
Application of Mathematical Software Packages in Chemical Engineering Education

DEMONSTRATION PROBLEMS

Sessions 16 and 116
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Workshop Presenters

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INTRODUCTION

Process computations often require the use numerical software packages for problem solving. Such a need frequently arises in ChE education and practice, where the main objectives are deriving the mathematical model of the physical phenomena and critically analyzing the results while technical details of the solution can be handled by a numerical software package. For professionals and ChE students who are involved with the development of mathematical models, there are considerable benefits in using numerical software packages for model development and implementation as compared to the use of source code programming. Process engineers often have to carry out computations that involve non-conventional processes and chemicals. Such processes cannot be modeled with the standard flowsheeting programs, and the use of numerical software packages in such cases is usually most effective.

The objective of this workshop is to provide basic knowledge of the capabilities of several software packages so that the participants will be able to select the package that is most suitable for a particular need. Important considerations will be that the package will provide accurate solutions and will enable precise, compact and clear documentation of the models along with the results with minimal effort on the part of the user.

A summary of the workshop problems is given in Table (D1). Solutions of realistic process computational examples obtained with different software packages will be presented, and similar assignments will be solved during the hands on sessions. The problems have been solved by each of the mathematical packages: Excel*, MATLAB* and Polymath*. Separate solution sets will be provided for each software package.

* Excel is a trademark of Microsoft Corporation (<http://www.microsoft.com>), MATLAB is a trademark of The Math Works, Inc. (<http://www.mathworks.com>), and POLYMATH is copyrighted by Michael B. Cutlip and M. Shacham (<http://www.polymath-software.com>).

Table (D1) Demonstration Problems Illustrating Mathematical Software

COURSE	PROBLEM DESCRIPTION	MATHEMATICAL MODEL	DEMO PROBLEM
Introduction to Ch. E.	Steady State Material Balances on a Separation Train*	Simultaneous Linear Equations	D1
Introduction to Ch. E. & Thermodynamics	Molar Volume and Compressibility Factor from Van Der Waals Equation	Single Nonlinear Equation	D2
Thermodynamics & Separation Processes	Three Phase Equilibrium - Bubble Point	Simultaneous Nonlinear Equations	D3
Fluid Dynamics	Terminal Velocity of Falling Particles	Single Nonlinear Equation	D4
Thermodynamics & Reaction Engineering	Reaction Equilibrium for Multiple Gas Phase Reactions*	Simultaneous Nonlinear Equations	D5
Mathematical Methods	Vapor Pressure Data Representation by Polynomials and Equations	Polynomial Fitting, Linear and Nonlinear Regression	D6
Heat Transfer	Unsteady State Heat Exchange in a Series of Agitated Tanks*	Simultaneous ODE's with Known Initial Conditions	D7
Mass Transfer & Reaction Engineering	Diffusion with Chemical Reaction in a One Dimensional Slab	Simultaneous ODE's with Split Boundary Conditions	D8
Reaction Engineering	Reversible, Exothermic, Gas Phase Reaction in a Catalytic Reactor*	Simultaneous ODE's and Explicit Algebraic Equations	D9
Process Dynamics and Control	Dynamics of a Heated Tank with PI Temperature Control**	Simultaneous Stiff ODE's	D10
Separation Processes	Binary Batch Distillation**	Simultaneous ODE's and Non-linear Algebraic Equations (Differential Algebraic Equations)	D11
Heat Transfer	Unsteady-state Heat Conduction in a Slab	Partial Differential Equation	D12

* Problem originally suggested by H. S. Fogler of the University of Michigan ** Problem preparation assistance by N. Brauner of Tel-Aviv University

These problem are taken in part from "Problem Solving in Chemical Engineering with Numerical Methods" by Michael B. Cutlip and Mordechai Shacham, Prentice-Hall (1999).

D1. STEADY STATE MATERIAL BALANCES ON A SEPARATION TRAIN

1.1 Numerical Methods

Solution of simultaneous linear equations.

1.2 Concepts Utilized

Material balances on a steady state process with no recycle.

1.3 Course Usage

Introduction to Chemical Engineering.

1.4 Problem Statement

Xylene, styrene, toluene and benzene are to be separated with the array of distillation columns that is shown below

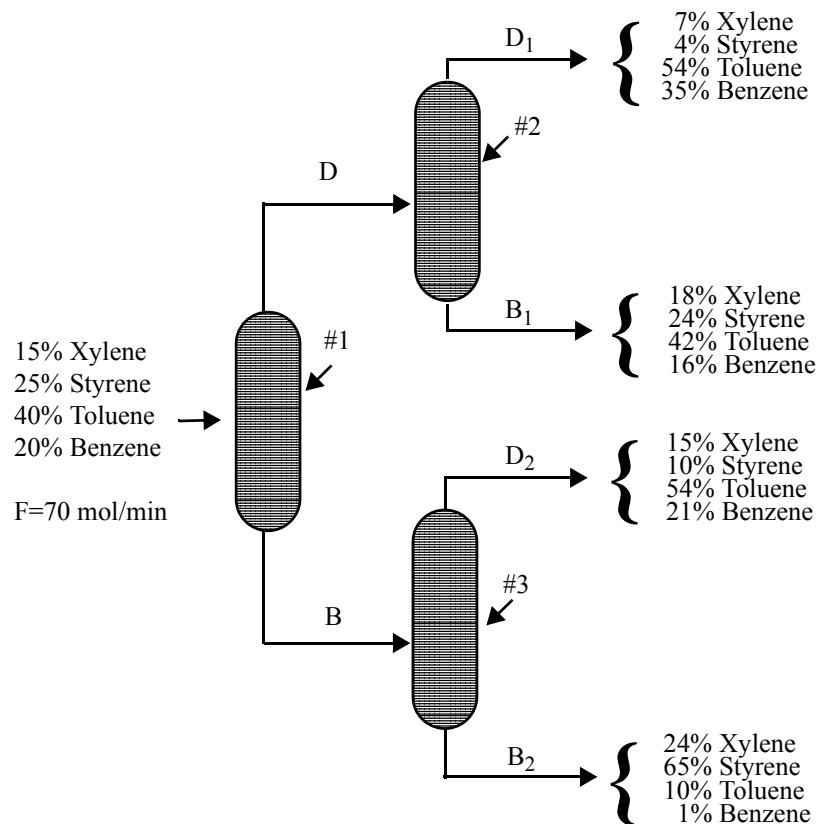


Figure (D1) Separation Train

where F , D , B , $D1$, $B1$, $D2$ and $B2$ are the molar flow rates in mol/min.

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

$$\begin{aligned}
 \text{Xylene: } & 0.07D_1 + 0.18B_1 + 0.15D_2 + 0.24B_2 = 0.15 \times 70 \\
 \text{Styrene: } & 0.04D_1 + 0.24B_1 + 0.10D_2 + 0.65B_2 = 0.25 \times 70 \\
 \text{Toluene: } & 0.54D_1 + 0.42B_1 + 0.54D_2 + 0.10B_2 = 0.40 \times 70 \\
 \text{Benzene: } & 0.35D_1 + 0.16B_1 + 0.21D_2 + 0.01B_2 = 0.20 \times 70
 \end{aligned}
 \tag{D1}$$

Overall balances and individual component balances on column #2 can be used to determine the molar flow rate and mole fractions from the equation of stream D from

$$\begin{aligned}
 \text{Molar Flow Rates: } & D = D_1 + B_1 \\
 \text{Xylene: } & X_{Dx}D = 0.07D_1 + 0.18B_1 \\
 \text{Styrene: } & X_{Ds}D = 0.04D_1 + 0.24B_1 \\
 \text{Toluene: } & X_{Dt}D = 0.54D_1 + 0.42B_1 \\
 \text{Benzene: } & X_{Db}D = 0.35D_1 + 0.16B_1
 \end{aligned}
 \tag{D2}$$

where X_{Dx} = mole fraction of Xylene, X_{Ds} = mole fraction of Styrene, X_{Dt} = mole fraction of Toluene, and X_{Db} = mole fraction of Benzene.

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

$$\begin{aligned}
 \text{Molar Flow Rates: } & B = D_2 + B_2 \\
 \text{Xylene: } & X_{Bx}B = 0.15D_2 + 0.24B_2 \\
 \text{Styrene: } & X_{Bs}B = 0.10D_2 + 0.65B_2 \\
 \text{Toluene: } & X_{Bt}B = 0.54D_2 + 0.10B_2 \\
 \text{Benzene: } & X_{Bb}B = 0.21D_2 + 0.01B_2
 \end{aligned}
 \tag{D3}$$

- (a) Calculate the molar flow rates of streams D_1 , D_2 , B_1 and B_2 .
- (b) Determine the molar flow rates and compositions of streams B and D for part (a).

D2. MOLAR VOLUME AND COMPRESSIBILITY FACTOR FROM VAN DER WAALS EQUATION

2.1 Numerical Methods

Solution of a single nonlinear algebraic equation.

2.2 Concepts Utilized

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

2.3 Course Usage

Introduction to Chemical Engineering, Thermodynamics.

2.4 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

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad \text{(D4)}$$

where

$$a = \frac{27}{64} \left(\frac{R^2 T_c^2}{P_c} \right) \quad \text{(D5)}$$

and

$$b = \frac{RT_c}{8P_c} \quad \text{(D6)}$$

The variables are defined by

P = pressure in atm

V = molar volume in liters/g-mol

T = temperature in K

R = gas constant ($R = 0.08206$ atm·liter/g-mol·K)

T_c = critical temperature (405.5 K for ammonia)

P_c = critical pressure (111.3 atm for ammonia)

Reduced pressure is defined as

$$P_r = \frac{P}{P_c} \quad \text{(D7)}$$

and the compressibility factor is given by

$$Z = \frac{PV}{RT} \quad \text{(D8)}$$

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

D3. THREE PHASE EQUILIBRIUM - BUBBLE POINT

3.1 Numerical Methods

Solution of systems of nonlinear algebraic equations.

3.2 Concepts Utilized

Complex phase equilibrium involving non-ideal mixtures.

3.3 Course Usage

Thermodynamics and Separation Processes.

3.4 Problem Statement

Phase equilibrium at the bubble point in a system which is separated into two liquid phases and one vapor phase can be represented by the following equations.

A mole balance on component i yields

$$z_i = x_{i,1} \left[\beta + (1 - \beta) \frac{k_{i,1}}{k_{i,2}} \right] \quad (\text{D9})$$

where z_i is the mol fraction of component i in the feed, $x_{i,1}$ is the mol fraction of component i in the first liquid phase, $k_{i,1}$ is the phase equilibrium constant of component i in the 1st liquid phase, $k_{i,2}$ is the phase equilibrium constant of component i in the 2nd liquid phase, $\beta = L1/F$ where $L1$ is the total amount (moles) of the 1st liquid phase, and F is the total amount (moles) of the feed.

Phase equilibrium conditions can be expressed by

$$y_i = x_{i,1} k_{i,1} = x_{i,2} k_{i,2} \quad (\text{D10})$$

where y_i is the mol fraction of component i in the vapor phase.

Mole fractions summations can be written by

$$\sum_i x_{i,1} - \sum_i y_i = 0 \quad (\text{D11})$$

$$\sum_i x_{i,1} - \sum_i x_{i,2} = 0 \quad (\text{D12})$$

The phase equilibrium coefficients of component i in liquid phase j can be calculated from

$$k_{i,j} = \frac{\gamma_{i,j} P_i}{P} \quad (\text{D13})$$

where $\gamma_{i,j}$ is the activity coefficient of component i in liquid phase j , P_i is the vapor pressure of component i and P is the total pressure.

The Antoine equation is typically used to calculate the vapor pressure

$$\log P_i = A_{vp_i} - \frac{B_{vp_i}}{C_{vp_i} + t} \quad (\text{D14})$$

where P_i is the vapor pressure (mmHg), t is the temperature ($^{\circ}\text{C}$) and A_{vp_i} , B_{vp_i} and C_{vp_i} are Antoine equation constants of component i .

For a mixture of isobutanol (20%, component No. 1) and water (80%) calculate the composition of the two liquid and the vapor phase and the temperature at the bubble point for total pressure of 760 mmHg.

Suggestion:

Use the following equations to calculate the activity coefficients of the isobutanol and the water (Henley and Rosen⁴).

For isobutanol:

$$\log \gamma_{1,j} = \frac{1.7x_{2,j}^2}{\left(\frac{1.7}{0.7}x_{1,j} + x_{2,j}\right)^2} \quad (\text{D15})$$

For water:

$$\log \gamma_{2,j} = \frac{0.7x_{1,j}^2}{\left(x_{1,j} + \frac{0.7}{1.7}x_{2,j}\right)^2} \quad (\text{D16})$$

The following Antoine equation coefficients should be used (Henley and Rosen⁴): $A_{vp_1} = 7.62231$, $B_{vp_1} = 1417.09$ and $C_{vp_1} = 191.15$ (for isobutanol) $A_{vp_2} = 8.10765$, $B_{vp_2} = 1750.29$ and $C_{vp_2} = 235.0$ (for water).

D4. TERMINAL VELOCITY OF FALLING PARTICLES

4.1 Numerical Methods

Solution of a single nonlinear algebraic equation.

4.2 Concepts Utilized

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

4.3 Course Usage

Fluid dynamics.

4.4 Problem Statement

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

$$v_t = \sqrt{\frac{4g(\rho_p - \rho)D_p}{3C_D\rho}} \quad (\text{D17})$$

where v_t is the terminal velocity in m/s, g is the acceleration of gravity given by $g = 9.80665 \text{ m/s}^2$, ρ_p is the particles density in kg/m^3 , ρ is the fluid density in 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 Perry⁵).

$$C_D = \frac{24}{Re} \quad \text{for} \quad Re < 0.1 \quad (\text{D18})$$

$$C_D = \frac{24}{Re}(1 + 0.14Re^{0.7}) \quad \text{for} \quad 0.1 \leq Re \leq 1000 \quad (\text{D19})$$

$$C_D = 0.44 \quad \text{for} \quad 1000 < Re \leq 350000 \quad (\text{D20})$$

$$C_D = 0.19 - 8 \times 10^4 / Re \quad \text{for} \quad 350000 < Re \quad (\text{D21})$$

where $Re = D_p v_t \rho / \mu$ and μ is the viscosity in Pa·s or kg/m·s.

- (a) 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 $\mu = 8.931 \times 10^{-4} \text{ kg/m}\cdot\text{s}$.
- (b) Estimate the terminal velocity of the coal particles in water within a centrifugal separator where the acceleration is $30.0 g$.

D5. REACTION EQUILIBRIUM FOR MULTIPLE GAS PHASE REACTIONS

5.1 Numerical Methods

Solution of systems of nonlinear algebraic equations.

5.2 Concepts Utilized

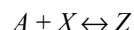
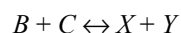
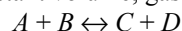
Complex chemical equilibrium calculations involving multiple reactions.

5.3 Course Usage

Thermodynamics or Reaction Engineering.

5.4 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 utilize the thermodynamic equilibrium expressions, and the linear relationships have been obtained from the stoichiometry of the reactions.

$$\begin{aligned} K_{C1} &= \frac{C_C C_D}{C_A C_B} & K_{C2} &= \frac{C_X C_Y}{C_B C_C} & K_{C3} &= \frac{C_Z}{C_A C_X} \\ C_A &= C_{A0} - C_D - C_Z & C_B &= C_{B0} - C_D - C_Y \\ C_C &= C_D - C_Y & C_Y &= C_X + C_Z \end{aligned} \quad \text{(D22)}$$

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.

(a) $C_D = C_X = C_Z = 0$

(b) $C_D = C_X = C_Z = 1$

(c) $C_D = C_X = C_Z = 10$

D6. FITTING EQUATIONS TO VAPOR PRESSURE DATA - POLYNOMIALS

6.1 Numerical Methods

Regression of polynomials of various degrees.

6.2 Concepts Utilized

Use of polynomials to model vapor pressure versus temperature data

6.3 Course Usage

Mathematical Methods, Thermodynamics.

6.4 Problem Statement

Table (D2) presents data of vapor pressure versus temperature for benzene. Some design calculations require these

Table (D2) Vapor Pressure of Benzene (Perry⁵)

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

data to be accurately correlated by various algebraic expressions which provide P in mmHg as a function of T in °C.

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

$$P = a_0 + a_1T + a_2T^2 + a_3T^3 + \dots + a_nT^n \quad (\text{D23})$$

where $a_0 \dots a_n$ 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

$$\log(P) = A - \frac{B}{T + 273.15} \quad (\text{D24})$$

where P is the vapor pressure in mmHg and T is the temperature in °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 Riedel equation (Perry et al.⁵) has the form

$$\log(P) = A + \frac{B}{T} + C\log(T) + DT^\beta \quad (\text{D25})$$

where A , B , C , and D are parameters determined by regression and β is an integer exponent. According to the recommendation in Perry et al.⁵, $\beta = 2$ can be used for this exponent

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

$$\log(P) = A - \frac{B}{T+C} \quad (\text{D26})$$

where typically P is the vapor pressure in mmHg and T is the temperature in °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 $C = 273.15$.

- (a) Regress the data with polynomials having the form of Equation (D23). Determine the degree of polynomial which best represents the data
- (b) Regress the data using linear regression on Equation (D24), the Clausius-Clapeyron equation.
- (c) Correlate the data using the Riedel Equation (D25).
- (d) Regress the data using nonlinear regression on Equation (D26), the Antoine equation.

D7. HEAT EXCHANGE IN A SERIES OF TANKS

7.1 Numerical Methods

Solution of simultaneous first order ordinary differential equations.

7.2 Concepts Utilized

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

7.3 Course Usage

Heat Transfer.

7.4 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 (D2). 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

$$Q = UA(T_{steam} - T) \tag{D27}$$

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

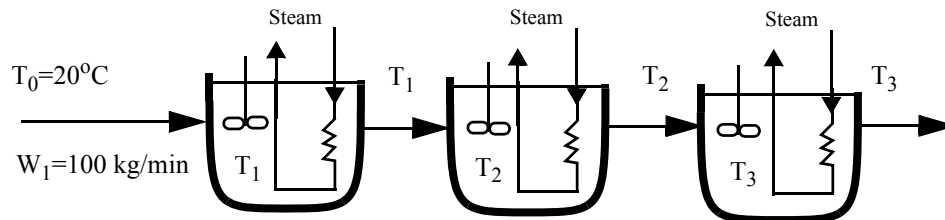


Figure (D2) Series of Tanks for Oil Heating

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

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

$$MC_p \frac{dT_1}{dt} = WC_p T_0 + UA(T_{steam} - T_1) - WC_p T_1 \tag{D28}$$

Note that the unsteady state mass balance is not needed for tank 1 or any other tanks 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.

$$\frac{dT_1}{dt} = [WC_p(T_0 - T_1) + UA(T_{steam} - T_1)] / (MC_p) \quad \text{(D29)}$$

Similarly for the second tank

$$\frac{dT_2}{dt} = [WC_p(T_1 - T_2) + UA(T_{steam} - T_2)] / (MC_p) \quad \text{(D30)}$$

For the third tank

$$\frac{dT_3}{dt} = [WC_p(T_2 - T_3) + UA(T_{steam} - T_3)] / (MC_p) \quad \text{(D31)}$$

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?

D8. DIFFUSION WITH CHEMICAL REACTION IN A ONE-DIMENSIONAL SLAB

8.1 Numerical Methods

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

8.2 Concepts Utilized

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

8.3 Course Usage

Transport Phenomena and Reaction Engineering.

8.4 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

$$\frac{d^2 C_A}{dz^2} = \frac{k}{D_{AB}} C_A \quad (\text{D32})$$

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 (D32) is that of a one dimension 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

$$C_A = C_{A0} \quad \text{for } z = 0 \quad (\text{D33})$$

$$\frac{dC_A}{dz} = 0 \quad \text{for } z = L \quad (\text{D34})$$

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

$$C_A = C_{A0} \frac{\cosh[L(\sqrt{k/D_{AB}})(1-z/L)]}{\cosh(L\sqrt{k/D_{AB}})} \quad (\text{D35})$$

- (a) Numerically solve Equation (D32) with the boundary conditions of Equation (D33) and Equation (D34) 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 (D34).
- (b) Compare the concentration profiles over the thickness as predicted by the numerical solution of (a) with the analytical solution of Equation (D35).

D9. REVERSIBLE, EXOTHERMIC, GAS PHASE REACTION IN A CATALYTIC REACTOR

9.1 Numerical Methods

Simultaneous ordinary differential equations with known initial conditions.

9.2 Concepts Utilized

Design of a gas phase catalytic reactor with pressure drop for a first order reversible gas phase reaction.

9.3 Course Usage

Reaction Engineering

9.4 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.

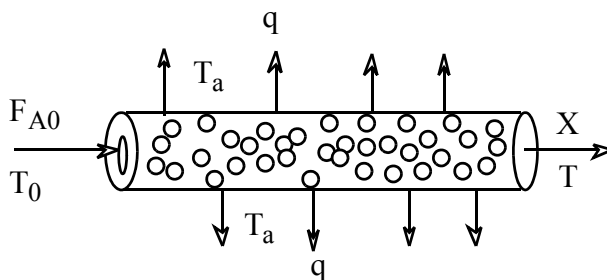


Figure (D3) Packed Bed Catalytic Reactor

The various parameters values for this reactor design problem are summarized in Table (D3).

Table (D3) Parameter Values for Problem 9.

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

- (a) 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.
- (b) Approximately midway down the reactor you will observe a “knee” in the conversion profile. Explain why this knee occurs and what parameters affect the knee.
- (c) Plot the concentration profiles for reactant A and product C from $W = 0$ kg up to $W = 20$ kg.

Addition 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 mole balance on reactant A given by

$$F_{A0} \frac{dX}{dW} = -r'_A \quad (\text{D36})$$

The simple catalytic reaction rate expression for this reversible reaction is

$$-r'_A = k \left[C_A^2 - \frac{C_C}{K_C} \right] \quad (\text{D37})$$

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

$$k = k(@T=450^\circ\text{K}) \exp \frac{E_A}{R} \left[\frac{1}{450} - \frac{1}{T} \right] \quad (\text{D38})$$

and the equilibrium constant variation with temperature can be determined from van't Hoff's equation with $\Delta C_P = 0$

$$K_C = K_C(@T=450^\circ\text{K}) \exp \frac{\Delta H_R}{R} \left[\frac{1}{450} - \frac{1}{T} \right] \quad (\text{D39})$$

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

$$C_A = C_{A0} \left(\frac{1-X}{1+\epsilon X} \right) \frac{P}{P_0} \frac{T_0}{T} = C_{A0} \left(\frac{1-X}{1-0.5X} \right) y \frac{T_0}{T} \quad (\text{D40})$$

and

$$y = \frac{P}{P_0} \quad (\text{D41})$$

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

The pressure drop can be expressed as a differential equation (see Fogler² for details)

$$\frac{d\left(\frac{P}{P_0}\right)}{dW} = \frac{-\alpha(1 + \varepsilon X)P_0 T}{2 P T_0} \quad \text{(D42)}$$

or

$$\frac{dy}{dW} = \frac{-\alpha(1 - 0.5X) T}{2y T_0} \quad \text{(D43)}$$

The general energy balance may be written at

$$\frac{dT}{dW} = \frac{U_a(T_a - T) + r'_A(\Delta H_R)}{F_{A0} \left(\sum \theta_i C_{Pi} + X \tilde{C}_P \right)} \quad \text{(D44)}$$

which for only reactant A in the reactor feed simplifies to

$$\frac{dT}{dW} = \frac{U_a(T_a - T) + r'_A(\Delta H_R)}{F_{A0}(C_{PA})} \quad \text{(D45)}$$

D10. DYNAMICS OF A HEATED TANK WITH PI TEMPERATURE CONTROL

10.1 Numerical Methods

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

10.2 Concepts Utilized

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

10.3 Course Usage

Process Dynamics and Control

10.4 Problem Statement

A continuous process system consisting of a well-stirred tank, heater and PI temperature controller is depicted in Figure (D4). The feed stream of liquid with density of ρ in kg/m^3 and heat capacity of C in $\text{kJ / kg}\cdot^\circ\text{C}$ flows into the heated tank at a constant rate of W in kg/min and temperature T_i in $^\circ\text{C}$. The volume of the tank is V in m^3 . It is desired to heat this stream to a higher set point temperature T_r in $^\circ\text{C}$. The outlet temperature is measured by a thermocouple as T_m in $^\circ\text{C}$, and the required heater input q in 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} .

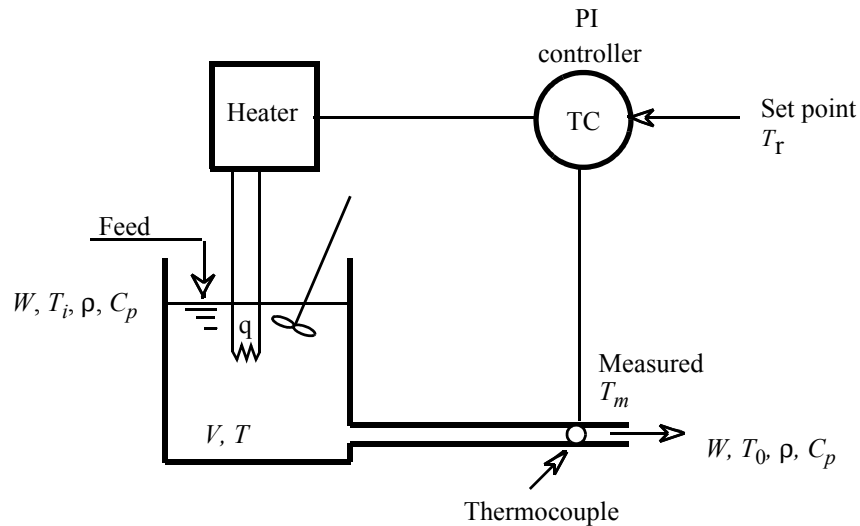


Figure (D4) Well Mixed Tank with Heater and Temperature Controller

Modeling and Control Equations

An energy balance on the stirred tank yields

$$\frac{dT}{dt} = \frac{WC_p(T_i - T) + q}{\rho VC_p} \quad (\text{D46})$$

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

$$T_0(t) = T(t - \tau_d) \quad (\text{D47})$$

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.

$$\frac{dT_0}{dt} = \left[T - T_0 - \left(\frac{\tau_d}{2} \right) \left(\frac{dT}{dt} \right) \right] \frac{2}{\tau_d} \quad \text{I. C. } T_0 = T_r \text{ at } t = 0 \text{ (steady state)} \quad (\text{D48})$$

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

$$\frac{dT_m}{dt} = \frac{T_0 - T_m}{\tau_m} \quad \text{I. C. } T_m = T_r \text{ at } t = 0 \text{ (steady state)} \quad (\text{D49})$$

where the thermocouple time constant τ_m is known.

The energy input to the tank, q , as manipulated by the proportional/integral (PI) controller can be described by

$$q = q_s + K_c(T_r - T_m) + \frac{K_c}{\tau_I} \int_0^t (T_r - T_m) dt \quad (\text{D50})$$

where K_c is the proportional gain of the controller, 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

$$q_s = WC_p(T_r - T_{is}) \quad (\text{D51})$$

The integral in Equation (D50) can be conveniently be calculated by defining a new variable as

$$\frac{d}{dt}(\text{errsum}) = T_r - T_m \quad \text{I. C. } \text{errsum} = 0 \text{ at } t = 0 \text{ (steady state)} \quad (\text{D52})$$

Thus Equation (D50) becomes

$$q = q_s + K_c(T_r - T_m) + \frac{K_c}{\tau_I}(\text{errsum}) \quad (\text{D53})$$

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 the system and control parameters in Table (D4) will be considered as leading to

baseline steady state operation.

Table (D4) Baseline System and Control Parameters for Problem 10

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

- (a) 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 (D48) is working properly.
- (b) Demonstrate the closed loop performance of the system for the conditions of part (a) and the baseline parameters from Table (D4). Plot temperatures T , T_0 , and T_m to steady state.
- (c) Repeat part (b) with $K_c = 500 \text{ kJ/min}\cdot^\circ\text{C}$.
- (d) Repeat part (c) for proportional only control action by setting the term $K_c/\tau_I = 0$.
- (e) Implement limits on q (as per Equation (D53)) 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 $t = 10 \text{ min}$. $K_c = 5000 \text{ kJ/min}\cdot^\circ\text{C}$. 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

D11. BINARY BATCH DISTILLATION

11.1 Numerical Methods

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

11.2 Concepts Utilized

Batch distillation of an ideal binary mixture.

11.3 Course Usage

Separation Processes.

11.4 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 mole fraction of the component 2, x_2 , can be expressed by the following equation

$$\frac{dL}{dx_2} = \frac{L}{x_2(k_2 - 1)} \quad \text{(D54)}$$

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 utilizes three parameters A , B , and C for component i as given below where T is the temperature in °C.

$$P_i = 10^{\left(A - \frac{B}{T+C}\right)} \quad \text{(D55)}$$

The temperature in the batch still follow 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

$$k_1x_1 + k_2x_2 = 1 \quad \text{(D56)}$$

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 $C_2 = 219.482$ (Dean¹). P is the pressure in mm Hg and T the temperature in °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 are 100 moles of liquid in the still, comprised of 60% benzene and 40% toluene (mole fraction basis). Calculate the amount of liquid remaining in the still when concentration of toluene reaches 80%.

D12. METHOD OF LINES FOR PARTIAL DIFFERENTIAL EQUATIONS

12.1 Numerical Methods

Unsteady-state heat conduction in one-dimensional slab with one face insulated and constant thermal diffusivity.

12.2 Concepts Utilized

Application of the numerical method of lines to solve a partial differential equation which involves the solution of simultaneous ordinary differential equations and explicit algebraic equations.

12.3 Course Useage

Heat Transfer.

12.4 Problem Statement*

Unsteady-state heat transfer in a slab in the x direction is described by the partial differential equation (see Geankoplis³ for derivation)

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad (\text{D57})$$

where T is the temperature in K, t is the time in s, and α is the thermal diffusivity in m^2/s given by $k/\rho c_p$. In this treatment, the thermal conductivity k in $\text{W}/\text{m}\cdot\text{K}$, the density ρ in kg/m^3 , and the heat capacity c_p in $\text{J}/\text{kg}\cdot\text{K}$ are all considered to be constant.

Consider an example problem posed by Geankoplis³ where a slab of material with a thickness 1.00 m is supported on nonconducting insulation. This slab is shown in Figure (D5). For a numerical problem solution, the slab is divided into N sections with $N + 1$ node points. The slab is initially at a uniform temperature of 100°C . This gives the initial condition that all the internal node temperatures are known at time $t = 0$.

$$T_n = 100 \text{ for } n = 2 \dots (N + 1) \text{ at } t = 0 \quad (\text{D58})$$

If at time zero the exposed surface is suddenly held constant at a temperature of 0°C , this gives the boundary condition at node 1:

$$T_1 = 0 \text{ for } t \geq 0 \quad (\text{D59})$$

Another boundary condition is that the insulated boundary at node $N + 1$ allows no heat conduction. Thus

$$\frac{\partial T_{N+1}}{\partial x} = 0 \text{ for } t \geq 0 \quad (\text{D60})$$

Note that this problem is equivalent to having a slab of twice the thickness exposed to the initial temperature on both faces.

When convection is considered as the only mode of heat transfer to the surface of the slab, an energy balance can be made at the interface that relates the energy input by convection to the energy output by conduction. Thus at

* Adapted from Geankoplis³, pp. 353–56, with permission.

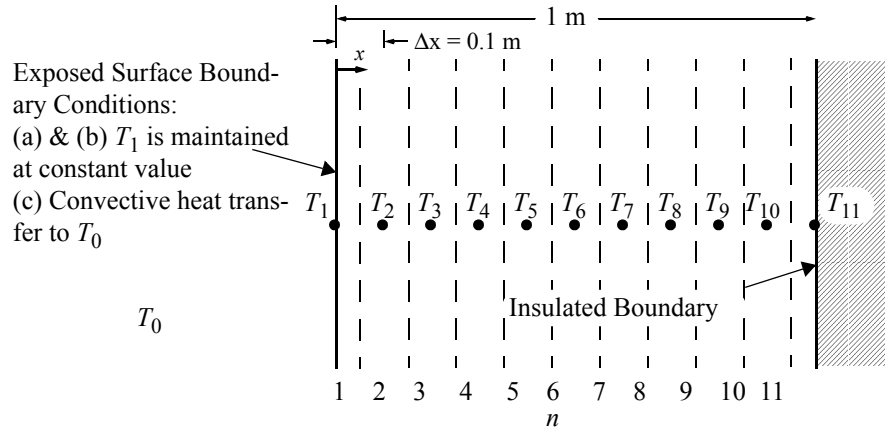


Figure (D5) Unsteady-State Heat Conduction in a One-Dimensional Slab

any time for transport normal to the slab surface in the x direction

$$h(T_0 - T_1) = -k \frac{\partial T}{\partial x} \Big|_{x=0} \quad (\text{D61})$$

where h is the convective heat transfer coefficient in $\text{W}/\text{m}^2 \cdot \text{K}$ and T_0 is the ambient temperature.

- Numerically solve Equation (D57) with the initial and boundary conditions of Equation (D58), Equation (D59), and Equation (D60) for the case where $\alpha = 2 \times 10^{-5} \text{ m}^2/\text{s}$ and the slab surface is held constant at $T_1 = 0 \text{ }^\circ\text{C}$. This solution should utilize the numerical method of lines with 10 sections. Plot the temperatures T_2 , T_3 , T_4 , and T_5 as functions of time to 6000 s.
- Repeat part (a) with 20 sections. Compare results with part (a) to verify that solution for part (a) is accurate.
- Repeat parts (a) and (b) for the case where heat convection is present at the slab surface. The heat transfer coefficient is $h = 25.0 \text{ W}/\text{m}^2 \cdot \text{K}$, and the thermal conductivity is $k = 10.0 \text{ W}/\text{m} \cdot \text{K}$.

The Numerical Method of Lines

The method of lines is a general technique for solving partial differential equations (PDEs) by typically using finite difference relationships for the spatial derivatives and ordinary differential equations for the time derivative, as discussed by Schiesser⁵. For this problem with $N = 10$ sections of length $\Delta x = 0.1 \text{ m}$, Equation (D57) can be rewritten using a central difference formula for the second derivative as

$$\frac{\partial T_n}{\partial t} = \frac{\alpha}{(\Delta x)^2} (T_{n+1} - 2T_n + T_{n-1}) \quad \text{for } (2 \leq n \leq 10) \quad (\text{D62})$$

The boundary condition given in Equation (D59) can be expressed as

$$T_1 = 0 \quad (\text{D63})$$

The second boundary condition represented by Equation (D60) can be written using a second-order backward finite

difference as

$$\frac{\partial T_{11}}{\partial x} = \frac{3T_{11} - 4T_{10} + T_9}{2\Delta x} = 0 \quad (\text{D64})$$

which can be solved for T_{11} to yield

$$T_{11} = \frac{4T_{10} - T_9}{3} \quad (\text{D65})$$

Surface Boundary Condition

The energy balance at the slab surface given by Equation (D61) can be used to determine a relationship between the slab surface temperature T_1 , the ambient temperature T_0 , and the temperatures at internal node points. In this case, the second-order forward difference equation for the first derivative can be applied to T_1

$$\frac{\partial T_1}{\partial x} = \frac{(-T_3 + 4T_2 - 3T_1)}{2\Delta x} \quad (\text{D66})$$

and can be substituted into Equation (D61) to yield

$$h(T_0 - T_1) = -k \left. \frac{\partial T}{\partial x} \right|_{x=0} = -k \frac{(-T_3 + 4T_2 - 3T_1)}{2\Delta x} \quad (\text{D67})$$

The preceding equation can be solved for T_1 to give

$$T_1 = \frac{2hT_0\Delta x - kT_3 + 4kT_2}{3k + 2h\Delta x} \quad (\text{D68})$$

and this can be used to calculate T_1 during the method of lines solution.

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