Elements of Chemical Reaction Engineering

Seventh Edition

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International Series in the Physical and Chemical Engineering Sciences

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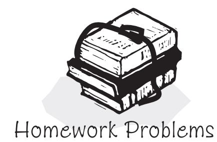
QUESTIONS, SIMULATIONS, AND PROBLEMS

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

A = ● B = ■ C = ◆ D = ◆◆



Questions

Q7-1$_A$ **QBR** (*Question Before Reading*). If you need to determine the rate law, what methods would you use to collect the data and how would you analyze it?

Q7-2$_A$ **i>clicker.** Go to the Web site (*http://www.umich.edu/~elements/7e/07chap/iclicker_ch7_q1.html*) and view at least five i>clicker questions. Choose one that could be used as is, or a variation thereof, to be included on the next exam. You also could consider the opposite case: explaining why the question should *not* be on the next exam. In either case, explain your reasoning.

Q7-3$_A$ (**a**) Listen to the audios  on the CRE Web site. Pick one and say why it could be eliminated.
(**b**) Create an original problem based on Chapter 7 material.
(**c**) 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 CRE Web site.
(**d**) **K-12 Experiment.** 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.)

Q7-4$_B$ **Example 7-1.** What is the error in assuming the concentration of species B is constant and what limits can you put on the calculated value of k? (i.e., $k = 0.24 \pm ?$)

Q7-5$_A$ **Example 7-3.** Explain *why* the regression was carried out twice to find k' and k.

Q7-6$_A$ AWFOS–S. Which of the four Safety Snippets Videos most impressed you with getting across the safety aspect that the video was trying to highlight? Which of the four 1- to 2-minute Snippets Videos was the most humorous while at the same time getting its point across?

Q7-7$_A$ Go to the LearnChemE screencasts link for Chapter 7 (*http://www.umich.edu/~elements/7e/07chap/learn-cheme-videos.html*).
(**a**) View the two screencasts on nonlinear regression and describe or list any differences between the two videos. Would you recommend these screencasts be assigned to next year's class?
(**b**) In the nonlinear regression screencast, what type of data do you need to regress for the reaction order?

Computer Simulations and Experiments

P7-1$_A$ (**a**) **LEP Example Problem 7-3$_A$.** The reaction $A+B \rightarrow C$ occurs in the liquid phase. The proposed empirical rate law is $-r_A = A\exp(-E_A/RT)\,C_A^{\alpha}C_B^{\beta}$. Look at the values of s^2 as a function of α. At what value of α is s^2 minimized?
(i) Vary β keeping A fixed and describe what you find.
(ii) Vary A keeping β fixed and describe what you find.
(iii) Suggest a rate law that minimizes s^2.

(b) **Example 7-4: Nonlinear Regression**
Follow the Polymath tutorial to regress the data given in this example to fit the rate law

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

What is the difference in the correlation and sums of squares compared with those given in Example 7-4?

Interactive Computer Games

P7-2$_A$ (a) Download the Interactive Computer Game (ICG) from the CRE Web site (*http://www.umich.edu/~elements/7e/icm/ecology.html*). Play the game and then record your performance number for the module that indicates your mastery of the material. Your professor has the key to decode your performance number.

ICM Ecology Performance # ________________.

(b) Go to Professor Herz's **Reactor Lab** on the Web at *www.reactorlab.net*. Do (a) one quiz, or (b) two quizzes from Division 1. 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 it 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 random 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.

Problems

P7-3$_A$ Skiing Hand Warmers.† Once a year, Professor Dr. Sven Köttlov loves to go skiing with his students in the mountains of Jofostan. Before going, he retires to his basement in his small but adequate university housing to make hand warmers for everyone.

Here he mixes iron (steel wool), sodium chloride, and a few other proprietary ingredients, then seals them in an airtight Ziploc® compartment. When the warmers are needed, the bag is broken and the iron is exposed to air generating heat by the exothermic reaction

$$4Fe(s) + 3O_2\,(g) \rightleftarrows 2Fe_2O_3(s)$$

To determine the reaction kinetics, a steel wool sample was weighed, cleaned, and put in a sealed container where the percent of oxygen was measured as a function of time and the following data was recorded:

t (min)	0	3	5	8	15	20	25
[% O_2]	21	15	12	10	5	3	2

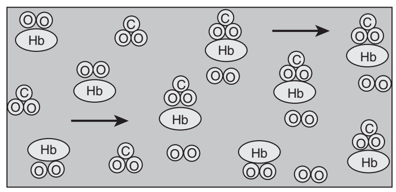
For a specified steel wool weight and surface area, the proposed relationship for the percent oxygen in the bag as a function of time is

$$[\%\ O_2] = 3\exp(-kt) \qquad \text{(P7-3.1)}$$

† J. Gordon and K. Chancy, *J. Chem. Educ.*, 82(7), 1065 (July 2005).

(**a**) Assuming the surface area of steel wool is approximately constant and the bag is sealed, use the CRE algorithm to derive Equation (P7-3.1).
(**b**) Compare the rate law and data. By inspection, without carrying out any data analysis, can you determine immediately that the rate law is correct or not? Explain.
(**c**) Use the data to determine the rate law and rate-law parameters.
(**d**) The data shows the reaction is virtually complete after 25 minutes, while the students will be skiing for 5–7 hours. Professor Köttlov had finger nail polish removed from his nails with acetic acid immediately before performing the experiment. It is known that acid accelerates the reaction. Can you take this information into account? If so, how would you do it?

P7-4$_A$ 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).

$$HbO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Hb + O_2$$

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 solution 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 cm^3/s with $C_{A0} = 2.33 \times 10^{-6}$ mol/cm^3.

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 reaction order and the forward specific reaction-rate constant k_1 for the deoxygenation of hemoglobin.
(**b**) Repeat using regression.

P7-5$_A$ The irreversible isomerization

$$A \longrightarrow B$$

was carried out in a constant-volume **batch** reactor and the following concentration–time data were obtained:

t (min)	0	5	8	10	12	15	17.5	20
C_A (mol/dm^3)	4.0	2.25	1.45	1.0	0.65	0.25	0.06	0.008

Determine the reaction order α and the specific reaction rate k in appropriate units.

P7-6$_B$ **OEQ** (*Old Exam Question*). The liquid-phase irreversible reaction

$$A \rightarrow B + C$$

is carried out in a CSTR. To learn the rate law, the volumetric flow rate, υ_0, (hence $\tau = V/\upsilon_0$) is varied and the effluent concentrations of species A are 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 constant.
(b) What experiments would you do to determine the activation energy?
(c) If you were to take more data, where would you place the measurements (e.g., τ)?
(d) It is believed that the technician may have made a dilution factor-of-10 error in one of the concentration measurements. What do you think?

Note: All measurements were taken at steady-state conditions. Be careful; this problem is sneaky.

P7-7$_A$ 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 to determine the reaction order, α, and the specific reaction rate, k.
(b) Nicolas Bellini wants to know, if you were to take more data, where would you place the points? Why?
(c) Prof. Dr. Sven Köttlov from Jofostan University always asks his students, 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 what you think he is expecting them to say and why.
(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?

P7-8$_A$ **OEQ** (*Old Exam Question*). The following data were reported (from 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

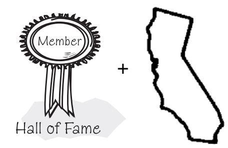
$$(CH_3)_2O \rightarrow CH_4 + H_2 + CO$$

is irreversible and goes virtually to completion, determine the reaction order and specific reaction rate k. (***Ans:*** k = 0.00048 min⁻¹)

(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 temperature? A lower temperature?

P7-9$_A$ **OEQ** (*Old Exam Question*). 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 per hour) into a sunlit body of water, 25000 gal in volume, in order to maintain a sterilizing level of bromine of 1.0 ppm. (***Ans:*** 0.43 lb/h)
(c) Apply to this problem one or more of the six ideas discussed in Table P-4 in the Complete Preface-Introduction on the Web site (***http://www.umich.edu/~elements/7e/toc/Preface-Complete.pdf***).

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.)

P7-10$_C$ The reactions of ozone were studied in the presence of alkenes (from R. Atkinson et al., *Int. J. Chem. Kinet., 15(8)*, 721). The data in Table P7-10$_C$ 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 P7-10$_C$ RATE AS A FUNCTION OF OZONE AND BUTENE CONCENTRATIONS

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.

P7-11$_A$ **OEQ** (*Old Exam Question*). 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 P7-11$_A$. 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 m^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). Determine as many rate-law parameters as you can.

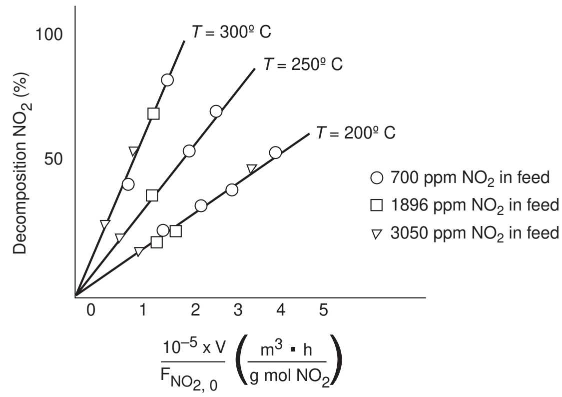


Figure P7-11$_A$ Auto exhaust data.

P7-12$_A$ The thermal decomposition of isopropyl isocyanate was studied in a *differential packed-bed reactor*. From the data in Table P7-12$_A$, determine the reaction-rate-law parameters.

TABLE P7-12$_A$ 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

† *Jofostan Journal of Chemical Engineering*, Vol. 15, page 743 (1995).

SUPPLEMENTARY READING

1. A wide variety of techniques for measuring the concentrations of the reacting species may or may not be found in

THORNTON W. BURGESS, *Mr. Toad and Danny the Meadow Mouse Take a Walk*. New York: Dover Publications, Inc., 1915.

H. SCOTT FOGLER AND STEVEN E. LEBLANC, with BENJAMIN RIZZO, *Strategies for Creative Problem Solving,* 3rd ed. Upper Saddle River, NJ: Pearson, 2014.

CHESTER L. KARRASS, *In Business As in Life, You Don't Get What You Deserve, You Get What You Negotiate*. Hill, CA: Stanford Street Press, 1996.

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

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

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

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

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

G. E. P. BOX, J. S. HUNTER, and W. G. HUNTER, *Statistics for Experimenters: Design, Innovation, and Discovery*, 2nd ed. Hoboken, NJ: Wiley, 2005.