

S. R. Logan, *Fundamentals of Chemical Kinetics*, Longman, Essex (1996).  
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### 3.19 PROBLEMS

3.1 Define the following terms:

- (a) Conversion
- (b) Integral method
- (c) Differential method
- (d) Direct method
- (e) Indirect method
- (f) Powell's method
- (g) Essen's method
- (h) Van 't Hoff's method
- (i) Half-life
- (j) Batch reactor
- (k) CSTR
- (l) Plug-flow reactor
- (m) Residence time
- (n) Batch method
- (o) Flow method
- (p) Stopped-flow method
- (q) Temperature-Jump method
- (r) Shock tube
- (s) Flash photolysis
- (t) Molecular beam

3.2 What did you learn in this chapter that was new? Had you heard of direct methods before? How about indirect methods? Were you aware of the inaccuracies in Essen's method? What else did you learn that was new?

3.3 Compare integral methods and differential methods for the analysis of rate data. What are the advantages and disadvantages of each method?

3.4 Compare the various experimental methods in Table 3.1. How does each method work? What determines how long it takes to initiate the reaction?

3.5 Find 10 examples of kinetic processes in your home, such as cooking different kinds of meals, washing clothes, you digesting different types of food, or plants growing on your windowsill.

(a) What experiments would you do to determine a rate equation for each of them? What variables would you think were important?

(b) Find an approximation to the rate equation for each of the reactions from your everyday observations.

(c) Pick one of the examples and explain how you would go about determining a *direct* measurement of the rate equation. Be sure to say specifically what you would do.

(d) For the same example, explain how you would go about determining an *indirect* measurement of the rate equation. Be sure to say specifically what you would do.

3.6 The half-life of tritium is 13.6 years.

(a) Calculate a rate constant for the decomposition of tritium. Assume a first-order reaction.

(b) How long will it take for 99.99% of the tritium to disappear?

3.7 Assume that you are working in the semiconductor industry. IBM just announced that they have a new process to replace aluminum with copper in their chips. Your boss tells you, "We need a copper process, too. Get me one." You look in the literature, and find that you can deposit copper via the chemical vapor deposition (CVD) reaction:



where hfac is a hexafluoroacetylacetonate ligand. Your company already makes CVD reactors, so this seems like a good process for you to bring back to your boss. What would you do to measure the kinetics of the process to enable your company to sell a copper deposition process, too? Be sure to say what you would do during the experiment, what you would measure, and how you would analyze your data.

3.8 Assume that you are working in the pharmaceutical industry. Your company just started selling Interluken-II and noticed that it degrades when it sits in a bottle for about 4 weeks. How would you measure the kinetics of the process? Be sure to consider what criteria you would use to decide whether to make direct or indirect measurements, qualitatively how you would make the measurements, and how you will analyze your data.

3.9 A first-order polymerization reaction is being run in a batch reactor. A concentration of 0.007 mol/liter of monomer is loaded into the reactor, and then a catalyst is added to initiate the reaction. Experiments show that the reaction is 30% complete in 10 minutes.

(a) Calculate the rate constant.

(b) Calculate the half-life.

(c) How long will it take for the reaction to be 90% complete?

(d) How would the time in (c) change if you increased the concentration in the reactor to 0.16 mol/liter?

(e) Repeat for a second-order reaction.

3.10  $\text{N}_2\text{O}_5$  can be made via oxidation of ammonia over a platinum gauze. You do an experiment and find that you get 50% conversion of the ammonia with a 0.1-second residence time ( $\tau$ ) in the reactor at 1000 K.

(a) Estimate the rate constant for the reaction assuming that the reaction is first-order in the ammonia pressure and zero-order in the oxygen pressure.

(b) How long of a residence time will you need to get to 90% conversion at 1000 K?

(c) Now assume that the reaction is instead second-order in the ammonia pressure.

(d) Estimate the rate constant for the reaction assuming 50% conversion in 0.1 second. Assume a stoichiometric feed at 1 atm pressure.

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- (b) Calculate the half-life.
- (c) How long will it take for the reaction to be 90% complete?
- (d) How would the time in (c) change if you increased the concentration in the reactor to 0.16 mol/liter?
- (e) Repeat for a second-order reaction.

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- (a) Estimate the rate constant for the reaction assuming that the reaction is first-order in the ammonia pressure and zero-order in the oxygen pressure.
- (b) How long of a residence time will you need to get to 90% conversion at 1000 K?
- (c) Now assume that the reaction is instead second-order in the ammonia pressure.
- (d) Estimate the rate constant for the reaction assuming 50% conversion in 0.1 second. Assume a stoichiometric feed at 1 atm pressure.

**Table P3.12 Additional data for Example 3.12**

Time, minutes	Concentration, mol/liter	Time, minutes	Concentration, mol/liter
30	0.25	60	0.14
		90	0.10

- (e) What would your conversion be if you used the residence time you calculated in part (b)?
- (f) Calculate a rate constant that would give you 90% conversion for part (e).
- (g) The results in (F) have a lot of industrial significance. People often design their reactors assuming that they have a first-order reaction, and then adjust the temperature of the reactor to get the conversion that they want. Explain how you could change the temperature to increase the rate constant for the reaction.
- (h) Assume that you used your results in (a) to design your reactor, but in fact the reaction is second-order, so the actual conversion is the value you calculate in problem (e). How much would you have to increase the temperature to get 90% conversion?

**3.11** In Example 3.A we fit some data for the growth of paramecium.

- (a) Reproduce the results yourself. A suitable spreadsheet is available in the instructions materials.
- (b) Change the first point. Assume that the measured rate at a paramecium concentration of 2 is 5.4, not 10.4. How will your results change?
- (c) Next, compare the fits obtained with the various methods. How do the  $r^2$  values compare? How do the variances compare?
- (d) What do your results in (c) tell you about the influence of errors in data on the various methods to analyze data?
- (e) Do an F test as in Example 3.B. Are the differences between the two models significant?
- (f) Try the model in Example 3.C. How well does it work?

**3.12** In Example 3.D we used a number of methods to analyze the rate data in Table 3.5.

- (a) Reproduce the results yourself. A suitable spreadsheet is in the instructions materials.
- (b) Assume that we have three more points as given in Table P3.12. How will that change your results?
- (c) How does  $r^2$  change?
- (d) Now assume that you mixed up the point for time = 90 and recorded a concentration of 0.05 mol/liter. How will that change your results?
- (e) According to the Essen plot, which model has the lowest value of  $r^2$  with the one bad point?
- (f) What do you conclude about the utility of  $r^2$  as a way of assessing the reliability of kinetic data?

- 3.13** In Example 3.F, we used Van't Hoff's method to analyze the data in Table 3.F.1.
  - (a) Set up your own spreadsheet to calculate the conversions from the data.
  - (b) Verify the numbers in Table 3.F.2.
  - (c) Verify the numbers in Table 3.F.3.
  - (d) Analyze the data using Essen's method.
  - (e) Analyze the data using Powell's method.
  - (f) How do your results differ?

- 3.14** In Example 3.K, we used Van't Hoff's method to analyze the data in Table 3.K.1.
  - (a) Set up your own spreadsheets and verify the results.
  - (b) Analyze the data using Essen's method.
  - (c) How do your results in (b) differ from those in Example 3.K?

**3.15** Steger and Masel examined the etching of copper in a reactor used to produce electronic materials. The main reaction is  $\text{Cu} + 2\text{hfach} + 0.5\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Cu}(\text{hfach})_2$  where hfach is a hexafluoroacetylacetonate ligand. The following data were obtained:

HfACH Pressure, torr	Etch Rate, $\mu\text{m}/\text{minute}$	HfACH Pressure, torr	Etch Rate, $\mu\text{m}/\text{minute}$	HfACH Pressure, torr	Etch Rate, $\mu\text{m}/\text{minute}$
0.25	0.031	0.35	0.081	0.45	0.113
0.30	0.055	0.40	0.099	0.50	0.126

- (a) Fit these data to equation (2.12) to determine the order of the reaction.
- (b) Steger and Masel also measured the temperature dependence of the rate, and obtained the following data:

Temperature, K	Etch rate, $\mu\text{m}/\text{minute}$	Temperature, K	Etch rate, $\mu\text{m}/\text{minute}$	Temperature, K	Etch rate, $\mu\text{m}/\text{minute}$
548	0.101	573	0.132	598	0.189
563	0.123	583	0.162	613	0.214

Estimate the activation barrier for the reaction.

- (c) How well do these data fit Perrin's equation? Which fits better, Arrhenius' law or Perrin's equation?
  - (d) Does the activation barrier agree with equation (2.31)? What is the significance of this result?
- 3.16** Assume that you have modeled a reaction,  $\text{A} + \text{B} \Rightarrow \text{products}$ , and find that it follows the rate equation

$$-r_B = \frac{k_1 K_2 [A]}{1 + K_2 [A]} (k_4 + K_3 [B])$$

with known values of  $k_1$  and  $K_2$ . You do not know  $K_3$  and  $k_4$  so you decide to go into the lab and measure it. Your data are given in Table P3.16.

- (a) Use linear regression to estimate a value of  $K_3$ . (Hint: Plot  $r_B/(k_1K_2[A])/1 + K_2[A]$ ) versus  $[B]$ .)
- (b) How good is your regression coefficient?
- (c) Make a plot of the calculated rate versus the predicted rate. How well does the model actually fit the data? Now assume that the reaction follows the rate equation:

$$-r_B = \left( \frac{k_1K_2[A]}{1 + K_2[A]} \right)^2 (k_4 + K_3[B])$$

- (d) Use linear regression to estimate a value of  $K_3$ . Hint: Plot  $r_B/\left(\frac{k_1K_2[A]}{1 + K_2[A]}\right)^2$  versus  $[B]$ .
- (e) How good is your regression coefficient?
- (f) Make a plot of the calculated rate versus the predicted rate. How well does the model actually fit the data?
- (g) Notice that the first model fits the data to two significant figures, even though the regression coefficient is  $4 \times 10^{-5}$ . In contrast, the second model has a much better regression coefficient but does not fit the data at all. What does this result tell you about the utility of using regression coefficients to distinguish between kinetic models?
- (h) Use the variances to see which model works best.
- (i) Do an F test to see if the difference is statistically significant.

**3.17** Table P3.17 gives Schneider and Rabinovitz' data for the isomerization of  $CH_3CN$  to  $CH_3NC$ .

- (a) Try to fit the data with a simple first- or second-order rate law. How well does it work?
- (b) Try fitting the data to rate  $= k_1[CH_3NC]^2/(1 + K_2[CH_3NC])$ . How well does the equation fit? (Hint: You could plot  $[CH_3NC]/\text{rate}$  vs.  $1/[CH_3NC]$ . However, I find it more accurate to simply program the rate equation in a spreadsheet and use the solver function to find  $k_1$  and  $K_2$  until the rate equation fits all the data.)
- (c) Are the differences statistically significant? Do an F test on the error in the natural logarithm of the rate.

**Table P3.16** Rate data for Example 3.16

[B], mol/liter	$k_1K_2[A]/1 + K_2[A]$ , mol/(liter-hour)	$-r_B$ , mol/(liter-hour)	[B], mol/liter	$k_1K_2[A]/1 + K_2[A]$ , mol/(liter-hour)	$-r_B$ , mol/(liter-hour)
0.25	1.001	1.0	2.8	5.002	5.0
1.5	2.001	2.0	3.5	6.001	6.0
2	3.000	3.0	4.6	7.003	7.0
2.3	4.001	4.0	5	8.008	8.0

**Table P3.17** The rate of methyl isocyanide isomerization

Methylisocyanide Pressure (mol/liter)	Rate (mol/liter)	Methylisocyanide Pressure (mol/liter)	Rate (mol/liter)
10,520	9.8	18.1	0.0047
10,250	9.4	10.1	0.0019
9,880	9.1	8	0.0012
5,580	5.1	7.14	0.0010
4,020	3.5	5.1	0.00062
3,850	3.5	2.2	0.00014
3,610	3.3	1.39	0.00067
3,580	3.2	1.05	0.00039
1,757	1.5	0.95	0.00036
1,349	1.2	0.59	0.00014
1,050	0.85	0.56	0.00012
486	0.39	0.41	0.000073
309	0.23	0.286	0.000036
222	0.15	0.272	0.000035
100	0.05	0.13	0.0000092
80.6	0.04	0.101	0.0000054
59.6	0.027	0.0876	0.0000040
40.8	0.015	0.0725	0.0000029
29.8	0.010		

Source: Data of Schneider and Rabinovitz (1962).

**3.18** In our undergraduate labs, we measure the rate of oxidation of Red Dye 40 with bleach. The main reaction is



Over the years, we have done many different measurements, and the data in Table P3.18 were obtained:

The objective of this problem is to fit the data to equation (2.13) and determine the order of the reaction in bleach and dye. The easiest way to solve this problem is to use the regression capabilities of your spreadsheet.

**Table P3.18** Rate data for Example 3.18

Dye Concentration, mol/liter	Bleach Concentration, mol/liter	Rate, mol/(liter-minute)	Dye Concentration, mol/liter	Bleach Concentration, mol/(liter-minute)	Rate, mol/liter
0.011	0.031	0.018	0.033	0.030	0.053
0.015	0.0315	0.023	0.034	0.039	0.073
0.018	0.0270	0.024	0.039	0.044	0.092
0.022	0.039	0.041	0.041	0.051	0.115
0.023	0.036	0.032	0.045	0.024	0.053
0.025	0.009	0.009	0.044	0.010	0.028
0.028	0.0189	0.023	0.052	0.052	0.145

- (a) Convert equation (2.13) so that you can use linear regression.  
 (b) Set up your spreadsheet to do the regression using the Data-Analysis/Regression tool in Microsoft Excel.  
 (c) Try nonlinear regression as in Table 3.A.4 to see how that changes your answers.

**3.19** Commercial sterilizers work by heating bacteria to high temperatures where the bacteria die. The FDA (U.S. Food and Drug Administration) requires all sterilizers to meet a standard of an overkill of  $10^{12}$ ; specifically, that each bacterial or bacteria spore has one chance in  $10^{12}$  of surviving. Generally people test sterilizers with a thermobacteria spore that is particularly able to survive high temperatures. It is hard to detect a  $10^{12}$  overkill, so people measure the time to a  $10^6$  overkill and assume that if they double the sterilization time, a  $10^{12}$  overkill will be achieved.

- (a) Show that if the death of bacteria follow a first-order rate law, the time to achieve a  $10^{12}$  overkill is twice the time to achieve a  $10^6$  overkill.  
 (b) What will the overkill be if the reaction is instead second-order? (Hint: Assume an initial concentration of  $10^8/\text{cm}^3$ . At a  $10^6$  overkill, you need to get to a final concentration of  $10^2/\text{cm}^3$ . At a  $10^{12}$  overkill, you need to get to a final concentration of  $10^{-4}/\text{cm}^3$ . Calculate the time in each case.)  
 (c) You can increase the overkill by increasing the temperature. How much would you have to increase the temperature to get the overkill up to  $10^{12}$  in the case in (b)?  
 (d) Assume that you are a canned milk manufacturer who uses a sterilizer to kill the bacteria in the cans before the cans leave your plant. The cans start out with 10,000 thermobacteria each. If the reaction is first-order, what fraction of the cans will have at least one bacterium left after sterilization?  
 (e) If you produce 50,000,000 cans/year, how many will go bad?  
 (f) How would your results in (e) change if the reaction were second-order?

**3.20** Ammonium dinitramide (ADN),  $\text{NH}_4\text{N}(\text{NO}_2)_2$ , is an oxidant used in solid fuel rockets and plastic explosives. The ADN is difficult to process because it can blow up. Oxley et al. *J. Phys Chem A*, **101** (1997) 5646, examined the decomposition of ADN to try to understand the kinetics of the explosion process. At  $160^\circ\text{C}$  they obtained the data in Table P3.20.

- (a) Is this a direct or indirect measurement of the rate?  
 (b) Use Essen's method to fit these data to a rate equation. Assume an initial concentration of  $10^{-3}$  molar.

**Table P3.20** Oxley's measurements of the decomposition of dinitramide at  $160^\circ\text{C}$

Time, seconds	Fraction of the ADN Remaining	Time, seconds	Fraction of the ADN Remaining		
			Time, seconds	Fraction of the ADN Remaining	
0	1.0	900	0.58	2400	0.24
300	0.84	1200	0.49	—	—
600	0.70	1500	0.41	—	—

- (c) Use Van't Hoff's method to fit these data to a rate equation.  
 (d) Use Powell's method to fit these data to a rate equation.  
 (e) If you had to process ADN at  $160^\circ\text{C}$ , how long could you run the process without blowing anything up? Assume that there is an explosion hazard once 5% of the ADN has reacted to form unstable intermediates.  
 (f) If you wanted to process for 5 minutes, what temperature would you choose? Assume that the reaction follows Arrhenius' law with a preexponential of  $10^{13}/\text{second}$ . (Hint: First, estimate the activation energy from your value of the rate constant and the known preexponential.)

**3.21** Chlebicki, et al. *Int J. Chem. Kinetics*, **29** (1997) 73, examined the sodium cresolate (S) catalyzed decomposition of epichlorohydrin (E). At  $71^\circ\text{C}$  they obtained the results in Table P3.21.

- (a) Is this a direct or indirect measurement of the rate?  
 (b) Fit these data to a rate equation. (Hint: Assume that  $C_S$  is constant during each run. First, fit the rate data at each  $C_S$  to a rate equation, and then determine how the rate constant varies with  $C_S$ . Assume an initial concentration of 0.1 mol/liter.)
- 3.22** In Problem 3.21 we noted that Chlebicki, et al. *Int J. Chem. Kinetics*, examined the sodium cresolate (S)-catalyzed decomposition of epichlorohydrin (E) in a batch reactor. However, they could have instead run the reaction in a CSTR.
- (a) Explain what they would have needed to do to measure the rate in a CSTR.  
 (b) What value of the residence time,  $\tau$ , will give a conversion of 0.45 at  $C_S = 0.76 \text{ mol/dm}^3$  (mole per cubic decimeter)?

**3.23** Bodenstein and Lund Z. *Physik Chem*, **57**, (1907)(168), examined the kinetics of the reaction

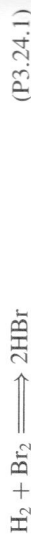


by loading equal amounts of bromine and hydrogen into a reactor and measuring the concentration as a function of time. Table P3.23 shows some of their data.

**Table P3.21** The decomposition of epichlorohydrin in the presence of sodium cresolate

Time, minutes	$C_S = 1.2 \text{ mol/dm}^3$		$C_S = 0.88 \text{ mol/dm}^3$		$C_S = 0.76 \text{ mol/dm}^3$		$C_S = 0.65 \text{ mol/dm}^3$	
	Fraction of the E Remaining	Time, minutes	Fraction of the E Remaining	Time, minutes	Fraction of the E Remaining	Time, minutes	Fraction of the E Remaining	Time, minutes
0	1.0	0	1	0	1.0	0	1.0	0
5	0.90	5	0.93	5	0.94	5	0.94	5
15	0.74	15	0.80	15	0.82	15	0.84	15
25	0.61	25	0.69	25	0.72	25	0.75	25
35	0.50	35	0.59	35	0.63	35	0.66	35
45	0.41	45	0.51	45	0.55	45	0.59	45
55	0.33	55	0.44	55	0.48	55	0.53	55

- (a) Is this a direct or indirect measurement of the rate?  
 (b) Use Essen's method to fit these data to a simple rate equation.  
 (c) Use Van't Hoff's method to fit these data to a simple rate equation.  
 (d) Use Powell's method to fit these data to a simple rate equation.  
 (e) What do you conclude from the nonlinearity of your plots?
- 3.24 In Problem 3.23 we noted that Bodenstein and Lund *Z. Physik Chem*, **57**, (1907) 168, examined the kinetics of the reaction



by loading equal amounts of bromine and hydrogen into a reactor and measuring the concentration as a function of time. Table P3.23 shows some of their data. Bodenstein and Lund fit their data to the expression

$$r_{\text{HBr}} = \frac{k_1[\text{H}_2][\text{Br}_2]^{1/2}}{1 + K_2 \frac{[\text{HBr}]^2}{[\text{Br}_2]}} \quad (\text{P3.24.2})$$

- (a) Use the stoichiometric table to derive an expression for  $[\text{H}_2]$  and  $[\text{HBr}]$  as a function of the  $\text{Br}_2$  conversion.  
 (b) Plug into equation (P3.24.2) to prove

$$\frac{dX_{\text{Br}_2}}{dt} = \frac{K_1(1 - X_{\text{Br}_2})^{1/2}(C_{\text{H}_2}^0 - X_{\text{Br}_2}C_{\text{Br}_2}^0)}{1 + 2K_2 \frac{X_{\text{Br}_2}}{(1 - X_{\text{Br}_2})}} \quad (\text{P3.24.3})$$

where  $X_{\text{Br}_2}$  is the conversion of  $\text{Br}_2$  and  $C_{\text{H}_2}^0$  and  $C_{\text{Br}_2}^0$  are the initial  $\text{H}_2$  and  $\text{Br}_2$  concentrations.

- (c) Show that the solution of equation (P3.24.3) is

$$\frac{C_{\text{Br}_2}^0 k_1}{4K_2} \tau = \left( \frac{1 - 2K_2}{2K_2 \sqrt{1 - X_{\text{Br}_2}}} + \frac{1}{3(1 - X_{\text{Br}_2})^{3/2}} - \frac{1}{2K_2} + \frac{2}{3} \right)$$

when  $C_{\text{Br}_2}^0 = C_{\text{H}_2}^0$

$$\frac{C_{\text{H}_2}^0 k_1}{4K_2} \tau = \frac{\sqrt{C_{\text{Br}_2}^0}}{\sqrt{C_{\text{H}_2}^0 - C_{\text{Br}_2}^0}} \left( \frac{1 - 2K_2}{2K_2} - \frac{C_{\text{Br}_2}^0}{C_{\text{H}_2}^0 - C_{\text{Br}_2}^0} \right)$$

Table P3.23 Bodenstein and Lund's data for the reaction  $\text{H}_2 + \text{Br}_2 \rightleftharpoons 2\text{HBr}$

Time, minutes	$[\text{H}_2]=[\text{Br}_2]$ , mol/liter	Time, minutes	$[\text{H}_2]=[\text{Br}_2]$ , mol/liter
0	0.2250	90	0.1158
20	0.1898	128	0.0967
60	0.1323	180	0.0752

$$\times \arctan \left( \frac{(1 - \sqrt{1 - X_{\text{Br}_2}})(\sqrt{C_{\text{H}_2}^0 - C_{\text{Br}_2}^0} - C_{\text{Br}_2}^0 \sqrt{C_{\text{Br}_2}^0})}{(C_{\text{H}_2}^0 - C_{\text{Br}_2}^0 + C_{\text{Br}_2}^0 \sqrt{1 + X_{\text{Br}_2}})} \right) + \frac{C_{\text{Br}_2}^0}{C_{\text{H}_2}^0 - C_{\text{Br}_2}^0} \left( \frac{1}{\sqrt{1 - X_{\text{Br}_2}}} - 1 \right)$$

when  $C_{\text{H}_2}^0 > C_{\text{Br}_2}^0$

$$\frac{C_{\text{H}_2}^0 k_1}{2K_2} \tau = \frac{\left( \frac{1 - 2K_2}{K_2} \right) + \left( \frac{C_{\text{Br}_2}^0}{C_{\text{Br}_2}^0 - C_{\text{H}_2}^0} \right) \sqrt{C_{\text{Br}_2}^0}}{\sqrt{C_{\text{Br}_2}^0 - C_{\text{H}_2}^0}} \times \ln \left( \frac{(\sqrt{C_{\text{Br}_2}^0} \sqrt{1 - X_{\text{Br}_2}} + \sqrt{C_{\text{Br}_2}^0 - C_{\text{H}_2}^0})(C_{\text{Br}_2}^0 - \sqrt{C_{\text{Br}_2}^0 - C_{\text{H}_2}^0})}{(\sqrt{C_{\text{Br}_2}^0} \sqrt{1 - X_{\text{Br}_2}} - \sqrt{C_{\text{Br}_2}^0 - C_{\text{H}_2}^0})(C_{\text{Br}_2}^0 - \sqrt{C_{\text{Br}_2}^0 - C_{\text{H}_2}^0})} \right) - \frac{2C_{\text{Br}_2}^0}{C_{\text{Br}_2}^0 - C_{\text{H}_2}^0} \left( \frac{1}{\sqrt{1 - X_{\text{Br}_2}}} - 1 \right)$$

- (d) Use your results in (c) to devise new Van't Hoff and Essen plots for the reaction.  
 (e) Construct the Van't Hoff and Essen plots and see if they work.
- 3.25 Ranley, Rust and Vaughn, *JACS* **70** (1948) 88 examined the decomposition of di-tertiary butyl peroxide. The main reaction is



Ranley et al. loaded the di-tertiarybutyl peroxide into a batch reactor at 154.6°C and measured the pressure as a function of time. They obtained the data listed in Table P3.25.

- (a) Is this a direct or indirect measurement of the rate?  
 (b) Develop a stoichiometric table for the reaction.  
 (c) Calculate the conversion as a function of time from the data in Table (P3.25).  
 (d) Use Essen's method to fit these data to a simple rate equation.  
 (e) Use Van't Hoff's method to fit these data to a simple rate equation.  
 (f) Use Powell's method to fit these data to a simple rate equation.  
 (g) How long of a residence time would you need to decompose 99.9% of the di-tertiarybutyl peroxide in a CSTR?

- 3.26 Silicon dioxide ( $\text{SiO}_2$ ) films are used as dielectrics in electronic devices.  $\text{SiO}_2$  films are made by decomposing TEOS [tetraethylorthosilicate,  $(\text{Si}(\text{OC}_2\text{H}_5)_4)$ ] on a silicon wafer. Kim and Gill *J. Electrochemical Society* **142** (1995) 676, examined the thermal decomposition of TEOS in a microbalance. The data shown in Table P3.2.6 were obtained.

**Table P3.25** Raney, et al.'s data for reaction (P3.25)

Time, minutes	Pressure, atm	Time, minutes	Pressure, atm	Time, minutes	Pressure, atm
0	0.223	9	0.295	18	0.355
3	0.249	12	0.316	21	0.372
6	0.273	15	0.336	—	—

**Table P3.26** The rate of SiO<sub>2</sub> deposition from TEOS at 1070 K

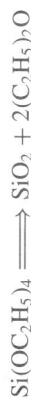
TEOS Pressure, torr	Deposition Rate, µg/hour	TEOS Pressure, torr	Deposition Rate, µg/hour
0.15	148	0.29	175
0.55	200	0.68	209
		0.42	190
		0.81	215

- (a) Is this a direct or indirect measurement of the rate?  
 (b) What is the order of the reaction?  
 (c) Kim and Gill fit the data to

$$r_{\text{SiO}_2} = \frac{k_1 P_{\text{TEOS}}^{1/2}}{1 + k_2 P_{\text{TEOS}}^{1/2}} \quad (\text{P3.26.1})$$

How well does equation (P3.26) fit the data?

- (d) Assume that the reaction follows equation (P3.26.1). Derive an equation for the TEOS pressure as a function of time when TEOS is loaded in a batch reactor and the reactor is heated to 1070°C. Assume the following overall reaction:



where Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> is TEOS. Calculate the TEOS pressure as a function of time, starting with an initial TEOS pressure of 1 torr. Calculate for a long enough period that 60% of the TEOS is used up.

- (e) Use Essen's method to fit your results in (d) to a zero-order, half-order, first-order, or second-order rate equation. How well do your calculated results fit zero-order, half-order, first-order or second-order rate expressions?  
 (f) Do an F test to see which model fits best.

**3.27** Chung and Lu, *J. Polymer Sci A*, **36** (1998) 1017, studied the production of polyethylene-styrene copolymer. Chung and Lu loaded ethylene into a reactor, added a small amount of styrene, and then initiated the reaction. Chung and Lu then measured the conversion of styrene as a function of time. They repeated the same experiments substituting methylstyrene for styrene. (The styrene and methylstyrene runs were done separately.) Some of Chung and Lu's results are given in Table P3.27.

- (a) Is this a direct or indirect measurement of the rate?  
 (b) Use Essen's method to fit these data to a rate equation.

**Table P3.27** The conversion of styrene as a function of time and the conversion of methylstyrene as a function of time, and reported by Chung and Lu

Time, minutes	Styrene Conversion	Methylstyrene Conversion
5	—	13
15	19	27
30	38	55
45	52	70
60	60	85

- (c) Use Van't Hoff's method to fit these data to a rate equation.  
 (d) Use Powell's method to fit these data to a rate equation.  
 (e) How long would you have to run to get 90% conversion of styrene?

**3.28** The growth of bacteria is often thought to follow Monod kinetics, where the growth rate of bacteria,  $r_B$ , in bacteria/(liter-hour) is related to the bacteria concentration by

$$r_B = k_B [B] \frac{K_F [F]}{1 + K_F [F]} \quad (\text{P3.28.1})$$

where [B] is the bacteria concentration in bacteria/liter and [F] is the food concentration in mol/liter.

- (a) What are the units of  $k_B$  and  $K_F$ ?  
 (b) Assume that the bacteria are growing under conditions where there is a large excess of food ( $K_F [F] \gg 1$ ). Develop an equation expressing how quickly the population of bacteria doubles.  
 (c) In the literature, it is common to report values at a constant  $k_G$ , where  $k_G$  is given by

$$k_G = \frac{r_B}{B}$$

Chang and Hong, *J. Biotechnology*, **42** (1995) 189, examined the growth of a potentially toxic bacteria, *Pseudomonas aeruginosa*, PU21 in a glucose solution, and obtained the data in Table P3.28. How well do these data fit Monod kinetics?

**3.29** The adsorption and destruction of alcohol in a human body can be modeled as two first-order reactions in series. When you drink an alcoholic beverage, the alcohol in the beverage reacts with the blood in your stomach walls to yield an alcohol/blood complex. The alcohol/blood complex is then quickly transported throughout your entire body, including your liver. In a second process, the enzymes in your liver break down the alcohol into other products.

- (a) Assume that the adsorption and destruction of alcohol are first-order processes. Use the equations in this chapter to obtain an expression for your blood alcohol level as a function of time.

**Table P3.28**  $k_0$  for the growth of *Pseudomonas aeruginosa* PU21 in glucose solution

Glucose Concentration grams/ml	$k_0$ , hour <sup>-1</sup>	Glucose Concentration grams/ml	$k_0$ , hour <sup>-1</sup>
0.0	0.0	0.7	0.80
0.01	0.4	1.0	0.82
0.05	0.65	1.25	0.85
0.3	0.74	2	0.91

- (b) How would you get values for the rate constants in your model? Assume that you had a Breathalyzer available. What experiments would you do? Would you do experiments only on yourself, or would you include friends?
- (c) Welling et al. *J. Clinical Pharmacology* 17 (1977) 199, measured the alcohol level in subjects and the data in Table P3.29 were obtained. How well does your model fit Welling's data?
- (d) What is the maximum amount of alcohol you can drink and still keep your blood alcohol level below 0.1 gram/liter? (*Hint*: I am looking for you to calculate the answer, NOT do an experiment.)

**3.30** Aranda et al. *Int. J. Chemical Kinetics* 30 (1998) 249, used the swamping method to measure the kinetics of the reaction



They produced the bromine atoms via a reaction with chlorine, while the CH<sub>3</sub>O was produced via photolysis of methanol. They ran their experiments so that there was always a large excess of bromine in the reactor.

- (a) Is this a direct or an indirect measurement of the rate equation?  
 (b) Set up a stoichiometric table for the reaction.  
 (c) Assume that the kinetics follow

$$r_{\text{CH}_2\text{O}} = k_2[\text{CH}_3\text{O}][\text{Br}] \quad (\text{P3.30.2})$$

**Table P3.29** Blood alcohol levels measured on a 75-kg test subject after fasting and then drinking 15 ml of 95% alcohol

Time, minutes	Blood Alcohol Concentration, mg/liter		Time, minutes	Blood Alcohol Concentration, mg/liter	
	Concentration	mg/liter		Concentration	mg/liter
0	0	160	90	60	
10	150	130	110	40	
20	200	70	170	20	

Source: Data of Welling et al. (1977).

Show that when there is a large excess of bromine atoms in the reactor, the CH<sub>3</sub>O concentration will follow

$$\ln \left( \frac{[\text{CH}_3\text{O}]_0}{[\text{CH}_3\text{O}]} \right) = k_2[\text{Br}]t \quad (\text{P3.30.3})$$

where [CH<sub>3</sub>O]<sub>0</sub> is the initial CH<sub>3</sub>O concentration and t is time.

- (d) Table P3.30.1 shows some data for the reaction. Use Essen's method to determine the order of the reaction.
- (e) Use Van't Hoff's method to determine the order of the reaction.
- (f) Use Powell's method to determine the order of the reaction.
- (g) Aranda et al. also report values of  $\ln([\text{CH}_3\text{O}]_0/[\text{CH}_3\text{O}])/t$  for various bromine concentrations. Table P3.30.2 shows the data. Use an Essen plot (i.e.,  $\ln([\text{CH}_3\text{O}]_0/[\text{CH}_3\text{O}])/t$  vs. [Br]) to see how well these data follow equation (P3.30.2).
- (h) Repeat part (g) using a Van't Hoff plot (i.e.,  $k_2$  vs. [Br]).
- (i) Can you find another rate law that fits the data better?
- 3.31** In Section 3.9.1, we derived an expression for the average rate of a reaction as a function of the conversion. The objective of this problem is to see how the average rate compares to the rate at the average concentration.
- (a) Derive an expression for the average rate of a first-order reaction and a second-order reaction as a function of the conversion in a batch reactor.

**Table P3.30.1** The CH<sub>3</sub>O conversion versus time reported by Aranda et al

Time, ms	CH <sub>3</sub> O Conversion	CH <sub>3</sub> O Conversion	CH <sub>3</sub> O Conversion
	$[\text{Br}] = 2.22 \times 10^{11}$ molecules/cm <sup>3</sup>	$[\text{Br}] = 4.48 \times 10^{11}$ molecules/cm <sup>3</sup>	$[\text{Br}] = 6.52 \times 10^{11}$ molecules/cm <sup>3</sup>
0	0	0	0
0.5	0.08	0.15	0.21
1	0.15	0.28	0.38
1.5	0.21	0.39	0.51
2	0.27	0.48	0.61
2.5	0.33	0.56	0.7
3	0.38	0.63	0.76
5	0.55	0.81	0.91

**Table P3.30.2** Values of  $\ln([\text{CH}_3\text{O}]_0/[\text{CH}_3\text{O}])/t$  reported by Aranda et al

$[\text{Br}] \times 10^{11}$ molecules/cm <sup>3</sup>	$\ln([\text{CH}_3\text{O}]_0/[\text{CH}_3\text{O}])/t \times 10^{11}$ molecules/cm <sup>3</sup>	$[\text{Br}] \times 10^{11}$ molecules/cm <sup>3</sup>	$\ln([\text{CH}_3\text{O}]_0/[\text{CH}_3\text{O}])/t \times 10^{11}$ molecules/cm <sup>3</sup>
1.59	116	6.96	503
2.94	210	7.26	506
3.38	250	8.71	578
4.78	334	10.8	755
5.07	427	11.84	913
6.23	505	12.46	823



- (b) Derive an expression for the rate at the average concentration.
- (c) How do the two compare?
- (d) Find a concentration where the average rate equals that rate at that concentration.

**3.32** In Section 3.13 we derived a number of equations for the behavior of a reaction



- (a) Show that equation (3.60) goes to equation (3.61) in the limit that  $[B] \gg [A]$ .
- (b) Show that equation (3.60) goes to equation (3.64) in the limit that  $[A] = [B]$ .
- (c) How can you use the results in (a) and (b) to determine the kinetics of a reaction?
- (d) Assume that you try to run reaction (P3.32.1) with  $[A] = [B]$ , but make a mistake so  $[A] = 0.30$  mol/liter, and  $[B] = 0.32$  mol/liter. Calculate the concentration as a function of time with  $k_2 = 0.45$  liter/(mol·hour). Assume that your final A concentration is 0.01 mol/liter.
- (e) Make an Essen plot of your results in (d) assuming that the reaction follows equation (3.64).
- (f) Make a Van't Hoff plot of your results.
- (g) Repeat for  $[A] = 0.30$   $[B] = 0.62$ .
- (h) What do the results in (e)-(g) tell you about the utility of running the reaction with  $[A] = [B]$ ?

**3.33** Estenfelder, Lintz, Stein Gaube, *Chemical Engineering & Processing*, **37**, (1998) 109, compared the use of an integral and differential reactor to measure the partial oxidation of an unsaturated aldehyde.

- (a) Describe the integral reactor use in these studies.
- (b) Describe the differential reactor used in these studies.
- (c) How do the data obtained by the two methods compare?
- (d) Are there any unexpected findings in the paper?
- (e) When do the authors say that each method should be used?
- (f) How do the findings compare to your expectations from this chapter?

**3.34** The hydrolysis of ethylacetate is a reversible reaction, which is catalyzed by acids. The main reaction is



The reaction obeys

$$r_{\text{EA}} = -k_1[\text{H}^+][\text{CH}_3\text{COOCH}_2\text{CH}_3] + k_2[\text{H}^+][\text{CH}_3\text{COOH}][\text{HOCH}_2\text{CH}_3] \quad (\text{P3.34.2})$$

- (a) Develop a stoichiometric table for the reaction.
- (b) Rearrange equation (P3.30.2) to prove that if there is no ethanol or acetic acid in the reactor at the beginning of the reaction, then

$$\frac{dX_{\text{EA}}}{dt} = -k_1[\text{H}^+](1 - X_{\text{EA}}) + k_2C_{\text{EA}}^0[\text{H}^+](X_{\text{EA}})^2 \quad (\text{P3.34.3})$$

where  $X_{\text{EA}}$  is the conversion of ethylacetate and  $C_{\text{EA}}^0$  is the initial ethylacetate concentration.

- (c) Show that the solution of equation (P3.34.3) is

$$k_1[\text{H}^+]\tau = \left( \frac{1}{1 + 2X_{\text{EA}}^{\text{eq}}} \right) \ln \left( \frac{X_{\text{EA}}^{\text{eq}} - X_{\text{EA}}}{X_{\text{EA}}^{\text{eq}}(X_{\text{EA}} + 1 + X_{\text{EA}}^{\text{eq}})} (1 + X_{\text{EA}}^{\text{eq}}) \right) \quad (\text{P3.34.4})$$

with

$$2X_{\text{EA}}^{\text{eq}} = \left( \sqrt{4 \left( \frac{k_2 C_{\text{EA}}^0}{k_1} \right) + 1} \right) - 1$$

- (d) Make a plot of the rate with various values of the parameters. How does the rate of reaction vary as you vary  $k_1$  and  $X_{\text{EA}}^{\text{eq}}$ ?

**More Advanced Problems**

**3.35** People often use bacteria to digest hazardous materials in wastestreams. The rate usually follows Monod kinetics:

$$\frac{d[\text{B}]}{dt} = k_{\text{B}}[\text{B}] \frac{K_{\text{F}}[\text{W}]}{1 + K_{\text{F}}[\text{W}]} \quad (\text{P3.35.1})$$

$$\frac{d[\text{W}]}{dt} = -k_{\text{W}}[\text{B}] \frac{K_{\text{F}}[\text{W}]}{1 + K_{\text{F}}[\text{W}]} \quad (\text{P3.35.2})$$

where  $[\text{B}]$  is the bacteria concentration in bacteria/liter and  $[\text{W}]$  is the waste concentration in mol/liter. Assume  $K_{\text{F}} = 220$  liters/mol,  $k_{\text{B}} = 0.35$ /hour, and  $k_{\text{W}} = 2.5 \times 10^{-6}$  (mol·hour)/bacteria.

- (a) Derive an expression for  $\frac{d[\text{B}]}{d[\text{W}]}$ .
- (b) Integrate your expression in (a) to derive an expression for  $[\text{B}]$  as a function of  $[\text{W}]$ , the waste concentration at any time,  $t$ , and  $[\text{W}]_0$  and  $[\text{B}]_0$ , the initial bacteria and waste concentrations.
- (c) Rearrange your expression in (b) to derive an expression for  $[\text{B}]$  as a function of the  $X_{\text{W}}$ , the fractional conversion of the waste.
- (d) Compare your results to those in the stoichiometric table. Can you see that you are converting waste into bacteria?
- (e) Substitute your expression into equation (P3.35.2) to calculate the rate of waste reduction as a function of  $X_{\text{W}}$ .
- (f) Integrate your expression to obtain an expression for the time to get a conversion  $X_{\text{W}}$ .

- (g) Assume that you start with  $10^6$  bacteria/liter and 1 mol/liter of waste. You have a choice of two bacteria: one with a  $K_F = 2.2 \times 10^2$  liters/mol,  $k_B = 0.35$ /hour,  $k_W = 2.5 \times 10^{-6}$  (mol-hour)/bacteria a second with a  $K_F = 2.2 \times 10^5$  liters/mol,  $k_B = 0.35$ /hour,  $k_W = 2.5 \times 10^{-7}$  (mol-hour)/bacteria. Which bacteria will get to 99% conversion first?
- (h) Repeat (f) for 99.999% conversion.
- (i) How would your results change with a CSTR?
- (j) On the basis of your results in (f) and (g), could you design a system that starts with one bacteria, then adds a second bacteria to finish the job?

## 3.36

Read the following papers and write a one-page report on the kinetics described in each paper. Why were kinetics measured? What techniques were used to do the kinetic measurements? How were the kinetic data analyzed? What were the key results?

- (a) Koch, R., Palm, Wu., and Setzsch, C. The first rate constants for the reactants of OH radicals with amides. *Int. J. Chem. Kinet.*, **29**, 81 (1997).
- (b) Crivello, J. V., and Liu, S. S. Synthesis and cationic polymerization of glycidyl ether. *Poly. Sci. A*, **36**, 1017 (1998).
- (c) Simakov, P. A., Martínez, F. N., Horner, J. H., and Newcomb, M. Absolute rate constants for alkoxy-carbonyl radical reactions. *J. Org. Chem.*, **63**, 1226 (1998).
- (d) Musa, O. M., Choi, S. Y., Horner, J. H., and Newcomb, M. Absolute rate constants for alpha-amide radical reactions. *J. Org. Chem.*, **63**, 786 (1998).
- (e) Ketting, U., Koltermann, A., Schwille, P., and Eigen, M. Real-time enzyme kinetics monitored by dual-color fluorescence cross-correlation spectroscopy. *Proc. Nat. Acad. Sci. U.S.A.*, **95**, 1416 (1998).
- (f) Wallington, T. J., Guschin, A., Steinn, T. N. N., Platz, J., Sehested, J., Christensen, L. K., and Nielsen, O. J. Atmospheric chemistry of  $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CF}_3$ -UV spectra and kinetic data for  $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$  and  $\text{CF}_3\text{CH}(\text{OCH}_2\text{CF}_3)$  radicals and atmospheric fate of  $\text{CF}_3\text{CH}(\text{OCH}_2\text{CF}_3)$  radicals. *J. Phys. Chem.*, **102**, 1152 (1998).
- (g) Tolti, N. P., and Leigh, W. J. Direct detection of 1,1-diphenylgermene in solution and absolute rate constants for germene trapping reactions. *J. Amer. Chem. Soc.*, **120**, 1172 (1998).
- (h) Lepicard, S. D., and Canosa, A. Measurement of the rate constant for the association reaction  $\text{CH} + \text{N}_2$  at 53 K and its relevance to tritons atmosphere. *Geophys. Res. Lett.*, **25**, 485 (1998).
- (i) Johnson, K. A. Advances in transient-state kinetics (review). *Curr. Opin. Biotechnol.*, **9**, 87 (1998).
- (j) Campbell, M. L. Gas-phase kinetics of ground-state platinum with  $\text{O}_2$ , NO,  $\text{N}_2\text{O}$  and  $\text{CH}_4$ . *J. Chem. Soc. Faraday Trans.*, **94**, 353 (1998).
- (k) Decker, C. The use of UV irradiation in polymerization (review). *Polym. Int.*, **45**, 133 (1998).
- (l) Wolter, S. D., Mohny, S. E., Venugopalan, H., Wickenden, A. E., and Koleske, D. D. Kinetic study of the oxidation of gallium nitride in dry air. *J. Electrochem. Soc.*, **145**, 629 (1998).

- (m) Bedjanian, Y., Laverdet, G., and Lebras, G. Low-pressure study of the reaction of CL atoms with isoprene. *J. Phys. Chem.*, **102**, 953 (1998).
- (n) Blaser, H. U., Jalett, H. P., Garland, M., Studer, M., Thies, H., and Wirthmüller, A. Kinetic studies of the enantioselective hydrogenation of ethyl pyruvate catalyzed by a cinchona modified Pt/Al2O3 catalyst. *J. Catal.*, **173**, 282 (1998).
- (o) Bradford, M. C. J.  $\text{CO}_2$  reforming of  $\text{CH}_4$  over supported Pt catalysts. *J. Catal.*, **173**, 157 (1998).
- (p) Madras, G., Smith, J. M., and McCoy, B. J. Thermal degradation kinetics of polystyrene in solution. *Polym. Degradation Stab.*, **58**, 131 (1997).
- (q) Deters, R., Oetting, M., Wagner, H. G., Temps, F., Laszlo, B., Dobe, S., and Berces, T. A direct investigation of the reaction  $\text{CH}_3\text{OH}$ —Overall rate constant and  $\text{CH}_2$  formation at  $T = 298$  K. *Ber. Bunsenges. Phys. Chem.*, **102**, 58 (1998).
- (r) Kunz, A., and Roth, P. A high temperature study of the reaction  $\text{SiH}_4 + \text{H} \rightarrow \text{H}_2$ . *Ber. Bunsenges. Phys. Chem.*, **102**, 73 (1998).
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- (y) Manke, G. C., and Setser, D. W. Measuring gas-phase chlorine atom concentrations—Rate constants for  $\text{Cl} + \text{HN}_3$ ,  $\text{CF}_3$ , and  $\text{C}_2\text{F}_5$ . *J. Phys. Chem.*, **102**, 153 (1998).

## 3.37

Go to the (a) *International Journal of Chemical Kinetics*, or if this journal is not available in your library, try (b) the kinetics section of *Physical Chemistry A*, (c) *Physical Organic Chemistry*, (d) *Biotechnology and Bioengineering*, (e) *Reaction Kinetics and Catalysis Letters*, (f) *J. Polymer Science A*. Find an article where someone measures the kinetics of a reaction. Write a one-page report on the findings in the article to describe:

- (a) Why the study was undertaken
- (b) What techniques were used
- (c) How the data were analyzed
- (d) What the key results were