

A Collection of 10 Numerical Problems in Chemical Engineering Solved by Various Mathematical Software Packages

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ABSTRACT: Current personal computers provide exceptional computing capabilities to engineering students that can greatly improve speed and accuracy during sophisticated problem solving. The need to actually create programs for mathematical problem solving has been reduced if not eliminated by available mathematical software packages. This article summarizes a collection of 10 typical problems from throughout the chemical engineering curriculum that require numerical solutions. These problems involve most of the

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standard numerical methods familiar to undergraduate engineering students. Complete problem solution sets have been generated by experienced users in six of the leading mathematical software packages. These detailed solutions including a writeup, and the electronic files for each package are available through the Internet at www.che.utexas.edu/cache/, and via FTP from [ftp.engr.uconn.edu/pub/ASEE/](ftp://ftp.engr.uconn.edu/pub/ASEE/). The written materials illustrate the differences in these mathematical software packages. The electronic files allow hands-on experience with the packages during execution of the actual software packages. This article and the provided resources should be of considerable value during mathematical problem solving and/or the selection of a package for classroom or personal use. © 1998 John Wiley & Sons, Inc. Comput Appl Eng Educ 6: 169–180, 1998

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INTRODUCTION

Session 12 of the Chemical Engineering Summer School [Ch. E. Summer School, sponsored by the Chemical Engineering Division of the American Society for Engineering Education (ASEE)] at Snowbird, Utah, on August 13, 1997, was concerned with "The Use of Mathematical Software in Chemical Engineering." This session provided a major overview of three major mathematical software packages (MathCAD, Mathematica, and POLYMATH), and a set of 10 problems was distributed that uses the basic numerical methods in problems that are appropriate to a variety of chemical engineering subject areas. The problems are titled according to the chemical engineering principles that are used, and the numerical methods required by the mathematical modeling effort are identified. This problem set is summarized in Table 1.

ADDITIONAL CONTRIBUTED SOLUTION SETS

After the ASEE summer school, three more sets of solutions were provided by authors who had considerable experience with additional mathematical software packages. The current total is now six packages, and the packages (listed alphabetically) and authors are given below.

Excel—Edward M. Rosen, EMR Technology Group

Maple—Ross Taylor, Clarkson University

MathCAD—John J. Hwalek, University of Maine

MATLAB—Joseph Brule, John Widmann, Tae Han, and Bruce Finlayson, University of Washington

Mathematica—H. Eric Nuttall, University of New Mexico

POLYMATH—Michael B. Cutlip, University of Connecticut; and Mordechai Shacham, Ben-Gurion University of the Negev

The complete problem set has now been solved with the following mathematical software packages: Excel [Microsoft Corporation (<http://www.microsoft.com>)], Maple [Waterloo Maple, Inc. (<http://www.maplesoft.com>)], MathCAD [Mathsoft, Inc. (<http://www.mathsoft.com>)], MATLAB [Math Works, Inc. (<http://www.mathworks.com>)], Mathematica [Wolfram Research, Inc. (<http://www.wolfram.com>)], and Polymath [Copyright M. B. Cutlip and M. Shacham (<http://www.polymath-software.com>)]. As a service to the academic community, the CACHE Corporation provides this problem set as well as the individual package writeups, and problem solution files for downloading on the World Wide Web at <http://www.che.utexas.edu/cache/>. [The CACHE Corporation is nonprofit educational corporation supported by most chemical engineering departments and many chemical corporations. CACHE stands for computer aides for chemical engineering. CACHE can be contacted at P.O. Box 7939, Austin, TX 78713-7939. Phone: (512)471-4933. Fax: (512) 295-4498. E-mail: cache@uts.cc.utexas.edu. Internet: <http://www.che.utexas.edu/cache/>.] The problem set and details of the various solutions (about 300 pages) are given in separate documents as Adobe PDF files. The problem solution files can be executed with the particular mathematical software package. Alternately, all of these materials can also be obtained from an FTP site at the University of Connecticut: [ftp.engr.uconn.edu/pub/ASEE/](ftp://ftp.engr.uconn.edu/pub/ASEE/).

USE OF THE PROBLEM SET

The complete problem writeups from the various packages allow potential users to examine the de-

Table 1 Problem Set for Use with Mathematical Software Packages

Subject Area	Problem Title	Mathematical Model	Problem
Introduction to Ch. E.	Molar Volume and Compressibility Factor from Van Der Waals Equation	Single nonlinear equation	1
Introduction to Ch. E.	Steady State Material Balances on a Separation Train*	Simultaneous linear equations	2
Mathematical methods	Vapor Pressure Data Representation by Polynomials and Equations	Polynomial fitting, linear, and nonlinear regression	3
Thermodynamics	Reaction Equilibrium for Multiple Gas Phase Reactions*	Simultaneous nonlinear equations	4
Fluid dynamics	Terminal Velocity of Falling Particles	Single nonlinear equation	5
Heat transfer	Unsteady State Heat Exchange in a Series of Agitated Tanks*	Simultaneous ODEs with known initial conditions	6
Mass transfer	Diffusion with Chemical Reaction in a One-Dimensional Slab	Simultaneous ODEs with split boundary conditions	7
Separation processes	Binary Batch Distillation†	Simultaneous differential and nonlinear algebraic equations	8
Reaction engineering	Reversible, Exothermic, Gas Phase Reaction in a Catalytic Reactor*	Simultaneous ODEs and algebraic equations	9
Process dynamics and control	Dynamics of a Heated Tank with PI Temperature Control†	Simultaneous stiff ODEs	10

These problems are adapted in part from a new book entitled *Problem Solving in Chemical Engineering with Numerical Methods*, by Michael B. Cutlip and Mordechai Shacham, to be published by Prentice Hall.

* Problem originally suggested by H. S. Fogler of the University of Michigan.

† Problem preparation assistance by N. Brauner of Tel-Aviv University.

tailed treatment of a variety of typical problems. This method of presentation should indicate the convenience and strengths or weaknesses of each mathematical software package. The problem files can be executed with the corresponding software package to obtain a sense of the package operation. Parameters can be changed and the problems can be resolved. These activities should be very helpful in the evaluation and selection of appropriate software packages for personal or educational use.

Additionally attractive for engineering faculty is that individual problems from the problem set can be easily integrated into existing coursework. Problem variations or even open-ended problems can quickly be created. This problem set and the various writeups should be helpful to engineering faculty who are continually faced with the selection of a mathematical problem-solving package for use in conjunction with their courses.

THE 10-PROBLEM SET

The complete problem set is given in the Appendix to this article. Each problem statement carefully identifies the numerical methods used, the concepts used, and the general problem content.

APPENDIX

Problem 1: Molar Volume and Compressibility Factor from van der Waals Equation

Numerical Methods. Solution of a single nonlinear algebraic equation.

Concepts Used. Use of the van der Waals equation of state to calculate molar volume and compressibility factor for a gas.

Course Usage. Introduction to Chemical Engineering, Thermodynamics.

Problem Statement. The ideal gas law can represent the pressure–volume–temperature (PVT) relationship of gases only at low (near atmospheric) pressures. For higher pressures, more complex equations of state should be used. The calculation of the molar volume and the compressibility factor using complex equations of state typically requires a numerical solution when the pressure and temperature are specified.

The van der Waals equation of state is given by

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad (\text{A.1})$$

where

$$a = \frac{27}{64} \left(\frac{R^2 T_c^2}{P_c} \right) \quad (\text{A.2})$$

and

$$b = \frac{RT_c}{8P_c} \quad (\text{A.3})$$

where P is the pressure (atm), V is the molar volume ($\text{L g}^{-1} \text{mol}^{-1}$), T is the temperature (K), R is the gas constant ($R = 0.08206 \text{ atm L g}^{-1} \text{mol}^{-1} \text{K}^{-1}$), T_c is the critical temperature (405.5 K for ammonia), and P_c is the critical pressure (111.3 atm for ammonia). Reduced pressure is defined as

$$P_r = \frac{P}{P_c} \quad (\text{A.4})$$

and the compressibility factor is given by

$$Z = \frac{PV}{RT} \quad (\text{A.5})$$

1. Calculate the molar volume and compressibility factor for gaseous ammonia at a pressure $P = 56 \text{ atm}$ and a temperature $T = 450 \text{ K}$ using the van der Waals equation of state.
2. Repeat the calculations for the following reduced pressures: $P_r = 1, 2, 4, 10$, and 20 .
3. How does the compressibility factor vary as a function of P_r ?

Problem 2: Steady-State Material Balances on a Separation Train

Numerical Methods. Solution of simultaneous linear equations.

Concepts Used. Material balances on a steady-state process with no recycle.

Course Usage. Introduction to Chemical Engineering.

Problem Statement. Xylene, styrene, toluene, and benzene are to be separated with the array of distilla-

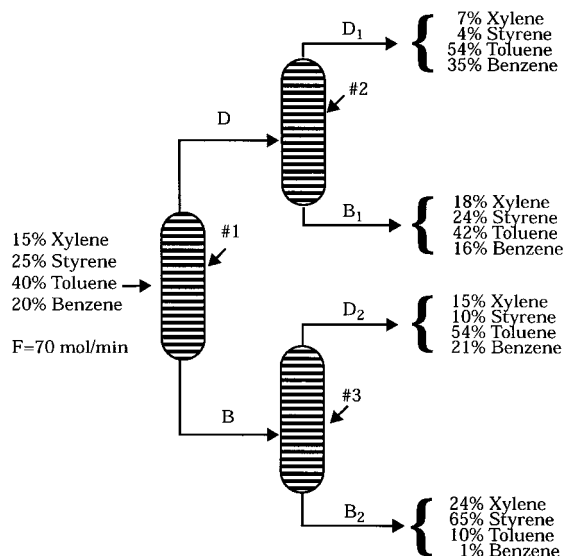


Figure A.1 Separation train.

tion columns that is shown in Figure A.1, where F , D , B , D_1 , B_1 , D_2 , and B_2 are the molar flow rates (mol/min).

Material balances on individual components on the overall separation train yield the equation set

$$\begin{aligned} \text{Xylene: } 0.07D_1 + 0.18B_1 + 0.15D_2 \\ + 0.24B_2 &= 0.15 \times 70 \\ \text{Styrene: } 0.04D_1 + 0.24B_1 + 0.10D_2 \\ + 0.65B_2 &= 0.25 \times 70 \\ \text{Toluene: } 0.54D_1 + 0.42B_1 + 0.54D_2 \\ + 0.10B_2 &= 0.40 \times 70 \\ \text{Benzene: } 0.35D_1 + 0.16B_1 + 0.21D_2 \\ + 0.01B_2 &= 0.20 \times 70 \end{aligned} \quad (\text{A.6})$$

Overall balances and individual component balances on Column 2 can be used to determine the molar flow rate and molar fractions from the equation of Stream D from

$$\text{Molar flow rates: } D = D_1 + B_1$$

$$\begin{aligned} \text{Xylene: } X_{Dx}D &= 0.07D_1 + 0.18B_1 \\ \text{Styrene: } X_{Ds}D &= 0.04D_1 + 0.24B_1 \\ \text{Toluene: } X_{Dt}D &= 0.54D_1 + 0.42B_1 \\ \text{Benzene: } X_{Db}D &= 0.35D_1 + 0.16B_1 \end{aligned} \quad (\text{A.7})$$

Table A.1 Vapor Pressure of Benzene (Perry³)

Temperature, T (°C)	Pressure, P (mmHg)
-36.7	1
-19.6	5
-11.5	10
-2.6	20
+7.6	40
15.4	60
26.1	100
42.2	200
60.6	400
80.1	760

where X_{Dx} is the molar fraction of xylene, X_{Ds} is the molar fraction of styrene, X_{Dt} is the molar fraction of toluene, and X_{Db} is the molar fraction of benzene.

Similarly, overall balances and individual component balances on Column 3 can be used to determine the molar flow rate and molar fractions of Stream B from the equation set

$$\text{Molar flow rates: } B = D_2 + B_2$$

$$\text{Xylene: } X_{Bx}B = 0.15D_2 + 0.24B_2$$

$$\text{Styrene: } X_{Bs}B = 0.10D_2 + 0.65B_2 \quad (\text{A.8})$$

$$\text{Toluene: } X_{Bt}B = 0.54D_2 + 0.10B_2$$

$$\text{Benzene: } X_{Bb}B = 0.21D_2 + 0.01B_2$$

1. Calculate the molar flow rates of streams D_1 , D_2 , B_1 , and B_2 .
2. Determine the molar flow rates and compositions of Streams B and D .

Problem 3: Vapor Pressure Data Representation by Polynomials and Equations

Numerical Methods. Regression of polynomials of various degrees. Linear regression of mathematical models with variable transformations. Nonlinear regression.

Concepts Used. Use of polynomials, a modified Clausius–Clapeyron equation, and the Antoine equation to model vapor pressure versus temperature data.

Course Usage. Mathematical Methods, Thermodynamics.

Problem Statement. Table A.1 presents data of vapor pressure versus temperature for benzene. Some

design calculations require these data to be accurately correlated by various algebraic expressions which provide P (mmHg) as a function of T (°C).

A simple polynomial is often used as an empirical modeling equation. This can be written in general form for this problem as

$$P = a_0 + a_1T + a_2T^2 + a_3T^3 + \cdots + a_nT^n \quad (\text{A.9})$$

where $a_0 \cdots a_n$ are the parameters (coefficients) to be determined by regression, and n is the degree of the polynomial. Typically, the degree of the polynomial is selected which gives the best data representation when using a least-squares objective function.

The Clausius–Clapeyron equation, which is useful for the correlation of vapor pressure data, is given by

$$\log(P) = A - \frac{B}{T + 273.15} \quad (\text{A.10})$$

where P is the vapor pressure (mmHg) and T is the temperature (°C). Note that the denominator is just the absolute temperature in K. Both A and B are the parameters of the equation which are typically determined by regression.

The Antoine equation, which is widely used for the representation of vapor pressure data, is given by

$$\log(P) = A - \frac{B}{T + C} \quad (\text{A.11})$$

where typically P is the vapor pressure (mmHg) and T is the temperature (°C). Note that this equation has parameters A , B , and C which must be determined by nonlinear regression as it is not possible to linearize this equation. The Antoine equation is equivalent to the Clausius–Clapeyron equation when $C = 273.15$.

1. Regress the data with polynomials having the form of Equation (A.9). Determine the degree of polynomial which best represents the data.
2. Regress the data using linear regression on Equation (A.10), the Clausius–Clapeyron equation.
3. Regress the data using nonlinear regression on Equation (A.11), the Antoine equation.

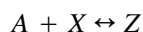
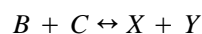
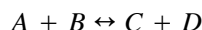
Problem 4: Reaction Equilibrium for Multiple Gas-Phase Reactions

Numerical Methods. Solution of systems of nonlinear algebraic equations.

Concepts Used. Complex chemical equilibrium calculations involving multiple reactions.

Course Usage. Thermodynamics or Reaction Engineering.

Problem Statement. The following reactions are taking place in a constant-volume, gas-phase batch reactor.



A system of algebraic equations describes the equilibrium of the above reactions. The nonlinear equilibrium relationships used the thermodynamic equilibrium expressions, and the linear relationships have been obtained from the stoichiometry of the reactions.

$$\begin{aligned} K_{C1} &= \frac{C_C C_D}{C_A C_B} & K_{C2} &= \frac{C_X C_Y}{C_B C_C} \\ K_{C3} &= \frac{C_Z}{C_A C_X} \\ C_A &= C_{A0} - C_D - C_Z \\ C_B &= C_{B0} - C_D - C_Y \\ C_C &= C_D - C_Y & C_Y &= C_X + C_Z \end{aligned} \quad (\text{A.12})$$

In this equation set, C_A , C_B , C_C , C_D , C_X , C_Y , and C_Z are concentrations of the various species at equilibrium resulting from initial concentrations of only C_{A0} and C_{B0} . The equilibrium constants K_{C1} , K_{C2} , and K_{C3} have known values.

Solve this system of equations when $C_{A0} = C_{B0} = 1.5$, $K_{C1} = 1.06$, $K_{C2} = 2.63$, and $K_{C3} = 5$, starting from three sets of initial estimates.

1. $C_D = C_X = C_Z = 0$
2. $C_D = C_X = C_Z = 1$
3. $C_D = C_X = C_Z = 10$.

Problem 5: Terminal Velocity of Falling Particles

Numerical Methods. Solution of a single nonlinear algebraic equation.

Concepts Used. Calculation of terminal velocity of solid particles falling in fluids under the force of gravity.

Course Usage. Fluid dynamics.

Problem Statement. A simple force balance on a spherical particle reaching terminal velocity in a fluid is given by

$$v_t = \sqrt{\frac{4g(\rho_p - \rho)D_p}{3C_D\rho}} \quad (\text{A.13})$$

where v_t is the terminal velocity (m/s), g is the acceleration of gravity given by $g = 9.80665 \text{ m/s}^2$, ρ_p is the particles density (kg/m^3), ρ is the fluid density (kg/m^3), D_p is the diameter of the spherical particle in (m), and C_D is a dimensionless drag coefficient.

The drag coefficient on a spherical particle at terminal velocity varies with the Reynolds number (Re) as follows (pp. 5–63, 5–64 in Perry [3]).

$$C_D = \frac{24}{Re} \quad \text{for } Re < 0.1 \quad (\text{A.14})$$

$$C_D = \frac{24}{Re} (1 + 0.14 Re^{0.7}) \quad \text{for } 0.1 \leq Re \leq 1000 \quad (\text{A.15})$$

$$C_D = 0.44 \quad \text{for } 1000 < Re \leq 350,000 \quad (\text{A.16})$$

$$C_D = 0.19 - 8 \times 10^4 / Re \quad \text{for } 350,000 < Re \quad (\text{A.17})$$

where $Re = D_p v_t \rho / \mu$, and μ is the viscosity (Pa s or $\text{kg m}^{-1} \text{ s}^{-1}$).

1. Calculate the terminal velocity for particles of coal with $\rho_p = 1800 \text{ kg/m}^3$ and $D_p = 0.208 \times 10^{-3} \text{ m}$ falling in water at $T = 298.15 \text{ K}$, where $\rho = 994.6 \text{ kg/m}^3$ and $\mu = 8.931 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$.
2. Estimate the terminal velocity of the coal particles in water within a centrifugal separator where the acceleration is $30.0 \times g$.

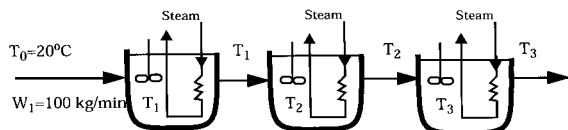


Figure A.2 Series of tanks for oil heating.

Problem 6: Heat Exchange in a Series of Tanks

Numerical Methods. Solution of simultaneous first-order ordinary differential equations.

Concepts Used. Unsteady-state energy balances, dynamic response of well-mixed heated tanks in series.

Course Usage. Heat Transfer.

Problem Statement. Three tanks in series are used to preheat a multicomponent oil solution before it is fed to a distillation column for separation, as shown in Figure (A.2). Each tank is initially filled with 1000 kg of oil at 20°C. Saturated steam at a temperature of 250°C condenses within coils immersed in each tank. The oil is fed into the first tank at the rate of 100 kg/min and overflows into the second and the third tanks at the same flow rate. The temperature of the oil fed to the first tank is 20°C. The tanks are well mixed so that the temperature inside the tanks is uniform, and the outlet stream temperature is the temperature within the tank. The heat capacity, C_p , of the oil is 2.0 kJ/kg. For a particular tank, the rate at which heat is transferred to the oil from the steam coil is given by the expression

$$Q = UA(T_{\text{steam}} - T) \quad (\text{A.18})$$

where $UA = 10 \text{ kJ min}^{-1} \text{ } ^\circ\text{C}^{-1}$ is the product of the heat transfer coefficient and the area of the coil for each tank, T is the temperature of the oil in the tank ($^\circ\text{C}$), and Q is the rate of heat transferred in kJ/min.

Energy balances can be made on each of the individual tanks. In these balances, the mass flow rate to each tank will remain at the same fixed value. Thus, $W = W_1 = W_2 = W_3$. The mass in each tank will be assumed constant, as the tank volume and oil density are assumed to be constant. Thus, $M = M_1 = M_2 = M_3$. For the first tank, the energy balance can be expressed by

$$\text{Accumulation} = \text{Input} - \text{Output}$$

$$MC_p \frac{dT_1}{dt} = WC_p T_0 + UA(T_{\text{steam}} - T_1) - WC_p T_1 \quad (\text{A.19})$$

Note that the unsteady-state mass balance is not needed for Tank 1 or any other tank, since the mass in each tank does not change with time. The above differential equation can be rearranged and explicitly solved for the derivative which is the usual format for numerical solution.

$$\frac{dT_1}{dt} = [WC_p(T_0 - T_1) + UA(T_{\text{steam}} - T_1)]/(MC_p) \quad (\text{A.20})$$

Similarly, for the second tank

$$\frac{dT_2}{dt} = [WC_p(T_1 - T_2) + UA(T_{\text{steam}} - T_2)]/(MC_p) \quad (\text{A.21})$$

For the third tank,

$$\frac{dT_3}{dt} = [WC_p(T_2 - T_3) + UA(T_{\text{steam}} - T_3)]/(MC_p) \quad (\text{A.22})$$

Determine the steady-state temperatures in all three tanks. What time interval will be required for T_3 to reach 99% of this steady-state value during startup?

Problem 7: Diffusion with Chemical Reaction in a One-Dimensional Slab

Numerical Methods. Solution of second-order ordinary differential equations with two point boundary conditions.

Concepts Used. Methods for solving second-order ordinary differential equations with two point boundary values typically used in transport phenomena and reaction kinetics.

Course Usage. Transport Phenomena and Reaction Engineering.

Problem Statement. The diffusion and simultaneous first-order irreversible chemical reaction in a single phase containing only Reactant A and Product B results in a second-order ordinary differential equation given by

$$\frac{d^2 C_A}{dz^2} = \frac{k}{D_{AB}} C_A \quad (\text{A.23})$$

where C_A is the concentration of Reactant A (kg mol m^{-3}); z is the distance variable (m); k is the homogeneous reaction rate constant (s^{-1}); and D_{AB} is the binary diffusion coefficient (m^2/s). A typical geometry for Equation (A.23) is that of a one-dimensional layer which has its surface exposed to a known concentration and allows no diffusion across its bottom surface. Thus, the initial and boundary conditions are

$$C_A = C_{A0} \quad \text{for} \quad z = 0 \quad (\text{A.24})$$

$$\frac{dC_A}{dz} = 0 \quad \text{for} \quad z = L \quad (\text{A.25})$$

where C_{A0} is the constant concentration at the surface ($z = 0$) and there is no transport across the bottom surface ($z = L$), so the derivative is zero.

This differential equation has an analytical solution given by

$$C_A = C_{A0} \frac{\cosh[L(\sqrt{k/D_{AB}})(1 - z/L)]}{\cosh(L\sqrt{k/D_{AB}})} \quad (\text{A.26})$$

1. Numerically solve Equation (A.23) with the boundary conditions of Equations (A.24) and (A.25) for the case where $C_{A0} = 0.2 \text{ kg mol m}^{-3}$, $k = 10^{-3} \text{ s}^{-1}$, $D_{AB} = 1.2 \cdot 10^{-9} \text{ m}^2/\text{s}$, and $L = 10^{-3} \text{ m}$. This solution should utilize an ODE solver with a shooting technique and employ Newton's method or some other technique for converging on the boundary condition given by Equation (A.25).
2. Compare the concentration profiles over the thickness as predicted by the numerical solution of part 1 with the analytical solution of Equation (A.26).

Problem 8: Binary Batch Distillation

Numerical Methods. Solution of a system of equations comprised of ordinary differential equations and nonlinear algebraic equations.

Concepts Used. Batch distillation of an ideal binary mixture.

Course Usage. Separation Processes.

Problem Statement. For a binary batch distillation process involving two components designated 1 and 2, the moles of liquid remaining, L , as a function of the molar fraction of the component 2, x_2 , can be expressed by the following equation:

$$\frac{dL}{dx_2} = \frac{L}{x_2(k_2 - 1)} \quad (\text{A.27})$$

where k_2 is the vapor liquid equilibrium ratio for Component 2. If the system may be considered ideal, the vapor liquid equilibrium ratio can be calculated from $k_i = P_i/P$, where P_i is the vapor pressure of component i , and P is the total pressure.

A common vapor pressure model is the Antoine equation, which uses three parameters, A , B , and C , for component i , as given below, where T is the temperature ($^{\circ}\text{C}$).

$$P_i = 10^{[A - (B/T + C)]} \quad (\text{A.28})$$

The temperature in the batch still follows the bubble point curve. The bubble point temperature is defined by the implicit algebraic equation which can be written using the vapor liquid equilibrium ratios as

$$k_1 x_1 + k_2 x_2 = 1 \quad (\text{A.29})$$

Consider a binary mixture of benzene (Component 1) and toluene (Component 2) which is to be considered as ideal. The Antoine equation constants for benzene are $A_1 = 6.90565$, $B_1 = 1211.033$, and $C_1 = 220.79$. For toluene, $A_2 = 6.95464$, $B_2 = 1344.8$, and $C_2 = 219.482$ (Dean [1]). P is the pressure (mmHg) and T the temperature ($^{\circ}\text{C}$).

The batch distillation of benzene (Component 1) and toluene (Component 2) mixture is being carried out at a pressure of 1.2 atm. Initially, there is 100 mol of liquid in the still, composed of 60% benzene and 40% toluene (molar fraction basis). Calculate the amount of liquid remaining in the still when the concentration of toluene reaches 80%.

Problem 9: Reversible, Exothermic, Gas-Phase Reaction in a Catalytic Reactor

Numerical Methods. Simultaneous ordinary differential equations with known initial conditions.

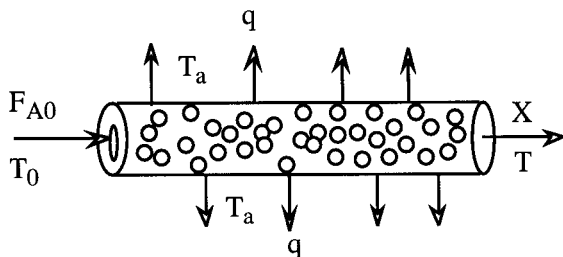


Figure A.3 Packed bed catalytic reactor.

Concepts Used. Design of a gas-phase catalytic reactor with pressure drop for a reversible gas-phase reaction.

Course Usage. Reaction Engineering.

Problem Statement. The elementary gas phase reaction $2A \rightleftharpoons C$ is carried out in a packed bed reactor. There is a heat exchanger surrounding the reactor, and there is a pressure drop along the length of the reactor (Fig. A.3).

The various parameters values for this reactor design problem are summarized in Table A.2.

1. Plot the conversion (X), reduced pressure (y), and temperature ($T \times 10^{-3}$) along the reactor from $W = 0$ kg up to $W = 20$ kg.
2. Around 16 kg of catalyst, you will observe a "knee" in the conversion profile. Explain why this knee occurs and what parameters affect it.
3. Plot the concentration profiles for Reactant A and Product C from $W = 0$ kg up to $W = 20$ kg.

Additional Information. The notation used here and the following equations and relationships for this particular problem are adapted from the textbook by Fogler [2]. The problem is to be worked assuming plug flow with no radial gradients of concentrations and temperature at any location within the catalyst bed. The reactor design will use the conversion of A designated by X and the temperature T , which are both functions of location within the catalyst bed specified by the catalyst weight W .

The general reactor design expression for a catalytic reaction in terms of conversion is a molar balance on Reactant A given by

$$F_{A0} \frac{dX}{dW} = -r'_A \quad (\text{A.30})$$

The simple catalytic reaction rate expression for this reversible reaction is

$$-r'_A = k \left[C_A^2 - \frac{C_C}{K_C} \right] \quad (\text{A.31})$$

where the rate constant is based on Reactant A and follows the Arrhenius expression

$$k = (k \text{ at } T = 450^\circ \text{ K}) \exp \frac{E_A}{R} \left[\frac{1}{450} - \frac{1}{T} \right] \quad (\text{A.32})$$

and the equilibrium constant variation with temperature can be determined from van't Hoff's equation with $\Delta \tilde{C}_p = 0$

$$K_C = (K_C \text{ at } T = 450^\circ \text{ K}) \times \exp \frac{\Delta H_R}{R} \left[\frac{1}{450} - \frac{1}{T} \right] \quad (\text{A.33})$$

The stoichiometry for $2A \rightleftharpoons C$ and the stoichiometric table for a gas allow the concentrations to be expressed as a function of conversion and temperature while allowing for volumetric changes due to decrease in moles during the reaction. Therefore,

$$\begin{aligned} C_A &= C_{A0} \left(\frac{1-X}{1+\epsilon X} \right) \frac{P}{P_0} \frac{T_0}{T} \\ &= C_{A0} \left(\frac{1-X}{1-0.5X} \right)^y \frac{T_0}{T} \end{aligned} \quad (\text{A.34})$$

and

Table A.2 Parameter Values for Problem 8

$C_{PA} = 40.0 \text{ J g}^{-1} \text{ mol}^{-1} \text{ K}^{-1}$
$C_{PC} = 80.0 \text{ J g}^{-1} \text{ mol}^{-1} \text{ K}^{-1}$
$\Delta H_R = -40,000 \text{ J g}^{-1} \text{ mol}^{-1} \text{ K}^{-1}$
$E_A = 41,800 \text{ J g}^{-1} \text{ mol}^{-1} \text{ K}^{-1}$
$k = 0.5 \text{ dm}^6 \text{ kg}^{-1} \text{ min}^{-1} \text{ mol}^{-1}$ at 450 K
$K_C = 25,000 \text{ dm}^3 \text{ g}^{-1} \text{ mol}^{-1}$ at 450 K
$C_{A0} = 0.271 \text{ g mol dm}^{-3}$
$T_0 = 450 \text{ K}$
$R = 8.314 \text{ J g}^{-1} \text{ mol}^{-1} \text{ K}^{-1}$
$F_{A0} = 5.0 \text{ g mol min}^{-1}$
$U_a = 0.8 \text{ J kg}^{-1} \text{ min}^{-1} \text{ K}^{-1}$
$T_a = 500 \text{ K}$
$\alpha = 0.015 \text{ kg}^{-1}$
$P_0 = 10 \text{ atm}$
$y_{A0} = 1.0$ (Pure A feed)

$$y = \frac{P}{P_0}$$

$$C_C = \left(\frac{0.5C_{A0}X}{1 - 0.5X} \right) y \frac{T_0}{T} \quad (\text{A.35})$$

The pressure drop can be expressed as a differential equation (see Fogler [2] for details)

$$\frac{d\left(\frac{P}{P_0}\right)}{dW} = \frac{-\alpha(1 + \varepsilon X)}{2} \frac{P_0}{P} \frac{T}{T_0} \quad (\text{A.36})$$

or

$$\frac{dy}{dW} = \frac{-\alpha(1 - 0.5X)}{2y} \frac{T}{T_0} \quad (\text{A.37})$$

The general energy balance may be written as

$$\frac{dT}{dW} = \frac{U_a(T_a - T) + r'_A(\Delta H_R)}{F_{A0}(\sum \theta_i C_{Pi} + X\Delta\tilde{C}_p)} \quad (\text{A.38})$$

which for only Reactant A in the reactor feed simplifies to

$$\frac{dT}{dW} = \frac{U_a(T_a - T) + r'_A(\Delta H_R)}{F_{A0}(C_{PA})} \quad (\text{A.39})$$

Problem 10: Dynamics of a Heated Tank with Proportional/Integral (PI) Temperature Control

Numerical Methods. Solution of ordinary differential equations, generation of step functions, simulation of a proportional integral controller.

Concepts Used. Closed-loop dynamics of a process including first-order lag and dead time. Padé approximation of time delay.

Course Usage. Process Dynamics and Control.

Problem Statement. A continuous process system consisting of a well-stirred tank, heater and PI temperature controller is depicted in Figure (A.4). The feed stream of liquid with density of ρ (kg/m³) and heat capacity of C (kJ kg⁻¹ °C⁻¹) flows into the heated tank at a constant rate of W (kg/min) and temperature T_i (°C). The volume of the tank is V (m³). It is desired to heat this stream to a higher set point temperature T_r (°C). The outlet temperature is

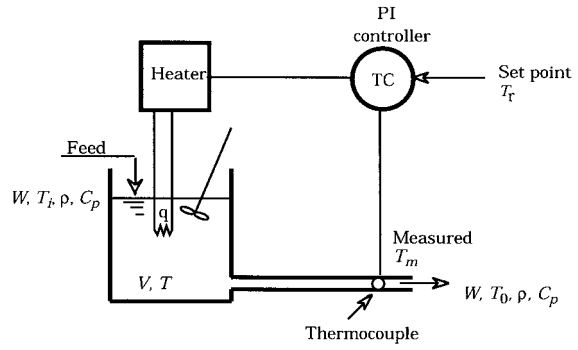


Figure A.4 Well-mixed tank with heater and temperature controller.

measured by a thermocouple as T_m (°C), and the required heater input q (kJ/min) is adjusted by a PI temperature controller. The control objective is to maintain $T_0 = T_r$ in the presence of a change in inlet temperature T_i , which differs from the steady-state design temperature of T_{is} .

Modeling and Control Equations. An energy balance on the stirred tank yields

$$\frac{dT}{dt} = \frac{WC_p(T_i - T) + q}{\rho VC_p} \quad (\text{A.40})$$

with initial condition $T = T_r$ at $t = 0$, which corresponds to steady-state operation at the set point temperature T_r .

The thermocouple for temperature sensing in the outlet stream is described by a first-order system plus the dead time τ_d , which is the time for the output flow to reach the measurement point. The dead time expression is given by

$$T_0(t) = T(t - \tau_d) \quad (\text{A.41})$$

The effect of dead time may be calculated for this situation by the Padé approximation, which is a first-order differential equation for the measured temperature.

$$\frac{dT_0}{dt} = \left[T - T_0 - \left(\frac{\tau_d}{2} \right) \left(\frac{dT}{dt} \right) \right] \frac{2}{\tau_d} \quad \text{I. C.} \quad (\text{A.42})$$

$$T_0 = T_r \quad \text{at} \quad t = 0 \quad (\text{steady state})$$

The above equation is used to generate the temperature input to the thermocouple, T_0 .

The thermocouple shielding and electronics are

modeled by a first-order system for the input temperature T_0 given by

$$\frac{dT_m}{dt} = \frac{T_0 - T_m}{\tau_m} \quad (\text{A.43})$$

I. C. $T_m = T_r$ at $t = 0$ (steady state)

where the thermocouple time constant τ_m is known.

The energy input to the tank, q , as manipulated by the PI controller can be described by

$$q = q_s + K_c(T_r - T_m) + \frac{K_c}{\tau_I} \int_0^t (T_r - T_m) dt \quad (\text{A.44})$$

where K_c is the proportional gain of the controller, and τ_I is the integral time constant or reset time. The q_s in the above equation is the energy input required at steady state for the design conditions as calculated by

$$q_s = WC_p(T_r - T_{is}) \quad (\text{A.45})$$

The integral in Equation (A.44) can be conveniently calculated by defining a new variable as

$$\frac{d}{dt}(\text{errsum}) = T_r - T_m$$

$$\text{I. C. errsum} = 0 \quad \text{at} \quad t = 0 \quad (\text{steady state}) \quad (\text{A.46})$$

Thus, Equation (A.44) becomes

$$q = q_s + K_c(T_r - T_m) + \frac{K_c}{\tau_I}(\text{errsum}) \quad (\text{A.47})$$

Let us consider some of the interesting aspects of this system as it responds to a variety of parameter and operational changes. The numerical values of

Table A.3 Baseline System and Control Parameters for Problem 10

$\rho VC_p = 4000 \text{ kJ/}^\circ\text{C}$	$WC_p = 500 \text{ kJ min}^{-1} ^\circ\text{C}^{-1}$
$T_{is} = 60^\circ\text{C}$	$T_r = 80^\circ\text{C}$
$\tau_d = 1 \text{ min}$	$\tau_m = 5 \text{ min}$
$K_c = 50 \text{ kJ min}^{-1} ^\circ\text{C}^{-1}$	$\tau_I = 2 \text{ min}$

the system and control parameters in Table A.3 will be considered as leading to baseline steady-state operation.

1. Demonstrate the open-loop performance (set $K_c = 0$) of this system when the system is initially operating at design steady state at a temperature of 80°C , and inlet temperature T_i is suddenly changed to 40°C at time $t = 10 \text{ min}$. Plot the temperatures T , T_0 , and T_m to steady state, and verify that Padé approximation for 1 min of dead time given in Equation (A.42) is working properly.
2. Demonstrate the closed-loop performance of the system for the conditions of part 1 and the baseline parameters from Table A.3. Plot temperatures T , T_0 , and T_m to steady state.
3. Repeat part 2 with $K_c = 500 \text{ kJ min}^{-1} ^\circ\text{C}^{-1}$.
4. Repeat part 3 for proportional-only control action by setting the term $K_c/\tau_I = 0$.
5. Implement limits on q [as per Eq. (A.47)] so that the maximum is 2.6 times the baseline steady-state value and the minimum is zero. Demonstrate the system response from baseline steady state for a proportional only controller when the set point is changed from 80°C to 90°C at $t = 10 \text{ min}$. $K_c = 5000 \text{ kJ min}^{-1} ^\circ\text{C}^{-1}$. Plot q and q_{lim} versus time to steady state to demonstrate the limits. Also, plot the temperatures T , T_0 , and T_m to steady state to indicate controller performance.

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BIOGRAPHIES



Michael B. Cutlip is a professor of chemical engineering and director of the university's honors programs at the University of Connecticut. He is active with the ASEE Chemical Engineering Division, serving as national program chair in 1997–1998, and he is the chair-elect for 1999–2000. He is also active with the CACHE Corporation, having served as a trustee since 1981 and president from 1992 to 1994. He is coauthor of the POLYMATH numerical analysis package, which is widely used in chemical engineering departments and made available through the CACHE Corporation. He has also coauthored a recent textbook for Prentice Hall entitled *Problem Solving in Chemical Engineering with Numerical Methods*. His research interests include chemical and electrochemical reaction engineering with a current emphasis on photocatalysis and fuel cell electrode processes.



Mordechai Shacham is a professor of chemical engineering at the Ben-Gurion University of the Negev, Beer-Sheva, Israel, where he has served since 1974. He received his BSc and DSc from the Technion, Israel Institute of Technology. He served for 8 years as department chairman at the Ben-Gurion University and for 2 years as the president of the Israel Institute of Chemical Engineers. His research interests include modeling and regression of data, applied numerical methods, computer-aided instruction and process simulation design and optimization. He is a coauthor of the POLYMATH numerical software package and the textbook *Problem Solving in Chemical Engineering with Numerical Methods*.

Ross Taylor is a professor of chemical engineering at Clarkson University in Potsdam, New York, where he has been since 1980. He received BSc, MSc, and PhD degrees from the University of Manchester, Institute of Science and Technology, in England. His research interests are in the areas of separation process modeling, multicomponent mass transfer, and developing applications of computer algebra to process engineering. He is a coauthor (with Professor R. Krishna of the University of Amsterdam) of the textbook *Multicomponent Mass Transfer* (John Wiley & Sons, 1993) and (with Harry Kooijman) of ChemSep, a software package for simulating multicomponent separation processes used in over 50 educational institutions around the world, as well as in industry. He is a trustee of the CACHE Corporation.



H. Eric Nuttall is a professor of chemical and nuclear engineering at the University of New Mexico and is an active user of Mathematica. He has published and presented many papers on Mathematica in engineering. At the University of New Mexico he has developed and team-taught courses in computer algebra systems with the Department of Mathematics. In the

Department of Chemical Engineering and Nuclear Engineering, Dr. Nuttall introduces Mathematica in a junior-level computational course and used it extensively in the process control course. Dr. Nuttall's research focus is on bioremediation of groundwater and colloid transport. His graduate students often use Mathematica to perform calculations for their theses.



Edward M. Rosen received his BS and MS degrees in chemical engineering from the Illinois Institute of Technology. After serving in the U.S. Army, he attended the University of Illinois, from which he received a PhD in chemical engineering in 1959. Subsequently, Dr. Rosen joined the Monsanto Chemical Company in St. Louis, where he worked in process simulation and computer

applications in chemical engineering. In 1962–1963 he received a Monsanto academic leave and attended Stanford University. With E. J. Henley, he is the coauthor of the book *Material and Energy Balance Computations* (John Wiley & Sons, 1969). A past chairman of the CAST division of AIChE, he is currently the chairman of the Process Engineering Task Force of the CACHE Corporation. Dr. Rosen retired from Monsanto as a senior fellow in 1993 and launched EMR Technology Group in 1994. He is a registered professional engineer in Missouri and a program accreditation evaluator for the AIChE.

John J. Hwalek, Joseph Brule, John Widmann, Tae Han, and Bruce Finlayson (*Biographical sketches and photographs not available.*)