We will see in Chapter 10 that this combination and similar rate laws which have reactant concentrations (or partial pressures) in the numerator and denominator are common in *heterogeneous catalysis*.

Let's see if the resulting rate law (E5-5.8) is qualitatively consistent with the rate observed.

1. *For condition 1*: At low P_{H_2}, $(b(P_{H_2})^{\beta_2} \ll 1)$ and Equation (E5-5.8) reduces to

$$r'_{CH_4} \sim P_{H_2}^{\beta_1} \qquad \text{(E5-5.9)}$$

Equation (E5-5.9) is consistent with the trend in comparing runs 4 and 5.

2. *For condition 2*: At high P_{H_2}, $b((P_{H_2})^{\beta_2} \gg 1)$ and Equation (E5-5.8) reduces to

$$r'_{CH_4} \sim \frac{(P_{H_2})^{\beta_1}}{(P_{H_2})^{\beta_2}} \sim \frac{1}{(P_{H_2})^{\beta_2 - \beta_1}} \qquad \text{(E5-5.10)}$$

where $\beta_2 > \beta_1$. Equation (E5-5.10) is consistent with the trends in comparing runs 5 and 6.

Combining Equations (E5-5.8) and (E5-5.5)

$$r'_{CH_4} = \frac{aP_{CO}P_{H_2}^{\beta_1}}{1 + bP_{H_2}^{\beta_2}} \qquad \text{(E5-5.11)}$$

We now use the Polymath regression program to find the parameter values a, b, β_1, and β_2. The results are shown in Table E5-5.3.

TABLE 5-5.3.   FIRST REGRESSION

POLYMATH Results
No Title 01-31-2004

Nonlinear regression (L-M)

Model: Rate = a*Pco*Ph2^beta1/(1+b*Ph2^beta2)

Variable	Ini guess	Value	95% confidence
a	1	0.0252715	0.4917749
beta1	1	0.6166542	6.9023286
b	1	2.4872569	68.002944
beta2	1	1.0262047	3.2344414

Nonlinear regression settings
Max # iterations = 64

Summary Notes

Polymath regression tutorial is in the Chapter 5 *Summary Notes*.

The corresponding rate law is

$$r_{CH_4} = \frac{0.025 P_{CO} P_{H_2}^{0.61}}{1 + 2.49 P_{H_2}} \qquad \text{(E5-5.12)}$$

We could use the rate law as given by Equation (E5-5.12) as is, but there are only six data points, and we should be concerned about extrapolating the rate law over a wider range of partial pressures. We could take more data, and/or we could carry out a theoretical analysis of the type discussed in Chapter 10 for heterogeneous reactions. If we assume hydrogen undergoes dissociative adsorption on the catalyst

surface one would expect a dependence of hydrogen to the $\frac{1}{2}$ power. Because (is close to 0.5, we are going to regress the data again setting $\beta_1 = (\frac{1}{2})$ and $\beta_2 =$ The results are shown in Table E5-5.4.

TABLE 5-5.4.   SECOND REGRESSION

POLYMATH Results
No Title 01-31-2004

Nonlinear regression (L-M)

Model: Rate = a*Pco*Ph2^0.5/(1+b*Ph2)

Variable	Ini guess	Value	95% confidence
a	1	0.018059	0.0106293
b	1	1.4898245	1.4787491

The rate law is now

$$r'_{CH_4} = \frac{0.018 P_{CO} P_{H_2}^{1/2}}{1 + 1.49 P_{H_2}}$$

where r'_{CH_4} is in mol/gcat · s and the partial pressure is in atm.

We could also have set $\beta_1 = \frac{1}{2}$ and $\beta_2 = 1.0$ and rearranged Equa (E5-5.11) in the form

Linearizing the rate
law to determine the
rate law parameters

$$\frac{P_{CO} P_{H_2}^{1/2}}{r'_{CH_4}} = \frac{1}{a} + \frac{b}{a} P_{H_2} \qquad (E5-5)$$

A plot of $P_{CO} P_{H_2}^{1/2} / r'_{CH_4}$ as a function of P_{H_2} should be a straight line with an in cept of $1/a$ and a slope of b/a. From the plot in Figure E5-5.2, we see that the law is indeed consistent with the rate law data.
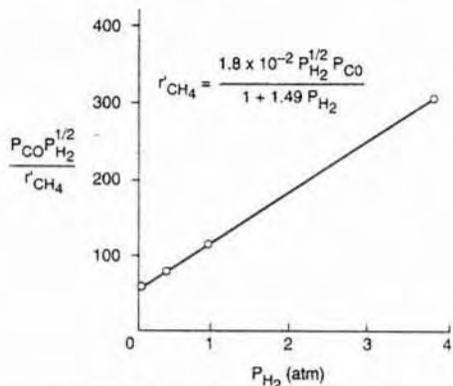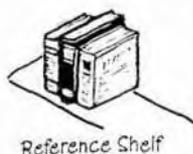

Figure E5-5.2 Linearized plot of data.

5.6 Experimental Planning

Reference Shelf

> Four to six weeks in the lab can save you an hour in the library.
>
> G. C. Quarderer, Dow Chemical Co.

So far, this chapter has presented various methods of analyzing rate data. It is just as important to know in which circumstances to use each method as it is to know the mechanics of these methods. On the CD-ROM, we give a thumbnail sketch of a heuristic to plan experiments to generate the data necessary for reactor design. However, for a more thorough discussion, the reader is referred to the books and articles by Box and Hunter.[9]

5.7 Evaluation of Laboratory Reactors

Reference Shelf

The successful design of industrial reactors lies primarily with the *reliability of the experimentally determined parameters used in the scale-up*. Consequently, it is imperative to design equipment and experiments that will generate accurate and meaningful data. Unfortunately, there is usually no single comprehensive laboratory reactor that could be used for all types of reactions and catalysts. In this section, we discuss the various types of reactors that can be chosen to obtain the kinetic parameters for a specific reaction system. We closely follow the excellent strategy presented in the article by V. W. Weekman of Mobil Oil, now ExxonMobil.[10]

5.7.1 Criteria

The criteria used to evaluate various types of laboratory reactors are listed in Table 5-2.

TABLE 5-2.   CRITERIA USED TO EVALUATE LABORATORY REACTORS

1. Ease of sampling and product analysis
2. Degree of isothermality
3. Effectiveness of contact between catalyst and reactant
4. Handling of catalyst decay
5. Reactor cost and ease of construction

Each type of reactor is examined with respect to these criteria and given a rating of good (G), fair (F), or poor (P). What follows is a brief description of each of the laboratory reactors. The reasons for rating each reactor for each of the criteria are given in *Professional Reference Shelf R5.4* on the CD-ROM.

---

[9] G. E. P. Box, W. G. Hunter, and J. S. Hunter, *Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building* (New York: Wiley, 1978).

[10] V. W. Weekman, *AIChE J., 20*, 833 (1974).

5.7.2 Types of Reactors

The criteria in Table 5-2 is applied to each of the reactors shown in Figure 5-12 and are also discussed on the CD-ROM in *Professional Reference Shelf R5.4*.
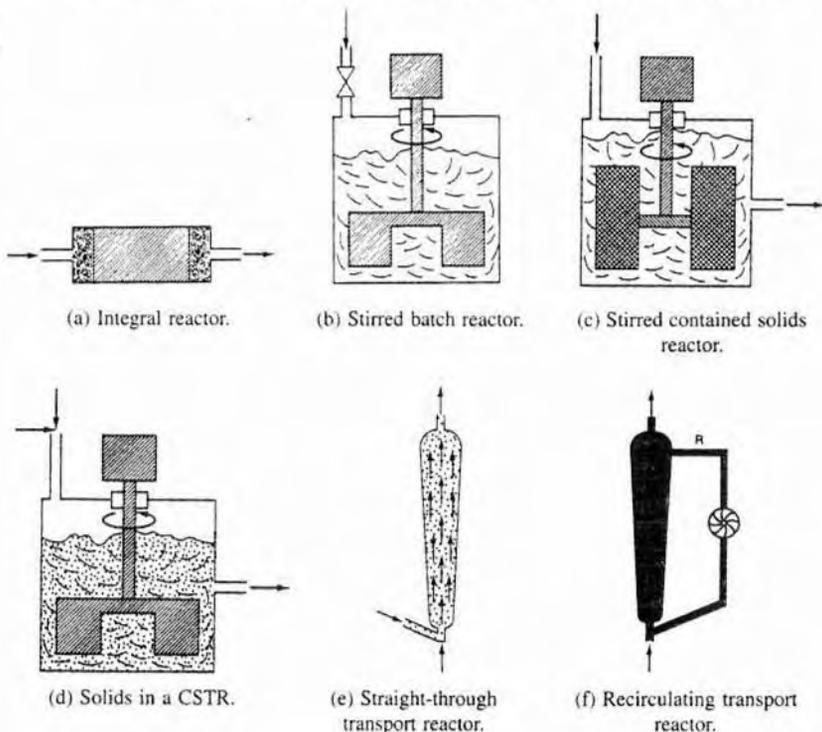
Reference Shelf

(a) Integral reactor. (b) Stirred batch reactor. (c) Stirred contained solids reactor.

(d) Solids in a CSTR. (e) Straight-through transport reactor. (f) Recirculating transport reactor.

Figure 5-12 [From V. Weekman, *AIChe J.*, 20, 833 (1974) with permission of the AIChE. Copyright © 1974 AIChE. All rights reserved.]

5.7.3 Summary of Reactor Ratings

The ratings of the various reactors are summarized in Table 5-3. From this table one notes that the CSTR and recirculating transport reactor appear to be the best choices because they are satisfactory in every category except for construction. However, if the catalyst under study does not decay, the stirred batch and contained solids reactors appear to be the best choices. If the system is not limited by internal diffusion in the catalyst pellet, larger pellets could be used, and the stirred-contained solids is the best choice. If the catalyst is nondecaying and heat effects are negligible, the fixed-bed (integral) reactor would be the top choice, owing to its ease of construction and operation. However, in practice, usually *more than one* reactor type is used in determining the reaction rate law parameters.

TABLE 5-3.   SUMMARY OF REACTOR RATINGS: GAS–LIQUID, POWDERED CATALYST, DECAYING CATALYST SYSTEM[a]

Reactor Type	Sampling and Analysis	Isothermality	Fluid–Solid Contact	Decaying Catalyst	Ease of Construction
Differential	P–F	F–G	F	P	G
Fixed bed	G	P–F	F	P	G
Stirred batch	F	G	G	P	G
Stirred-contained solids	G	G	F–G	P	F–G
Continuous-stirred tank	F	G	F–G	F–G	P–F
Straight-through transport	F–G	P–F	F–G	G	F–G
Recirculating transport	F–G	G	G	F–G	P–F
Pulse	G	F–G	P	F–G	G

[a]G, good; F, fair; P, poor.

Closure. After reading this chapter, the reader should be able to analyze data to determine the rate law and rate law parameters using the graphical and numerical techniques as well as software packages. Nonlinear regression is the easiest method to analyze rate-concentration data to determine the parameters, but the other techniques such as graphical differentiation help one get a feel for the disparities in the data. The reader should be able to describe the care that needs to be taken in using nonlinear regression to ensure you do not arrive on a false minimum for σ^2. Consequently, it is advisable to use more than one method to analyze the data. Finally, the reader should be able to carry out a meaningful discussion on reactor selection to determine the reaction kinetics along with how to efficiently plan experiments.

SUMMARY

1. Differential method for constant-volume systems

$$-\frac{dC_A}{dt} = kC_A^\alpha \tag{S5-1}$$

a. Plot $-\Delta C_A/\Delta t$ as a function of t.
b. Determine $-dC_A/dt$ from this plot.
c. Take the ln of both sides of (S5-1) to get

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + \alpha \ln C_A \tag{S5-2}$$

Plot $\ln(-dC_A/dt)$ versus $\ln C_A$. The slope will be the reaction order α, could use finite-difference formulas or software packages to evalu $(-dC_A/dt)$ as a function of time and concentration.

2. *Integral method*
   a. Guess the reaction order and integrate the mole balance equation.
   b. Calculate the resulting function of concentration for the data and plot i a function of time. If the resulting plot is linear, you have proba guessed the correct reaction order.
   c. If the plot is not linear, guess another order and repeat the procedure.

3. *Nonlinear regression*: Search for the parameters of the rate law that will n imize the sum of the squares of the difference between the measured rate reaction and the rate of reaction calculated from the parameter values cho: For N experimental runs and K parameters to be determined, use Polyma

$$\sigma_{min}^2 = \sum_{i=1}^{N} \frac{[r_i(\text{measured}) - r_i(\text{calculated})]^2}{N - K} \qquad (S:$$

$$s^2 = \sum_{i=1}^{N} (t_{mi} - t_{ci})^2 = \sum_{i=1}^{N} \left[t_{mi} - \frac{C_{A0}^{1-\alpha} - C_{Ai}^{1-\alpha}}{k(1-\alpha)} \right]^2 \qquad (S:$$

4. *Method of initial rates*:
   In this method of analysis of rate data, the slope of a plot of $\ln(-r_{A0})$ ve $\ln C_{A0}$ will be the reaction order.

5. *Modeling the differential reactor*:
   The rate of reaction is calculated from the equation

$$-r_A' = \frac{F_{A0}X}{W} = \frac{F_P}{W} = \frac{v_0(C_{A0} - C_{Ae})}{W} = \frac{C_P v_0}{W} \qquad (S:$$

In calculating the reaction order, α,

$$-r_A' = kC_A^{\alpha}$$

the concentration of A is evaluated either at the entrance conditions or mean value between C_{A0} and C_{Ae}.

CD-ROM MATERIAL

- **Learning Resources**
    1. *Summary Notes*
    3. *Interactive Computer Modules*
       A. Ecology

       B. Reactor Lab (*www.reactorlab.net*) See Reactor Lab Chapter 4 and P5-3$_B$.
    4. *Solved Problems*
       A. Example Differential Method of Analysis of Pressure-Time Data
       B. Example Integral Method of Analysis of Pressure-Time Data
       C. Example Oxygenating Blood
- **Living Example Problems**
    1. *Example 5-3 Use of Regression to Find the Rate Law Parameters*
- **FAQ [Frequently Asked Questions]—In Updates/FAQ icon section**
- **Professional Reference Shelf**
    R5.1 *Least Squares Analysis of the Linearized Rate Law*
          The CD-ROM describes how the rate law

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

is linearized

$$\ln(-r_A) = \ln k + \alpha \ln C_A + \beta \ln C_B$$

and put in the form

$$Y = a_0 + \alpha X_1 + \beta X_2$$

and used to solve for α, β, and k. The etching of a semiconductor, MnO_2, is used as an example to illustrate this technique.

    R5.2 *A Discussion of Weighted Least Squares*
          For the case when the error in measurement is not constant, we must use a weighted least squares.
    R5.3 *Experimental Planning*
          A. Why perform the experiment?
          B. Are you choosing the correct parameters?
          C. What is the range of your experimental variables?

D. Can you repeat the measurement? (Precision)

E. Milk your data for all it's worth.

F. We don't believe an experiment until it's proven by theory.

G. Tell someone about your result.

R5.4 *Evaluation or Laboratory Reactors (see Table 5-3)*

QUESTIONS AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet \quad B = \blacksquare \quad C = \blacklozenge \quad D = \blacklozenge\blacklozenge$$

Home Work Problems **P5-1_A**   (a) Compare Table 5-3 on laboratory reactors with a similar table on page 269 of Bisio and Kabel (see Supplementary Reading, listing 1). What are the similarities and differences?

(b) Which of the ICM's for Chapters 4 and 5 was the most fun?

(c) Choose a FAQ from Chapters 4 and 5 and say why it was the most helpful.

(d) Listen to the audios 🎧 on the CD and pick one and say why it could be eliminated.

Creative Thinking

(e) Create an original problem based on Chapter 5 material.

(f) Design an experiment for the undergraduate laboratory that demonstrates the principles of chemical reaction engineering and will cost less than $500 in purchased parts to build. (From 1998 AIChE National Student Chapter Competition) Rules are provided on the CD-ROM.

(g) Plant a number of seeds in different pots (corn works well). The plant and soil of each pot will be subjected to different conditions. Measure the height of the plant as a function of time and fertilizer concentration. Other variables might include lighting, pH, and room temperature. (Great Grade School or High School Science Project)

(h) **Example 5-1.** Discuss the differences for finding $\left[-\dfrac{dC_A}{dt}\right]$ shown in Table E5-3.1 by the three techniques.

(i) **Example 5-2.** Construct a table and plot similar to Table E5-2.1 and Figure E5-2.1, assuming a zero-order and a first-order reaction. Looking at the plots, can either of these orders possibly explain the data?

(j) **Example 5-3.** Explain why the regression had to be carried out twice to find k' and k.

(k) **Example 5-4.** Use regression to analyze the data in Table E5-4.1. What do you find for the reaction order?

(l) **Example 5-5.** Regress the data to fit the rate law

$$r_{CH_4} = kP_{CO}^{\alpha}\,P_{H_2}^{\beta}$$

Interactive

What is the difference in the correlation and sums-of-squares compared with those given in Example 5-5? Why was it necessary to regress the data twice, once to obtain Table E5-5.3 and once to obtain Table E5-5.4?

P5-2_A   Load the Interactive Computer Module (ICM) from the CD-ROM. Run the module and then record your performance number for the module which indicates your mastering of the material. Your professor has the key to decode your performance number.

Computer Modules   ICM Ecology Performance # _____.

Visit Reactor Lab   **P5-3$_A$**   Go to Professor Herz's **Reactor Lab** on the CD-ROM or on the web at
www.reactorlab.net. Do (a) one quiz, or (b) two quizzes from Division 1.

Links   When you first enter a lab, you see all input values and can vary them. In a
lab, click on the Quiz button in the navigation bar to enter the quiz for that lab.
In a quiz, you cannot see some of the input values: you need to find those with
"???" hiding the values. In the quiz, perform experiments and analyze your
data in order to determine the unknown values. See the bottom of the Example
Quiz page at *www.reactorlab.net* for equations that relate E and k. Click on the
"???" next to an input and supply your value. Your answer will be accepted if
is within ±20% of the correct value. Scoring is done with imaginary dollars to
emphasize that you should design your experimental study rather than do ran-
dom experiments. Each time you enter a quiz, new unknown values are
assigned. To reenter an unfinished quiz at the same stage you left, click the [i]
info button in the Directory for instructions. Turn in copies of your data, your
analysis work, and the Budget Report.

P5-4$_B$ When arterial blood enters a tissue capillary, it exchanges oxygen and carbon
dioxide with its environment, as shown in this diagram.
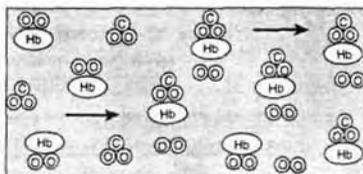
The kinetics of this deoxygenation of hemoglobin in blood was studied with the
aid of a **tubular reactor** by Nakamura and Staub [*J. Physiol., 173*, 161].

$$HbO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Hb + O_2$$
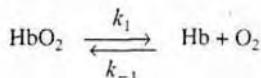
Although this is a reversible reaction, measurements were made in the initial
phases of the decomposition so that the reverse reaction could be neglected.
Consider a system similar to the one used by Nakamura and Staub: the solu-
tion enters a tubular reactor (0.158 cm in diameter) that has oxygen electrodes
placed at 5-cm intervals down the tube. The solution flow rate into the reactor
is 19.6 cm³/s.

Electrode Position	1	2	3	4	5	6	7
Percent Decomposition of HbO_2	0.00	1.93	3.82	5.68	7.48	9.25	11.00

(a) Using the method of differential analysis of rate data, determine the reac-
tion order and the forward specific reaction rate constant k for the deoxy-
genation of hemoglobin.

(b) Repeat using regression.

P5-5$_A$ The liquid-phase irreversible reaction

$$A \rightarrow B + C$$
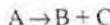
is carried out in a CSTR. To learn the rate law the volumetric flow rate, v (hence $\tau = V/v_0$) is varied and the effluent concentrations of species A recorded as a function of the space time τ. Pure A enters the reactor at a concentration of 2 mol/dm³. Steady-state conditions exist when the measurements are recorded.

Run	1	2	3	4	5
τ (min)	15	38	100	300	1200
C_A (mol/dm³)	1.5	1.25	1.0	0.75	0.5

(a) Determine the reaction order and specific reaction rate.
(b) If you were to repeat this experiment to determine the kinetics, what would you do differently? Would you run at a higher, lower, or the same temperature? If you were to take more data, where would you place the measurements (e.g., τ)?
(c) It is believed that the technician may have made a dilution factor-of-error in one of the concentration measurements. What do you think? How do your answers compare using regression (Polymath or other software) with those obtained by graphical methods?

Note: All measurements were taken at steady-state conditions.

P5-6$_B$ The reaction

$$A \rightarrow B + C$$
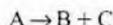
was carried out in a constant-volume batch reactor where the following concentration measurements were recorded as a function of time.

t (min)	0	5	9	15	22	30	40	60
C_A (mol/dm³)	2	1.6	1.35	1.1	0.87	0.70	0.53	0.35

(a) Use nonlinear least squares (i.e., regression) and one other method determine the reaction order α and the specific reaction rate.
(b) If you were to take more data, where would you place the points? Why
(c) If you were to repeat this experiment to determine the kinetics, what would you do differently? Would you run at a higher, lower, or the same temperature? Take different data points? Explain.
(d) It is believed that the technician made a dilution error in the concentration measured at 60 min. What do you think? How do your answers compare using regression (Polymath or other software) with those obtained by graphical methods?

P5-7$_B$ The liquid-phase reaction of methanol and triphenyl takes place in a batch reactor at 25°C

$$CH_3OH + (C_6H_5)_3 CCl \rightarrow (C_6H_5)_3COCH_3 + HCl$$

$$A \quad + \quad B \quad \rightarrow \quad C \quad + D$$
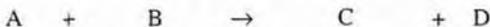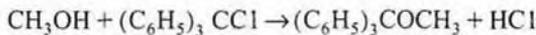
For an equal molar feed the following concentration–time data was obtained for methanol:

C_A (mol/dm³)	0.1	0.95	0.816	0.707	0.50	0.370
t (h)	0	0.278	1.389	2.78	8.33	16.66

The following concentration time data was carried out for an initial methanol concentration 0.01 and an initial triphenyl of 0.1:

C_A (mol/dm³)	0.01	0.0847	0.0735	0.0526	0.0357
t (h)	0	1	2	5	10

(a) Determine the rate law and rate law parameters.

(b) If you were to take more data points, what would be the reasonable settings (e.g., C_{A0}, C_{B0})? Why?

P5-8$_B$ The following data were reported [C. N. Hinshelwood and P. J. Ackey, *Proc. R. Soc. (Lond).*, *A115*, 215] for a gas-phase constant-volume decomposition of dimethyl ether at 504°C in a *batch reactor*. Initially, only $(CH_3)_2O$ was present.

Time (s)	390	777	1195	3155	∞
Total Pressure (mmHg)	408	488	562	799	931

(a) Why do you think the total pressure measurement at $t = 0$ is missing? Can you estimate it?

(b) Assuming that the reaction

$$(CH_3)_2O \rightarrow CH_4 + H_2 + CO$$

is irreversible and goes to completion, determine the reaction order and specific reaction rate k.

(c) What experimental conditions would you suggest if you were to obtain more data?

(d) How would the data and your answers change if the reaction were run at a higher or lower temperature?

P5-9$_B$ In order to study the photochemical decay of aqueous bromine in bright sunlight, a small quantity of liquid bromine was dissolved in water contained in a glass battery jar and placed in direct sunlight. The following data were obtained at 25°C:

Time (min)	10	20	30	40	50	60
ppm Br$_2$	2.45	1.74	1.23	0.88	0.62	0.44

(a) Determine whether the reaction rate is zero, first, or second order in bromine, and calculate the reaction rate constant in units of your choice.

(b) Assuming identical exposure conditions, calculate the required hourly rate of injection of bromine (in pounds) into a sunlit body of water, 25,000 gal in volume, in order to maintain a sterilizing level of bromine of 1.0 ppm. (*Ans.*: 0.43 lb/h)

(c) What experimental conditions would you suggest if you were to obtain more data?

(*Note:* ppm = parts of bromine per million parts of brominated water by weight. In dilute aqueous solutions, 1 ppm ≡ 1 milligram per liter.) (From California Professional Engineers Exam.)

P5-10$_C$ The gas-phase decomposition

$$A \longrightarrow B + 2C$$

is carried out in a *constant-volume batch reactor*. Runs 1 through 5 were carried out at 100°C, while run 6 was carried out at 110°C.

(a) From the data in Table P5-10, determine the reaction order and specific reaction rate.

(b) What is the activation energy for this reaction?

TABLE P5-10.   RAW DATA

Run	Initial Concentration, C_{A0} (g mol/L)	Half-Life, $t_{1/2}$ (min)
1	0.0250	4.1
2	0.0133	7.7
3	0.010	9.8
4	0.05	1.96
5	0.075	1.3
6	0.025	2.0

P5-11$_C$ The reactions of ozone were studied in the presence of alkenes [R. Atkinson et al., *Int. J. Chem. Kinet.*, *15(8)*, 721 (1983)]. The data in Table P5-11 are for one of the alkenes studied, *cis*-2-butene. The reaction was carried out isothermally at 297 K. Determine the rate law and the values of the rate law parameters.

TABLE P5-11.   RAW DATA

Run	Ozone Rate (mol/s · dm^3 × 10^7)	Ozone Concentration (mol/dm^3)	Butene Concentration (mol/dm^3)
1	1.5	0.01	10^{-12}
2	3.2	0.02	10^{-11}
3	3.5	0.015	10^{-10}
4	5.0	0.005	10^{-9}
5	8.8	0.001	10^{-8}
6	4.7	0.018	10^{-9}

(*Hint:* Ozone also decomposes by collision with the wall.)

P5-12$_A$ Tests were run on a small experimental reactor used for decomposing nitrogen oxides in an automobile exhaust stream. In one series of tests, a nitrogen stream containing various concentrations of NO_2 was fed to a reactor, and the kinetic data obtained are shown in Figure P5-12. Each point represents one

complete run. The reactor operates essentially as an *isothermal backmix reactor (CSTR)*. What can you deduce about the apparent order of the reaction over the temperature range studied?

The plot gives the fractional decomposition of NO_2 fed versus the ratio of reactor volume V (in cm^3) to the NO_2 feed rate, $F_{NO_{2,0}}$ (g mol/h), at different feed concentrations of NO_2 (in parts per million by weight).
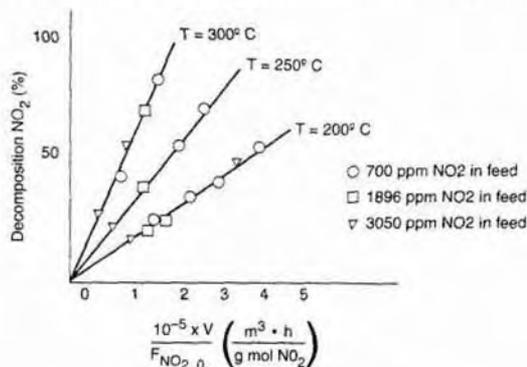

Figure P5-12   Auto exhaust data.

P5-13$_B$ *Microelectronic devices* are formed by first forming SiO_2 on a silicon wafer by chemical vapor deposition (Figure P5-13). This procedure is followed by coating the SiO_2 with a polymer called a photoresist. The pattern of the electronic circuit is then placed on the polymer and the sample is irradiated with ultraviolet light. If the polymer is a positive photoresist, the sections that were irradiated will dissolve in the appropriate solvent, and those sections not irradiated will protect the SiO_2 from further treatment. The wafer is then exposed to strong acids, such as HF, which etch (i.e., dissolve) the exposed SiO_2. It is extremely important to know the kinetics of the reaction so that the proper depth of the channel can be achieved. The dissolution reaction is

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$
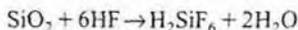
From the following initial rate data, determine the rate law.

Etching Rate (nm/min)	60	200	600	1000	1400
HF (wt %)	8	20	33	40	48

A total of 1000 thin wafer chips are to be placed in 0.5 dm^3 of 20% HF. If a spiral channel 10 μm wide and 10 m in length were to be etched to a depth of 50 μm on both sides of each wafer, how long should the chips be left in the solution? Assume that the solution is well mixed. (*Ans.*: 330 min)
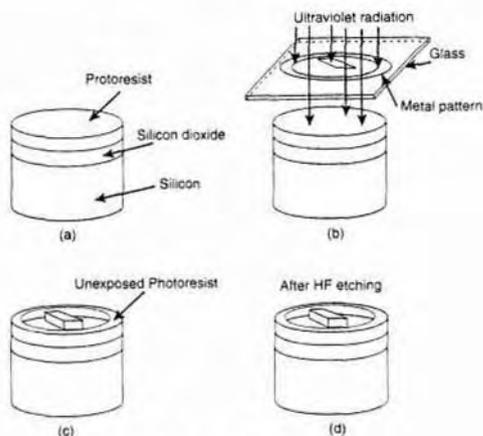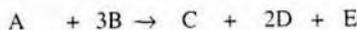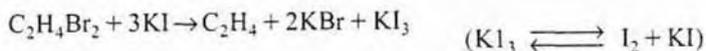
Figure P5-13 Semiconductor etching.

P5-14$_D$ The following reaction

$$C_2H_4Br_2 + 3KI \rightarrow C_2H_4 + 2KBr + KI_3 \qquad (KI_3 \rightleftharpoons I_2 + KI)$$

$$A \quad + 3B \rightarrow C \quad + 2D + E$$

is carried out in a differential reactor, and the flow rate of ethylene is recorᵈ
as a function of temperature and entering concentrations.

| T(K)	323	333	343	353	363	363
C_2H_4Br (mol/dm^3)	0.1	0.1	0.05	0.1	0.2	0.01
KI (mol/dm^3)	0.1	0.1	0.1	0.05	0.01	0.01
C_2H_4 (mol/dm^3)	0.002	0.006	0.008	0.02	0.02	0.01

The space time for the differential reactor is 2 minutes.
(a) Determine the rate law and rate law parameters.
(b) If you were to take more data points, what would be the reasonᵃ
settings (e.g., C_{A0})? Why?

P5-15$_B$ The following data as obtained in a batch reactor for the yeast *Saccharomy*
cerevisicae

Yeast Budding
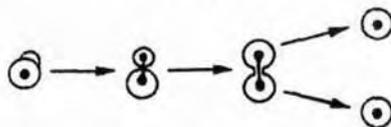
t (h)	0	1	2	3	4	6	8
C_C (g/dm^3)	1	1.39	1.93	2.66	3.7	7.12	13.7
C_S (g/dm^3)	250	245	238	229	216	197	94.4
C_P (g/dm^3)	0	2.17	5.22	9.3	15.3	34	71
$\left(\dfrac{dC_C}{dt}\right)$ (g/dm^3 · h)	0.30	0.45	0.63	0.87	1.21	2.32	4.42

(a) Determine the rate law parameters μ_{max} and K_S, assuming the data can be described by Monod Equation $\dfrac{dC_C}{dt} = r_g = \dfrac{\mu_{max}C_S C_C}{K_S + C_S}$

[*Hint*: It might be best to regress your data taking the reciprocal of the Monod equation in the form $(C_S C_C/r_g)$ vs. C_S.]
What is the residual sums of squares?

(b) Determine the rate parameters μ_{max} and k, assuming the data can be fit by the Tessier Equation

$$r_g = \mu_{max}\left[1 - \exp\left(-\frac{C_S}{k}\right)\right]C_C$$

What is the residual sums of squares?

(c) Determine the rate law parameters μ_{max}, k, and λ, assuming the data can be fit by the Moser Equation

$$r_g = \frac{\mu_{max}C_C}{1 + kC_S^{-\lambda}}$$

What is the residual sums of squares?

P5-16$_C$ The thermal decomposition of isopropyl isocyanate was studied in a *differential packed-bed reactor*. From the data in Table P5-16, determine the reaction rate law parameters.

TABLE P5-16.   RAW DATA

Run	Rate (mol/s · dm^3)	Concentration (mol/dm^3)	Temperature (K)
1	4.9×10^{-4}	0.2	700
2	1.1×10^{-4}	0.02	750
3	2.4×10^{-3}	0.05	800
4	2.2×10^{-2}	0.08	850
5	1.18×10^{-1}	0.1	900
6	1.82×10^{-2}	0.06	950

JOURNAL CRITIQUE PROBLEMS

P5C-1 A *packed-bed reactor* was used to study the reduction of nitric oxide with ethylene on a copper–silica catalyst [*Ind. Eng. Chem. Process Des. Dev., 9*, 455 (1970)]. Develop the integral design equation in terms of the conversion at various initial pressures and temperatures. Is there a significant discrepancy between the experimental results shown in Figures 2 and 3 in the article and the calculated results based on the proposed rate law? If so, what is the possible source of this deviation?

P5C-2 Equation (3) in the article [*J. Chem. Technol. Biotechnol., 31*, 273 (1981)] is the rate of reaction and is incorporated into design equation (2). Rederive the design equation in terms of conversion. Determine the rate dependence on H_2 based on this new equation. How does the order obtained compare with that found by the authors?

P5C-3 See "Kinetics of catalytic esterification of terephthalic acid with methanol vapour" [*Chem. Eng. Sci., 28*, 337 (1973)]. When one observes the data points in Figure 2 of this paper for large times, it is noted that the last data point always falls significantly off the straight-line interpretation. Is it possible to reanalyze these data to determine if the chosen reaction order is indeed correct? Substituting your new rate law into equation (3), derive a new form of equation (10) in the paper relating time and particle radius.

P5C-4 The selective oxidation of toluene and methanol over vanadium pentoxide-supported alkali metal sulfate catalysts was studied [*AIChE J., 27*(1), 41 (1981)]. Examine the experimental technique used (equipment, variables, etc.) in light of the mechanism proposed. Comment on the shortcomings of the analysis and compare with another study of this system presented in *AIChE J., 28*(5), 855 (1982).

- **Additional Homework Problems**

CDP5-A$_B$ The reaction of penicillin G with NH_2OH is carried out in a batch reactor. A colorimeter was used to measure the absorbency as a function of time. [1st Ed. P5-10]

CDP5-B$_B$ The isomerization $A \rightarrow B$ is carried out in a batch reactor. Find α and k. [3rd Ed. P5-3$_B$]

CDP5-C$_C$ The ethane hydrogenolysis over a commercial nickel catalyst was studied in a stirred contained solids reactor.

$$H_2 + C_2H_6 \rightarrow 2CH_4$$
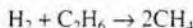
[*Ans:* $k = 0.48$ mol · atm / kg · h] [3rd ed. P5-14]

CDP5-D$_B$ The half-life of one of the pollutants, NO, in autoexhaust is required. [1st Ed. P5-11]

CDP5-E$_B$ The kinetics of a gas-phase reaction $A_2 \rightarrow 2A$ were studied in a constant-pressure batch reactor in which the volume was measured as a function of time. [1st Ed. P5-6]

CDP5-F$_B$ Reaction kinetics in a tubular reactor.

$$Et_3In(g) + AsH_3 \;\rightleftharpoons\; \text{Adduct}$$

GaInAs in fiber optics [3rd Ed. P5-6]

CDP5-G$_B$ Differential reactor data for the reaction

$$CH_3CH = CH_2 + O_2 \rightarrow CH_2 = CHCHO + H_2O$$
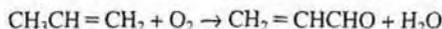
[3rd Ed. P5-13]

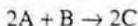**CDP5-H$_B$**   Lumping of species for hydrocarbon mixtures. [3rd Ed. P5-16]

CDP5-I$_B$ Prepare an experimental plan to find the rate law. [3rd Ed. P5-17]

CDP5-J$_B$ Batch data on the liquid phase reaction

$$A + B \rightarrow C$$

[3rd Ed. P5-18]

CDP5-K$_B$ Analyze data to see if it fits an elementary reaction

$$2A + B \rightarrow 2C$$

[3rd Ed. P5-21$_B$]

Green Engineering   **New Problems on the Web**

CDP5-New   From time to time new problems relating Chapter 5 material to every-day interests or emerging technologies will be placed on the web. Solutions to these problems can be obtained by emailing the author. Also, one can go to the web site, *www.rowan.edu/greenengineering*, and work the home problem specific to this chapter.

Links

SUPPLEMENTARY READING

1. A wide variety of techniques for measuring the concentrations of the reacting species may be found in

    BISIO, A., and R. L. KAPEL, *Scaleup of Chemical Processes*. New York: Wiley-Interscience, 1985.

    ROBINSON, J. W., *Undergraduate Instrumental Analysis*, 5th ed. New York: Marcel Dekker, 1995.

    SKOOG, DOUGLAS A., F. JAMES HOLLER, and TIMOTHY A. NIEMAN, *Principles of Instrumental Analysis*, 5th ed. Philadelphia: Saunders College Publishers, Harcourt Brace College Publishers, 1998.

2. A discussion on the methods of interpretation of batch reaction data can be found in

    CRYNES, B. L., and H. S. FOGLER, eds., *AIChE Modular Instruction Series E: Kinetics*, Vol. 2. New York: American Institute of Chemical Engineers, 1981, pp. 51–74.

3. The interpretation of data obtained from flow reactors is also discussed in

    CHURCHILL, S. W., *The Interpretation and Use of Rate Data*. New York: McGraw-Hill, 1974.

4. The design of laboratory catalytic reactors for obtaining rate data is presented in

    RASE, H. F., *Chemical Reactor Design for Process Plants*, Vol. 1. New York: Wiley, 1983, Chap. 5.

5. Model building and current statistical methods applied to interpretation of rate
   are presented in

   FROMENT, G. F., and K. B. BISCHOFF, *Chemical Reactor Analysis and Des*
       2nd ed. New York: Wiley, 1990.

   MARKERT, B. A., *Instrumental Element and Multi-Element Analysis of P
       Samples: Methods and Applications.* New York: Wiley, 1996.

6. The sequential design of experiments and parameter estimation is covered in

   BOX, G. E. P., W. G. HUNTER, and J. S. HUNTER, *Statistics for Experiment
       An Introduction to Design, Data Analysis, and Model Building.* New Yo
       Wiley, 1978.