times 10^{-3}}{100}$$

$$= -0.61 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min}$$

$$t = 250 \quad \left(\frac{dC_A}{dt}\right)_5 = \frac{C_{A6} - C_{A4}}{2\Delta t} = \frac{(17.4 - 22.2) \times 10^{-3}}{100}$$

$$= -0.48 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min}$$

$$t = 300 \quad \left(\frac{dC_A}{dt}\right)_6 = \frac{C_{A4} - 4C_{A5} + 3C_{A6}}{2\Delta t} = \frac{[22.2 - 4(19.5) + 3(17.4)] \times 10^{-3}}{100}$$

$$= -0.36 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min}$$

Summary Notes

A Polymath turorial
for fitting data can
be found on the
Summary Notes on
the CD.

Step 5A.1c Polynomial Method. Another method to determine (dC_A/dt) is to fit th concentration of A to a polynomial in time and then to differentiate the resultin polynomial.

We will use the Polymath software package to express concentration as a functio of time. Here we first choose the polynomial degree (in this case, fourth degree) an then type in the values of C_A at various times t to obtain

$$C_A = 0.04999 - 2.978 \times 10^{-4}t + 1.343 \times 10^{-6}t^2 - 3.485 \times 10^{-9}t^3 + 3.697 \times 10^{-12}t^4$$

(E5-1.7

C_A is in (mol/dm³) and t is in minutes. A plot of C_A versus t and the correspondin fourth-degree polynomial fit are shown in Figure E5-1.2.

TABLE E5–1.3 POLYMATH OUTPUT

Linear Regression Report

Model: $CA = a0 + a1*t + a2*t^2 + a3*t^3 + a4*t^4$

Variable	Value	95% confidence
a0	0.0499903	3.1E-04
a1	-2.978E-04	1.762E-05
a2	1.343E-06	2.72E-07
a3	-3.485E-09	1.418E-09
a4	3.697E-12	2.347E-12

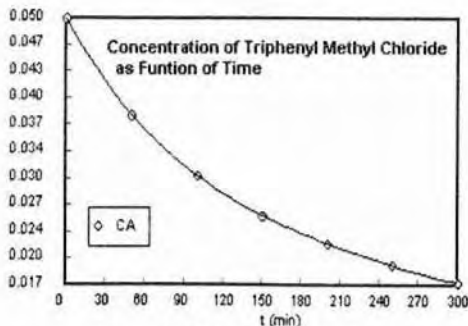**Concentration of Triphenyl Methyl Chloride as Funtion of Time**

◇ CA

t (min)

Figure E5-1.2 Polynomial fit.

Differentiating Equation (E5-1.7) yields

$$\frac{dC_A}{dt} \times 10^3 = -0.2987 + 0.002687t - 1.045 \times 10^{-5}t^2 + 1.479 \times 10^{-8}t^3 \qquad (E5-1.8)$$

Note: You can also obtain Equation (E5-1.9) directly from Polymath.

To find the derivative at various times, we substitute the appropriate time into Equation (E5-1.8) to arrive at the fourth column in Table E5-1.4 and multiply by (−1). We can see that there is quite a close agreement between the graphical technique, finite difference, and the polynomial methods.

TABLE E5-1.3.   SUMMARY OF PROCESSED DATA

t (min)	*Graphical* $-\dfrac{dC_A}{dt} \times 10{,}000$ (mol/dm^3 · min)	*Finite Difference* $-\dfrac{dC_A}{dt} \times 10{,}000$ (mol/dm^3 · min)	*Polynominal* $-\dfrac{dC_A}{dt} \times 10{,}000$ (mol/dm^3 · min)	$C_A \times 1{,}000$ (mol/dm^3)
0	3.0	2.86	2.98	50
50	1.86	1.94	1.88	38
100	1.20	1.24	1.19	30.6
150	0.80	0.84	0.80	25.6
200	0.68	0.61	0.60	22.2
250	0.54	0.48	0.48	19.5
300	0.42	0.36	0.33	17.4

We will now plot columns 2, 3, and 4 $\left(-\dfrac{dC_A}{dt} \times 10{,}000\right)$ as a function of column 5 ($C_A \times 1{,}000$) on log-log paper as shown in Figure E5-1.3. We could also substitute the parameter values in Table E5-1.4 into Excel to find α and k'. Note that most all of the points for all methods fall virtually on top of one another.

From Figure E5-1.3, we found the slope to be 2.05 so that the reaction is said to be second order wrt triphenyl methyl chloride. To evaluate k', we can evaluate the derivative and $C_{Ap} = 20 \times 10^{-3}$ mol/dm^3, which is

$$\left(-\frac{dC_A}{dt}\right)_p = 0.5 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min} \qquad (E5-1.9)$$

then

$$k' = \frac{\left(-\dfrac{dC_A}{dt}\right)_p}{C_{Ap}^2} \qquad (E5-1.10)$$

$$= \frac{0.5 \times 10^{-4} \text{mol/dm}^3 \cdot \text{min}}{\left(20 \times 10^{-3} \text{mol/dm}^3\right)^2} = 0.125 \text{ dm}^3 / \text{mol} \cdot \text{min}$$

As will be shown in Section 5.1.3, we could also use nonlinear regression on Equation (E5-1.7) to find k':

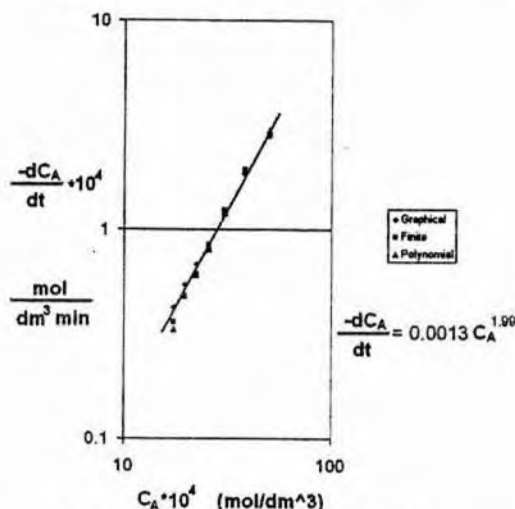$$k' = 0.122 \text{ dm}^3/\text{mol} \cdot \text{min} \qquad (E5-1.11)$$

Figure E5-1.3 Excel plot to determine α and k.

The Excel graph shown in Figure E5-1.3 gives $\alpha = 1.99$ and $k' = 0.13$ dm³/mol · min. We could set $\alpha = 2$ and regress again to find $k' = 0.122$ dm³/mol · min.

ODE Regression. There are techniques and software becoming available whereby an ODE solver can be combined with a regression program to solve differential equations, such as

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

to find k_A and α from concentration–time date.

Part (2) The reaction was said to be first order wrt methanol, $\beta = 1$,

$$k' = C_{B0}^{\beta} k = C_{B0} k \tag{E5-1.12}$$

Assuming C_{B0} is constant at 0.5 mol/dm³ and solving for k yields

$$k = \frac{k'}{C_{B0}} = \frac{0.122 \dfrac{dm^3}{mol \cdot min}}{0.5 \dfrac{mol}{dm^3}}$$

$$k = 0.244 \ (dm^3/mol)^2 / min$$

The rate law is

$$\boxed{-r_A = [0.244(dm^3/mol)^2/min]C_A^2 \, C_B} \tag{E5-1.13}$$

5.2.2 Integral Method

To determine the reaction order by the integral method, we guess the reaction order and integrate the differential equation used to model the batch system. If the order we assume is correct, the appropriate plot (determined from this integration) of the concentration–time data should be linear. The integral method is used most often when the reaction order is known and it is desired to evaluate the specific reaction rate constants at different temperatures to determine the activation energy.

The integral method uses a trial-and-error procedure to find reaction order.

In the integral method of analysis of rate data, we are looking for the appropriate function of concentration corresponding to a particular rate law that is linear with time. You should be thoroughly familiar with the methods of obtaining these linear plots for reactions of zero, first, and second order.

For the reaction

It is important to know how to generate linear plots of functions of C_A versus t for zero-, first-, and second-order reactions.

$$A \rightarrow \text{Products}$$
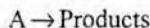
carried out in a constant-volume batch reactor, the mole balance is

$$\frac{dC_A}{dt} = r_A$$

For a zero-order reaction, $r_A = -k$, and the combined rate law and mole balance is

$$\frac{dC_A}{dt} = -k \tag{5-13}$$

Integrating with $C_A = C_{A0}$ at $t = 0$, we have

Zero order

$$\boxed{C_A = C_{A0} - kt} \tag{5-14}$$

A plot of the concentration of A as a function of time will be linear (Figure 5-3) with slope $(-k)$ for a zero-order reaction carried out in a constant-volume batch reactor.

If the reaction is first order (Figure 5-4), integration of the combined *mole balance and the rate law*

$$-\frac{dC_A}{dt} = kC_A$$

with the limit $C_A = C_{A0}$ at $t = 0$ gives

First order

$$\boxed{\ln \frac{C_{A0}}{C_A} = kt} \tag{5-15}$$

Consequently, we see that the slope of a plot of $[\ln(C_{A0}/C_A)]$ as a function of time is linear with slope k.

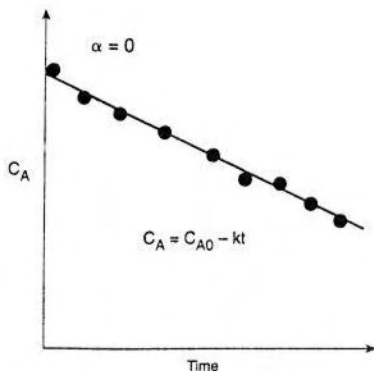If the reaction is second order (Figure 5-5), then

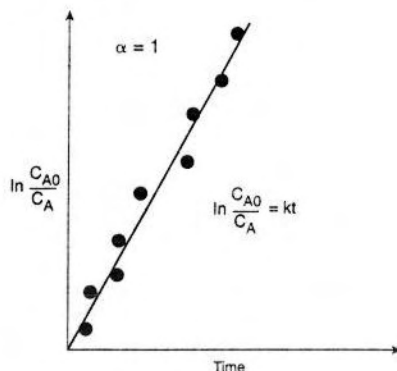**Figure 5-3**   Zero-order reaction.
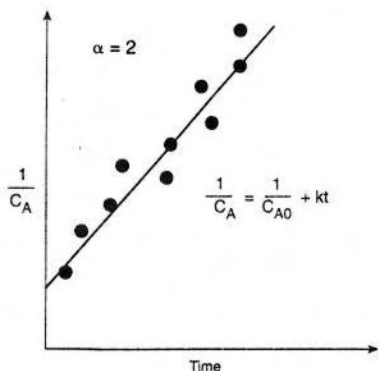

Figure 5-4   First-order reaction.

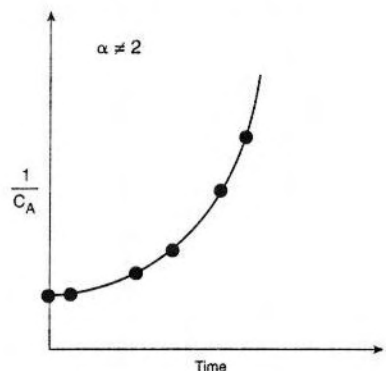

Figure 5-5   Second-order reaction.

Figure 5-6   Plot of reciprocal concentration as a function of time.

$$-\frac{dC_A}{dt} = kC_A^2$$

Integrating, with $C_A = C_{A0}$ initially, yields

Second order

$$\boxed{\frac{1}{C_A} - \frac{1}{C_{A0}} = kt}$$ (5-16

We see that for a second-order reaction a plot of $(1/C_A)$ as a function of tim should be linear with slope k.

In Figures 5-3, 5-4, and 5-5, we saw that when we plotted the appropriat function of concentration (i.e., C_A, $\ln C_A$, or $1/C_A$) versus time, the plots wer linear, and we concluded that the reactions were zero, first, or second order respectively. However, if the plots of concentration data versus time had turne

out **not to be linear**, such as shown in Figure 5-6, we would say that the proposed reaction order did not fit the data. In the case of Figure 5-6, we would conclude the reaction is not second order.

The idea is to arrange the data so that a linear relationship is obtained.

It is important to restate that, given a reaction rate law, you should be able to choose quickly the appropriate function of concentration or conversion that yields a straight line when plotted against time or space time.

Example 5–2   Integral Method of CRE Data Analysis

Use the integral method to confirm that the reaction is second order wrt triphenyl methyl chloride as described in Example 5-1 and to calculate the specific reaction rate k'

$$\text{Trityl (A) + Methanol (B)} \rightarrow \text{Products}$$
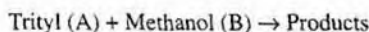
Solution

Substituting for $\alpha = 2$ in Equation (E5-1.5)

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

we obtain

$$-\frac{dC_A}{dt} = k' C_A^2 \tag{E5-2.1}$$

Integrating with $C_A = C_{A0}$ at $t = 0$

$$t = \frac{1}{k'}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right] \tag{E5-2.2}$$

Rearranging

$$\frac{1}{C_A} = \frac{1}{C_{A0}} + k' t \tag{E5-2.3}$$

We see if the reaction is indeed second order then a plot of $(1/C_A)$ versus t should be linear. The data in Table E5-1.1 in Example 5-1 will be used to construct Table E5-2.1.

TABLE E5-2.1.   PROCESSED DATA

t (min)	0	50	100	150	200	250	300
C_A (mol/dm³)	0.05	0.038	0.0306	0.0256	0.0222	0.0195	0.0174
$1/C_A$ (dm³/mol)	20	26.3	32.7	39.1	45	51.3	57.5

In a graphical solution, the data in Table E5-2.1 can be used to construct a plot of $1/C_A$ as a function of t, which will yield the specific reaction rate k'. This plot is shown in Figure E5-2.1. Again, one could use Excel or Polymath to find k' from the data in Table E5-2.1. The slope of the line is the specific reaction rate k'