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# Application of Mathematical Software Packages in Chemical Engineering Education

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## ASSIGNMENT PROBLEMS

Sessions 16 and 116  
ASEE Chemical Engineering Division Summer School  
University of Colorado - Boulder  
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### Workshop Presenters

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### INTRODUCTION TO ASSIGNMENT PROBLEMS

This set of Assignment Problems in Chemical Engineering is a companion set to the Demonstration Problems that were prepared for the ASEE Chemical Engineering Summer School. 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 Assignment Problems is given in Table (A1). Participants will be able to selected problems from this problem set to solve in the afternoon computer workshops. This problem solving will be individualized under the guidance of experienced faculty who are knowledgeable on the various mathematical packages: Excel\*, MATLAB\* and Polymath\*.

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**Table A1** Assignment Problems Illustrating Mathematical Software

COURSE	PROBLEM DESCRIPTION	MATHEMATICAL MODEL	ASSIGNMENT PROBLEM
Introduction to Ch. E.	Steady State Material Balances on a Separation Train*	Simultaneous Linear Equations	A1
Introduction to Ch. E. & Thermodynamics	Molar Volume and Compressibility Factor from Redlich-Kwong Equation	Single Nonlinear Equation	A2
Thermodynamics & Separation Processes	Dew Point and Two-Phase Flash in a Non-Ideal System	Simultaneous Nonlinear Equations	A3
Fluid Dynamics	Pipe and Pump Network	Simultaneous Nonlinear Equations	A4
Reaction Engineering	Operation of a Cooled Exothermic CSTR	Simultaneous Nonlinear Equations	A5
Mathematical Methods	Vapor Pressure Correlations for a Sulfur Compound Present in Petroleum	Polynomial Fitting, Linear and Nonlinear Regression	A6
Reaction Engineering	Catalyst Decay in a Packed Bed Reactor Modeled by a Series of CSTRs	Simultaneous ODE's with Known Initial Conditions	A7
Mass Transfer	Slow Sublimation of a Solid Sphere	Simultaneous ODE's with Split Boundary Conditions	A8
Reaction Engineering	Semibatch Reactor with Reversible Liquid Phase Reaction	Simultaneous ODE's and Explicit Algebraic Equations	A9
Process Dynamics and Control	Reset Windup in a Stirred Tank Heater	Simultaneous ODE's with Step Functions	A10
Reaction Engineering & Process Dynamics and Control	Steam Heating Stage of a Batch Reactor Operation	Simultaneous ODE's and Explicit Algebraic Equations	A11
Mass Transfer & Mathematical Methods	Unsteady State Mass Transfer in a Slab	Partial Differential Equation	A12

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).

## A1. 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

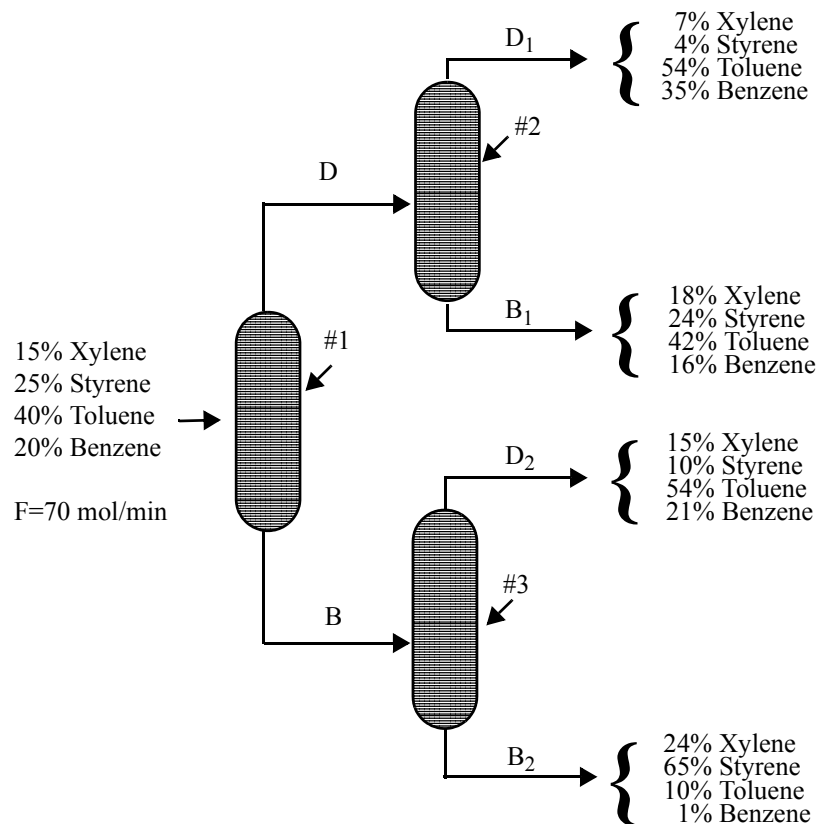


Figure A1 Separation Train

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

$$\begin{aligned}
 \text{Xylene: } & 0.07D_1 + 0.18B_1 + 0.15D_2 + 0.24B_2 = 0.15 \times 70 \\
 \text{Styrene: } & 0.04D_1 + 0.24B_1 + 0.10D_2 + 0.65B_2 = 0.25 \times 70 \\
 \text{Toluene: } & 0.54D_1 + 0.42B_1 + 0.54D_2 + 0.10B_2 = 0.40 \times 70 \\
 \text{Benzene: } & 0.35D_1 + 0.16B_1 + 0.21D_2 + 0.01B_2 = 0.20 \times 70
 \end{aligned}
 \tag{A1}$$

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

$$\begin{aligned}
 \text{Molar Flow Rates: } & D = D_1 + B_1 \\
 \text{Xylene: } & X_{Dx}D = 0.07D_1 + 0.18B_1 \\
 \text{Styrene: } & X_{Ds}D = 0.04D_1 + 0.24B_1 \\
 \text{Toluene: } & X_{Dt}D = 0.54D_1 + 0.42B_1 \\
 \text{Benzene: } & X_{Db}D = 0.35D_1 + 0.16B_1
 \end{aligned}
 \tag{A2}$$

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

$$\begin{aligned}
 \text{Molar Flow Rates: } & B = D_2 + B_2 \\
 \text{Xylene: } & X_{Bx}B = 0.15D_2 + 0.24B_2 \\
 \text{Styrene: } & X_{Bs}B = 0.10D_2 + 0.65B_2 \\
 \text{Toluene: } & X_{Bt}B = 0.54D_2 + 0.10B_2 \\
 \text{Benzene: } & X_{Bb}B = 0.21D_2 + 0.01B_2
 \end{aligned}
 \tag{A3}$$

Reduce the original feed flow rate to the first column in turn for each one of the components by first 1% then 2% and calculate the corresponding flow rates of  $D_1$ ,  $B_1$ ,  $D_2$ , and  $B_2$ . Explain your results.

## A2. MOLAR VOLUME AND COMPRESSIBILITY FACTOR FROM REDLICH-KWONG EQUATION

### 2.1 Numerical Methods

Solution of a single nonlinear algebraic equation.

### 2.2 Concepts Utilized

Use of the Redlich-Kwong 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 Redlich-Kwong equation of state is given by

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+b)\sqrt{T}} \quad (\text{A4})$$

where

$$a = 0.42747 \left( \frac{R^2 T_c^{5/2}}{P_c} \right) \quad (\text{A5})$$

$$b = 0.08664 \left( \frac{RT_c}{P_c} \right) \quad (\text{A6})$$

The variables are defined by

$P$  = pressure in atm

$V$  = molar volume in L/g-mol

$T$  = temperature in K

$R$  = gas constant ( $R = 0.08206 \text{ atm} \cdot \text{L/g-mol} \cdot \text{K}$ )

$T_c$  = the critical temperature (405.5 K for ammonia)

$P_c$  = the critical pressure (111.3 atm for ammonia)

Reduced pressure is defined as

$$P_r = \frac{P}{P_c} \quad (\text{A7})$$

and the compressibility factor is given by

$$Z = \frac{PV}{RT} \quad (\text{A8})$$

- (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 Redlich-Kwong 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  $P_r$ ?

### A3. DEW POINT AND TWO-PHASE FLASH IN A NON-IDEAL SYSTEM

#### 3.1 Numerical Methods

Solution of systems of nonlinear algebraic equations.

#### 3.2 Concepts Utilized

Complex chemical equilibrium involving non-ideal mixtures.

#### 3.3 Course Usage

Thermodynamics and Separation Processes.

#### 3.4 Problem Statement

Phase equilibrium in a system, which is separated into a liquid phase and a vapor phase, can be represented by the following equations.

A mole balance on component  $i$  yields

$$z_i = x_i [1 + \alpha(k_i - 1)] \quad (\text{A9})$$

where  $z_i$  is the mol fraction of component  $i$  in the feed,  $x_i$  is the mol fraction of component  $i$  in the liquid phase,  $k_i$  is the phase equilibrium constant of component  $i$ ,  $\alpha = V/F$  where  $V$  is the total amount (moles) of the vapor phase and  $F$  is the total amount of the feed.

Phase equilibrium conditions may be expressed by

$$y_i = x_i k_i \quad (\text{A10})$$

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

Mole fraction summation can be written as.

$$\sum_i x_i - \sum_i y_i = 0 \quad (\text{A11})$$

The phase equilibrium coefficients of component  $i$  can be calculated from the equation

$$k_i = \frac{\gamma_i P_i}{P} \quad (\text{A12})$$

where  $\gamma_i$  is the activity coefficient of component  $i$ ,  $P_i$  is the vapor pressure of component  $i$  and  $P$  is the total pressure.

The Antoine equation is used to calculate the vapor pressure

$$\log P_i = A v p_i - \frac{B v p_i}{C v p_i + t} \quad (\text{A13})$$

where  $P_i$  is the vapor pressure (mmHg),  $t$  is the temperature ( $^{\circ}$  C) and  $A v p_i$ ,  $B v p_i$  and  $C v p_i$  are Antoine equation con-

stants of component  $i$ .

For a mixture of isobutanol (20%, component No. 1)) and water (80%) calculate

(a) Calculate the composition of the liquid and the vapor phases and the temperature at the dew point for total pressure of 760 mmHg. (hint: at the dew point  $\alpha = 1$ ).

(b) Calculate the vapor fraction ( $\alpha$ ) and the composition of the liquid at temperature of 90 °C and total pressure of 760 mmHg.

### 3.5 Solution Suggestions:

Use the following equations to calculate the activity coefficients of the isobutanol and the water (Henley and Rosen<sup>4</sup>).

**For isobutanol:**

$$\log \gamma_{1,j} = \frac{1.7x_{2,j}^2}{\left(\frac{1.7}{0.7}x_{1,j} + x_{2,j}\right)^2} \quad (\text{A14})$$

**For water:**

$$\log \gamma_{2,j} = \frac{0.7x_{1,j}^2}{\left(x_{1,j} + \frac{0.7}{1.7}x_{2,j}\right)^2} \quad (\text{A15})$$

The following Antoine equation coefficients should be used (Henley and Rosen<sup>4</sup>):  $Avp_1 = 7.62231$ ,  $Bvp_1 = 1417.09$  and  $Cvp_1 = 191.15$  (for isobutanol)  $Avp_2 = 8.10765$ ,  $Bvp_2 = 1750.29$  and  $Cvp_2 = 235.0$  (for water).



## A4. PIPE AND PUMP NETWORK

### 4.1 Numerical Methods

Calculations of flow rates in a pipe and pump network using an overall mechanical energy balance and accounting for various frictional losses.

### 4.2 Concepts Utilized

Solution of systems of nonlinear algebraic equations.

### 4.3 Course Usage

Fluid Dynamics

### 4.4 Problem Statement

Water at 60 °F and one atmosphere is being transferred from tank 1 to tank 2 with a 2-hp pump that is 75% efficient, as shown in Figure (A2). All the piping is 4-inch schedule 40 steel pipe except for the last section, which is 2-inch schedule 40 steel pipe. All elbows are 4-inch diameter, and a reducer is used to connect to the 2-inch pipe. The change in elevation between points 1 and 2 is  $z_2 - z_1 = 60$  ft.

- (a) Calculate the expected flow rate in gal/min when all frictional losses are considered.
- (b) Repeat part (a) but only consider the frictional losses in the straight pipes.
- (c) What is the % error in flow rate for part (b) relative to part (a)?

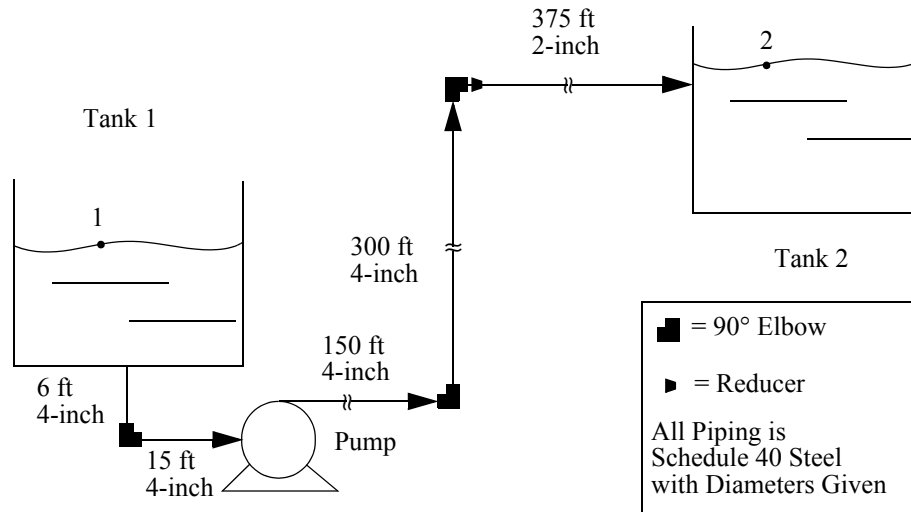


Figure A2 Pipe and Pump Network

### Additional Information and Data

The various frictional losses and the mechanical energy balance are discussed by Geankoplis<sup>3</sup> and Perry et al.<sup>6</sup> Frictional losses for this problem include contraction loss at tank 1 exit, friction in three 4-inch elbows, contraction loss from 4-inch to 2-inch pipe, friction in both the 2-inch and 4-inch pipes, and expansion loss at the tank 2 entrance.

The explicit equation given below can be used to calculate the friction factor for both sizes of pipe.

$$f_F = \frac{1}{16 \left\{ \log \left[ \frac{\epsilon/D}{3.7} - \frac{5.02}{Re} \log \left( \frac{\epsilon/D}{3.7} + \frac{14.5}{Re} \right) \right] \right\}^2} \quad \text{(Shacham}^8 \text{ equation)} \quad \text{(A16)}$$

The viscosity and density of water in English units can be calculated from

$$\rho = 62.122 + 0.0122T - 1.54 \times 10^{-4} T^2 + 2.65 \times 10^{-7} T^3 - 2.24 \times 10^{-10} T^4 \quad \text{(A17)}$$

$$\ln \mu = -11.0318 + \frac{1057.51}{T + 214.624} \quad \text{(A18)}$$

where T is in °F,  $\rho$  is in lb<sub>m</sub>/ft<sup>3</sup>, and  $\mu$  is in lb<sub>m</sub>/ft·s.

The effective surface roughness for commercial steel is 0.00015 ft. The inside diameters of schedule 40 steel pipes with 2-inch and 4-inch inside diameters are 2.067 and 4.026 inches respectively.

## A5. OPERATION OF A COOLED EXOTHERMIC CSTR

### 5.1 Numerical Methods

Material and energy balances on a CSTR with an exothermic reaction and cooling jacket.

### 5.2 Concepts Utilized

Solution of a system of simultaneous nonlinear algebraic equations, and conversion of the system of equations into one equation to examine multiple steady-state solutions.

### 5.3 Course Usage

Reaction Engineering, Mathematical Methods.

### 5.4 Problem Statement\*

An irreversible exothermic reaction  $A \xrightarrow{k} B$  is carried out in a perfectly mixed CSTR, as shown in Figure (A3). The

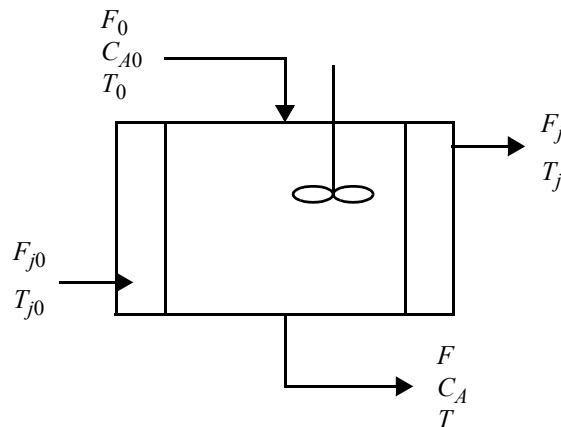


Figure A3 Cooled Exothermic CSTR

reaction is first order in reactant  $A$  and has a heat of reaction given by  $\lambda$ , which is based on reactant  $A$ . Negligible heat losses and constant densities can be assumed. A well-mixed cooling jacket surrounds the reactor to remove the heat of reaction. Cooling water is added to the jacket at a rate of  $F_j$  and at an inlet temperature of  $T_{j0}$ . The volume  $V$  of the contents of the reactor and the volume  $V_j$  of water in the jacket are both constant. The reaction rate constant changes as function of the temperature according to the equation

$$k = \alpha \exp(-E/RT) \quad (\text{A19})$$

The feed flow rate  $F_0$  and the cooling water flow rate  $F_j$  are constant. The jacket water is assumed to be completely mixed. Heat transferred from the reactor to the jacket can be calculated from

$$Q = UA(T - T_j) \quad (\text{A20})$$

where  $Q$  is the heat transfer rate,  $U$  is the overall heat transfer coefficient, and  $A$  is the heat transfer area. Detailed data

\* This problem is adapted from Luyben<sup>5</sup>.

for the process from Luyben<sup>5</sup> are shown in the Table (A2).

**Table A2** CSTR Parameter Values<sup>a</sup>

$F_0$	40 ft <sup>3</sup> /h	$U$	150 btu/h · ft <sup>2</sup> · °R
$F$	40 ft <sup>3</sup> /h	$A$	250 ft <sup>2</sup>
$C_{A0}$	0.55 lb-mol/ft <sup>3</sup>	$T_{j0}$	530 °R
$V$	48 ft <sup>3</sup>	$T_0$	530 °R
$F_j$	49.9 ft <sup>3</sup> /h	$\lambda$	-30,000 btu/lb-mol
$C_P$	0.75 btu/lb <sub>m</sub> · °R	$C_j$	1.0 btu/lb <sub>m</sub> · °R
$\alpha$	$7.08 \times 10^{10} \text{ h}^{-1}$	$E$	30,000 btu/lb-mol
$\rho$	50 lb <sub>m</sub> /ft <sup>3</sup>	$\rho_j$	62.3 lb <sub>m</sub> /ft <sup>3</sup>
$R$	1.9872 btu/lb-mol · °R	$V_j$	12 ft <sup>3</sup>

<sup>a</sup>Data are from Luyben<sup>5</sup>.

- (a) Formulate the material and energy balances that apply to the CSTR and the cooling jacket.
- (b) Calculate the steady-state values of  $C_A$ ,  $T_j$ , and  $T$  for the operating conditions of Table (A2).
- (c) Identify all possible steady-state operating conditions, as this system may exhibit multiple steady states.
- (d) Solve the unsteady-state material and energy balances to identify if any of the possible multiple steady states are unstable.

### 5.5 Solution (Partial)

(a) There are three balance equations that can be written for the reactor and the cooling jacket. These include the material balance on the reactor, the energy balance on the reactor, and the energy balance on the cooling jacket.

**Mole balance on CSTR for reactant A**

$$F_0 C_{A0} - F C_A - V k C_A = 0 \quad (\text{A21})$$

**Energy balance on the reactor**

$$\rho C_p (F_0 T_0 - F T) - \lambda V k C_A - U A (T - T_j) = 0 \quad (\text{A22})$$

**Energy balance on the cooling jacket**

$$\rho_j C_j F_j (T_{j0} - T_j) + U A (T - T_j) = 0 \quad (\text{A23})$$

(b) Nonlinear equations (A21), (A22), and (A23) along with explicit equation (A19) form the system of equations that can be solved for this problem. A reasonable initial assumption is that there is no reaction; therefore,  $C_{A0} = 0.55$ ,  $T_0 = 530$ , and  $T_{j0} = 530$ . The solution obtained with these initial estimates is summarized in Table (A3).

**Table A3** Steady-State Operating Conditions for CSTR

Solution		
Variable	Value	$f()$
$C_A$	0.52139	-4.441e-16
$T$	537.855	1.757e-9
$T_j$	537.253	-1.841e-9
$k$	0.0457263	

(c) Several different steady states may be possible with exothermic reactions in a CSTR. One possible method to determine these different steady states is to solve the system of nonlinear equations with different initial estimates of the final solution. While this approach is not very sophisticated, it can be of benefit in very complex systems of equations.

Another approach is to convert the system of equations into a single implicit and several explicit or auxiliary equations. (Incidentally, this is a good way to show that a particular system does not have a solution at all.) In this particular case, the material balance of Equation (A21) can be solved for  $C_A$ .

$$C_A = \frac{F_0 C_{A0}}{(F + V k)} \quad (\text{A24})$$

Also, the energy balance of Equation (A23) on the cooling jacket can be solved for  $T_j$ .

$$T_j = \frac{\rho_j C_j F_j T_{j0} + U A T}{(\rho_j C_j F_j + U A)} \quad (\text{A25})$$

Thus the problem has been converted to a single nonlinear equation given by Equation (A22) and three explicit equations given by Equations (A19), (A24), and (A25). When  $f(T)$  is plotted versus  $T$  in the range  $500 \leq T \leq 700$ , three solutions can be clearly identified. The first one is at low temperature as this is the solution that was initially identified. The second is at an intermediate temperature, and the third is at a high temperature. The three resulting solutions are summarized in Table (A4).

**Table A4** Multiple Steady-State Solutions for CSTR

Solution No.			
	1	2	3
$T$	537.86	590.35	671.28
$C_A$	0.5214	0.3302	0.03542
$T_j$	537.25	585.73	660.46

## A6. VAPOR PRESSURE CORRELATIONS FOR A SULFUR COMPOUND PRESENT IN PETROLEUM

### 6.1 Numerical Methods

Use of polynomials, the Clapeyron equation, and the Riedel equation to correlate vapor pressure versus temperature data

### 6.2 Concepts Utilized

Regression of polynomials of various degrees and linear regression of correlation equations with variable transformations.

### 6.3 Course Usage

Mathematical Methods, Thermodynamics.

### 6.4 Problem Statement

The Table given below provides data of vapor pressure ( $P$  in mm Hg) versus temperature ( $T$  in  $^{\circ}\text{C}$ ) for various sulfur compounds present in petroleum. Descriptions of the Clapeyron and Riedel equations are found in Problem (D6).

- Use polynomials of different degrees to represent the vapor pressure data for ethane-thiol. Consider  $T$  ( $^{\circ}\text{K}$ ) as the independent variable and  $P$  as the dependent variable. Determine the degree and the parameters of the best-fitting polynomial for your selected compound.
- Correlate the data with the Clapeyron equation.
- Correlate the data with the Riedel equation.
- Which one of these correlations represents these data best?

**Table A5** Vapor Pressure Data for Ethane-thiol

Pressure mm Hg	Temperature $^{\circ}\text{C}$	Pressure mm Hg	Temperature $^{\circ}\text{C}$
187.57	0.405	906.06	40.092
233.72	5.236	1074.6	45.221
289.13	10.111	1268	50.39
355.22	15.017	1489.1	55.604
433.56	19.954	1740.8	60.838
525.86	24.933	2026	66.115
633.99	29.944	906.06	40.092

## A7. CATALYST DECAY IN A PACKED BED REACTOR MODELED BY A SERIES OF CSTRs

### 7.1 Numerical Methods

Determination of the change of reactant and product concentration and catalyst decay with time in a packed bed reactor that is approximated by a series of CSTRs with and without pressure drop.

### 7.2 Concepts Utilized

Solution of simultaneous ordinary differential equations.

### 7.3 Course Usage

Reaction Engineering.

### 7.4 Problem Statement

A gas phase catalytic reaction  $A \xrightarrow{k} B$  is carried out in a packed bed reactor where the catalyst activity is decaying. The reaction with deactivation follows the rate expression given by

$$-r_A = akC_A \quad (\text{A26})$$

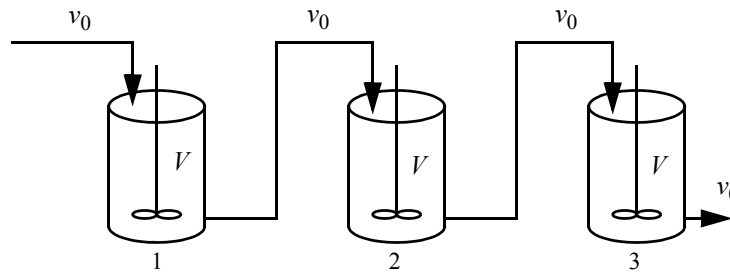
where  $a$  is the catalyst activity variable that follows either the deactivation kinetics

$$\frac{da}{dt} = -k_{d1}a \quad (\text{A27})$$

or

$$\frac{da}{dt} = -k_{d2}aC_B \quad (\text{A28})$$

The packed bed reactor can be approximated by three CSTRs in series, as shown in Figure (A4).



**Figure A4** Reactor Approximation by a Train of Three CSTRs

The volumetric flow rate to each reactor is  $v_0$ . The reactor feed is pure  $A$  at concentration  $C_{A0}$  to the first reactor. The pressure drop can be neglected. At time zero there is only inert gas in all of the reactors.

The following parameter values apply:

$$k_{d1} = 0.01 \text{ min}^{-1} \quad k_{d2} = 1.0 \frac{\text{dm}^3}{\text{g-mol} \cdot \text{min}}$$

$$k = 0.9 \frac{\text{dm}^3}{\text{dm}^3 (\text{of catalyst}) \text{min}}$$

$$C_{A0} = 0.01 \frac{\text{g-mol}}{\text{dm}^3} \quad V = 10 \text{ dm}^3 \quad v_0 = 5 \frac{\text{dm}^3}{\text{min}}$$

- (a) Plot the concentration of  $A$  in each of the three reactors as a function of time to 60 minutes using the activity function given by Equation (A27). Create a separate plot for the activities in all three reactors.
- (b) Repeat part (a) for the activity function as given in Equation (A28).
- (c) Compare the outlet concentration of  $A$  for parts (a) and (b) at 60 minutes deactivation to that from a plug-flow packed bed reactor with no deactivation (total volume of  $30 \text{ dm}^3$ ) and the three CSTR reactors in series model with no deactivation.

### 7.5 Solution (Partial)

The respective material balances on components  $A$  and  $B$  yield the following differential equations for the first CSTR, where the subscript 1 indicates the concentrations in the first reactor:

$$\frac{dC_{A1}}{dt} = \frac{(C_{A0} - C_{A1})v_0}{V} + r_{A1} \quad (\text{A29})$$

$$\frac{dC_{B1}}{dt} = \frac{-C_{B1}v_0}{V} - r_{A1}$$

For the second and third CSTR, where  $i = 2$  and  $3$ , the balances yield

$$\frac{dC_{Ai}}{dt} = \frac{(C_{A(i-1)} - C_{A(i)})v_0}{V} + r_{Ai} \quad (\text{A30})$$

$$\frac{dC_{Bi}}{dt} = \frac{(C_{B(i-1)} - C_{B(i)})v_0}{V} + r_{Ai}$$

These equations, together with Equations (A26) and (A27) or (A28), provide the equations that need to be solved simultaneously in this problem.

(a) For this part, only the material balances involving  $A$  are needed in addition to Equations (A26) and (A27).

(b) The material balances involving both components  $A$  and  $B$  are needed along with Equations (A26) and (A28). Note that the activities in each reactor will be different because of the dependency of the activity relationship of Equation (A28) on the concentration of  $B$ .



## A8. SLOW SUBLIMATION OF A SOLID SPHERE

### 8.1 Numerical Methods

Sublimation of a solid sphere by diffusion in still gas and by a mass transfer coefficient in a moving gas.

### 8.2 Concepts Utilized

Solution of simultaneous ordinary differential equations while optimizing a single parameter to achieve split boundary conditions.

### 8.3 Course Usage

Mass Transfer.

### 8.4 Problem Statement

Consider the sublimation of solid dichlorobenzene, designated by  $A$ , which is suspended in still air, designated by  $B$ , at 25 °C and atmospheric pressure. The particle is spherical with a radius of  $3 \times 10^{-3}$  m. The vapor pressure of  $A$  at this temperature is 1 mm Hg, and the diffusivity in air is  $7.39 \times 10^{-6}$  m<sup>2</sup>/s. The density of  $A$  is 1458 kg/m<sup>3</sup>, and the molecular weight is 147.

- Estimate the initial rate of sublimation (flux) from the particle surface by using an approximate analytical solution to this diffusion problem. (See the following discussion for more information.)
- Calculate the rate of sublimation (flux) from the surface of a sphere of solid dichlorobenzene in still air with a radius of  $3 \times 10^{-3}$  m with a numerical technique employing a shooting technique, with ordinary differential equations that describe the problem. Compare the result with part (a).
- Show that expression for the rate of sublimation (flux) from the particle as predicted in part (a) is the same as that predicted by the external mass transfer coefficient for a still gas.
- Calculate the time necessary for the complete sublimation of a single particle of dichlorobenzene if the particle is enclosed in a volume of 0.05 m<sup>3</sup>.

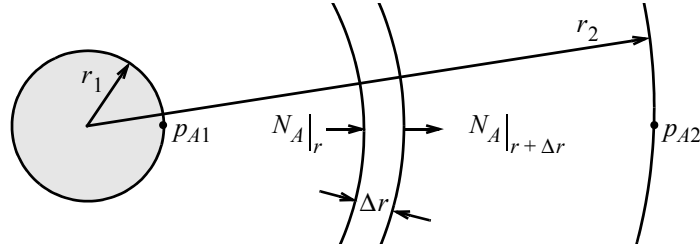
### Additional Information and Data

**Diffusion** The diffusion of  $A$  through stagnant  $B$  from the surface of a sphere is shown in Figure (A5). A material balance on  $A$  in a differential volume between radius  $r$  and  $r + \Delta r$  in a  $\Delta t$  time interval yields

$$\text{INPUT} + \text{GENERATION} = \text{OUTPUT} + \text{ACCUMULATION}$$

$$(N_A 4\pi r^2) \Big|_r \Delta t + 0 = (N_A 4\pi r^2) \Big|_{r+\Delta r} \Delta t + 0 \quad (\text{A31})$$

where  $N_A$  is the flux in kg-mol/m<sup>2</sup> · s at radius  $r$  in m. The  $4\pi r^2$  is the surface area of the sphere with radius  $r$ . Division



**Figure A5** Shell Balance for Diffusion from the Surface of a Sphere

by  $\Delta t$  and rearrangement of this equation while taking the limit as  $\Delta r \rightarrow 0$  yields

$$\frac{d(N_A r^2)}{dr} = 0 \quad (\text{A32})$$

Fick's law for the diffusion of  $A$  through stagnant  $B$  in terms of partial pressures is expressed as

$$N_A = -\frac{D_{AB} dp_A}{RT} + \frac{p_A}{P} N_A \quad (\text{A33})$$

where  $D_{AB}$  is the molecular diffusivity of  $A$  in  $B$  in  $\text{m}^2/\text{s}$ ,  $R$  is the gas constant with a value of  $8314.34 \text{ m}^3 \cdot \text{Pa}/\text{kg} \cdot \text{mol} \cdot \text{K}$ ,  $T$  is the absolute temperature in  $\text{K}$ , and  $P$  is the total pressure in  $\text{Pa}$ .

Rearrangement of Equation (A33) yields

$$\frac{dp_A}{dr} = -\frac{RTN_A \left(1 - \frac{p_A}{P}\right)}{D_{AB}} \quad (\text{A34})$$

where the initial condition is that  $p_A = (1/760)1.01325 \times 10^5 \text{ Pa} = 133.32 \text{ Pa}$ , which is the vapor pressure of the solid  $A$  at  $r = 3 \times 10^{-3} \text{ m}$ . The final value is that  $p_A = 0$  at some relatively large radius  $r$ .

The analytical solution to this problem can be obtained by integrating Equation (A32) and introducing the result for  $N_A$  into Equation (A34). The final solution as given by Geankoplis<sup>3</sup>, p. 391, is

$$N_{A1} = \frac{D_{AB} P (p_{A1} - p_{A2})}{RT r_1 p_{BM}} \quad (\text{A35})$$

where subscripts 1 and 2 indicate locations and  $p_{BM}$  is given by

$$p_{BM} = \frac{p_{B2} - p_{B1}}{\ln(p_{B2}/p_{B1})} = \frac{p_{A1} - p_{A2}}{\ln((P - p_{A2})/(P - p_{A1}))} \quad (\text{A36})$$

**Mass Transfer Coefficient** The transfer of  $A$  from the surface of the spherical particle to the surrounding gas can also be described by a mass transfer coefficient for transport of  $A$  through stagnant  $B$ .

A general relationship for gases that can be used to calculate the mass transfer coefficient for gases is presented by Geankoplis<sup>3</sup>, p. 446, as

$$N_{Sh} = 2 + 0.552 N_{Re}^{0.53} N_{Sc}^{1/3} \quad (\text{A37})$$

Note that for a quiescent gas, the limiting value of  $N_{Sh}$  is 2 because the  $N_{Re}$  is zero.

The Sherwood number is defined as

$$N_{Sh} = k'_c \frac{D_p}{D_{AB}}$$

where  $k'_c$  is the mass transfer coefficient in m/s based on concentration and equimolar counter diffusion, and  $D_p$  is the particle diameter in m. The particle Reynolds number is defined as

$$N_{Re} = \frac{D_p v \rho}{\mu}$$

where  $D_p$  is the particle diameter in m,  $v$  is the gas velocity in m/s, and  $\mu$  is the gas viscosity in Pa·s. The Schmidt number is given by

$$N_{Sc} = \frac{\mu}{\rho D_{AB}}$$

with  $\rho$  representing the density of the gas in kg/m<sup>3</sup>.

The mass transfer coefficient (see Geankoplis<sup>3</sup>, p. 435) can be used to describe the flux  $N_A$  from the surface of the sphere for transport through stagnant  $B$  by utilizing

$$N_A = \frac{k'_c P (p_{A1} - p_{A2})}{RT p_{BM}} \quad (\text{A38})$$

### 8.5 Solution (Partial with Suggestions)

(a) The analytical solution is given by Equations (A35) and (A36) which can be easily evaluated.

(b) The numerical solution involves the simultaneous solution of Equations (A32) and (A34) along with the following algebraic equation, which is needed to calculate the flux  $N_A$  from the quantity  $(N_A r^2)$ :

$$N_A = \frac{(N_A r^2)}{r^2} \quad (\text{A39})$$

The initial radius is the known radius of the sphere (initial condition), and the final value of the radius is much greater than the initial radius, so that the value of the partial pressure of  $A$  is effectively zero. The final value in this numerical solution is such that the desired value of the partial pressure of  $A$  is very nearly zero at a very “large” final radius of  $r$ . A comparison of the calculated  $N_A$  with the analytical  $N_A$  at the surface of the sphere should be in agreement with the value of  $1.326 \times 10^{-7}$  kg-mol/m<sup>2</sup>·s.

(c) The resulting solutions should be identical with each other.

(d) This is an unsteady-state problem that can be solved utilizing the mass transfer coefficient by making the pseudo-steady-state assumption that the mass transfer can be described by Equation (A38) at any time. The mass transfer coefficient increases as the particle diameter decreases because for a still gas

$$N_{Sh} = k'_c \frac{D_p}{D_{AB}} = 2 \quad (\text{A40})$$

as indicated by Equation (A38); thus, in terms of the particle radius,

$$k'_c = \frac{D_{AB}}{r} \quad (\text{A41})$$

A material balance on component  $A$  in the well-mixed gas phase volume  $V$  with the only input due to the sublimation of  $A$  yields

INPUT + GENERATION = OUTPUT + ACCUMULATION

$$(N_A 4\pi r^2) \Big|_r \Delta t + 0 = 0 + \left( \frac{V p_A}{RT} \right) \Big|_{t+\Delta t} - \left( \frac{V p_A}{RT} \right) \Big|_t \quad (\text{A42})$$

The limit as  $\Delta t \rightarrow 0$  and the use of Equation (38) for  $N_A$  give

$$\frac{dp_A}{dt} = \frac{4\pi r^2 k'_c P (p_{A1} - p_{A2})}{V p_{BM}} \quad (\text{A43})$$

with  $p_{A1}$  being the vapor pressure of  $A$  at the solid surface and  $p_{A2}$  being the partial pressure of  $A$  in the gas volume.

A material balance on  $A$  within the solid sphere of radius  $r$  gives

INPUT + GENERATION = OUTPUT + ACCUMULATION

$$0 + 0 = (N_A 4\pi r^2) \Big|_r \Delta t + \left( \frac{4}{3} \pi r^3 \frac{\rho_A}{M_A} \right) \Big|_{t+\Delta t} - \left( \frac{4}{3} \pi r^3 \frac{\rho_A}{M_A} \right) \Big|_t \quad (\text{A44})$$

where  $\rho_A$  is the density of the solid and  $M_A$  is the molecular weight of the solid. Rearranging Equation (A44) and taking the limit as  $\Delta t \rightarrow 0$  yields

$$\frac{d(r^3)}{dt} = 3r^2 \frac{dr}{dt} = - \frac{3N_A M_A r^2}{\rho_A} \quad (\text{A45})$$

Simplifying and introducing Equation (A38) for  $N_A$  gives

$$\frac{dr}{dt} = - \frac{M_A k'_c P (p_{A1} - p_{A2})}{\rho_A RT p_{BM}} \quad (\text{A46})$$

The complete sublimation of  $A$  is described by the simultaneous solution of differential Equations (A43) and (A46) along with Equation (A41).

## A9. SEMIBATCH REACTOR WITH REVERSIBLE LIQUID PHASE REACTION

### 9.1 Numerical Methods

Solution of simultaneous ordinary differential equations and explicit algebraic equations.

### 9.2 Concepts Utilized

Calculation of conversion in an isothermal liquid phase reaction carried out in a semibatch reactor under both equilibrium and rate-controlling assumptions.

### 9.3 Course Usage

Reaction Engineering.

### 9.4 Problem Statement

Pure butanol is to be fed into a semibatch reactor containing pure ethyl acetate to produce butyl acetate and ethanol. The reaction



which can be expressed as



is elementary and reversible. The reaction is carried out isothermally at 300 K. At this temperature the equilibrium constant based on concentrations is 1.08 and the reaction rate constant is  $9 \times 10^{-5} \text{ dm}^3/\text{g}\cdot\text{mol}$ . Initially there are  $200 \text{ dm}^3$  of ethyl acetate in the reactor, and butanol is fed at a rate of  $0.05 \text{ dm}^3/\text{s}$  for a period of 4000 seconds from the start of reactor operation. At the end of the butanol introduction, the reactor is operated as a batch reactor. The initial concentration of ethyl acetate in the reactor is  $7.72 \text{ g}\cdot\text{mol}/\text{dm}^3$ , and the feed butanol concentration is  $10.93 \text{ g}\cdot\text{mol}/\text{dm}^3$ .

- Calculate and plot the concentrations of  $A$ ,  $B$ ,  $C$ , and  $D$  within the reactor for the first 5000 seconds of reactor operation.
- Simulate reactor operation in which reaction equilibrium is always attained by increasing the reaction rate constant by a factor of 100 and repeating the calculations and plots requested in part (a). Note that this is a difficult numerical integration.
- Compare the conversion of ethyl acetate under the conditions of part (a) with the equilibrium conversion of part (b) during the first 5000 seconds of reactor operation.
- If the reactor down time between successive semibatch runs is 2000 seconds, calculate the reactor operation time that will maximize the rate of butyl acetate production.

### 9.5 Solution (Partial)

The mole balance, rate law, and stoichiometry equations applicable to the semibatch reactor are necessary in the problem solutions.

**Mole balances**

$$\frac{dN_A}{dt} = r_A V \quad \frac{dN_B}{dt} = r_A V \quad (\text{A49})$$

$$\frac{dN_C}{dt} = -r_A V \quad \frac{dN_D}{dt} = -r_A V \quad (\text{A50})$$

**Rate law**

$$-r_A = k \left( C_A C_B - \frac{C_C C_D}{K_e} \right) \quad (\text{A51})$$

**Stoichiometry**

$$C_A = \frac{N_A}{V} \quad C_B = \frac{N_B}{V} \quad (\text{A52})$$

$$C_C = \frac{N_C}{V} \quad C_D = \frac{N_D}{V} \quad (\text{A53})$$

**Overall material balance**

$$\frac{dV}{dt} = v_0 \quad (\text{A54})$$

**Definition of conversion**

$$x_A = \frac{N_{A0} - N_A}{N_{A0}} \quad (\text{A55})$$

**Definition of production rate of butyl acetate**

$$P = \frac{N_C}{(t_p + 2000)} \quad (\text{A56})$$

At equilibrium the net rate is equal to zero or  $r_A = 0$ . A convenient way to achieve this with the problem described with differential equations is to give the rate constant a large value such, as suggested in part (b).

(a) The equation set for part (a) consists of Equations (A49) through (A56). A special provision must be made to introduce the volumetric feed rate of butanol,  $v_0$ , to the reactor during the first 4000 s of operation, and then to set this feed rate to zero for the remaining reaction time  $t$ .

(c) An easy method for simulation of the equilibrium-based reactor operation is to simply increase the value of the rate constant  $k$  to a higher value so that equilibrium conversion is always maintained. A graphical comparison should indicate that the equilibrium conversion is higher than the rate-based conversion at all times.

## A10. RESET WINDUP IN A STIRRED TANK HEATER

### 10.1 Numerical Methods

Solution of ordinary differential equations, generation of step functions.

### 10.2 Concepts Utilized

Closed loop dynamics of a process including reset windup. Use of anti-windup provisions.

### 10.3 Course Usage

Process Dynamics and Control.

### 10.4 Problem Statement

The stirred tank heater described in Problem (D10) operates at steady state, where the PI controller settings are:  $K_c = 500$ ;  $K_r = 500$  and there is no measuring lag in the thermocouple ( $t_m, t_d = 0$ ). The output from the heater is limited to twice of its design value ( $q \leq 20000$  kJ/min).

- (a) At time  $t = 0$  the inlet temperature is reduced to half of its steady state value. At time  $t = 30$  min the inlet temperature is restored to its steady state value. Simulate the system behavior up to  $t = 50$  min and explain why the controller cannot restore the outlet temperature to its steady state value even after 20 minutes.
- (b) Many industrial controllers have anti-windup provisions. One option to prevent reset windup is to switch off the error accumulation term when the required heat supply exceeds the bounds. Include this feature in your model and repeat the simulation. Compare the results to the results of part (a). What differences can you notice?

## A11. STEAM HEATING STAGE OF A BATCH REACTOR OPERATION

### 11.1 Numerical Methods

Solution of systems of equations comprised of ordinary differential equations and nonlinear algebraic equations.

### 11.2 Concepts Utilized

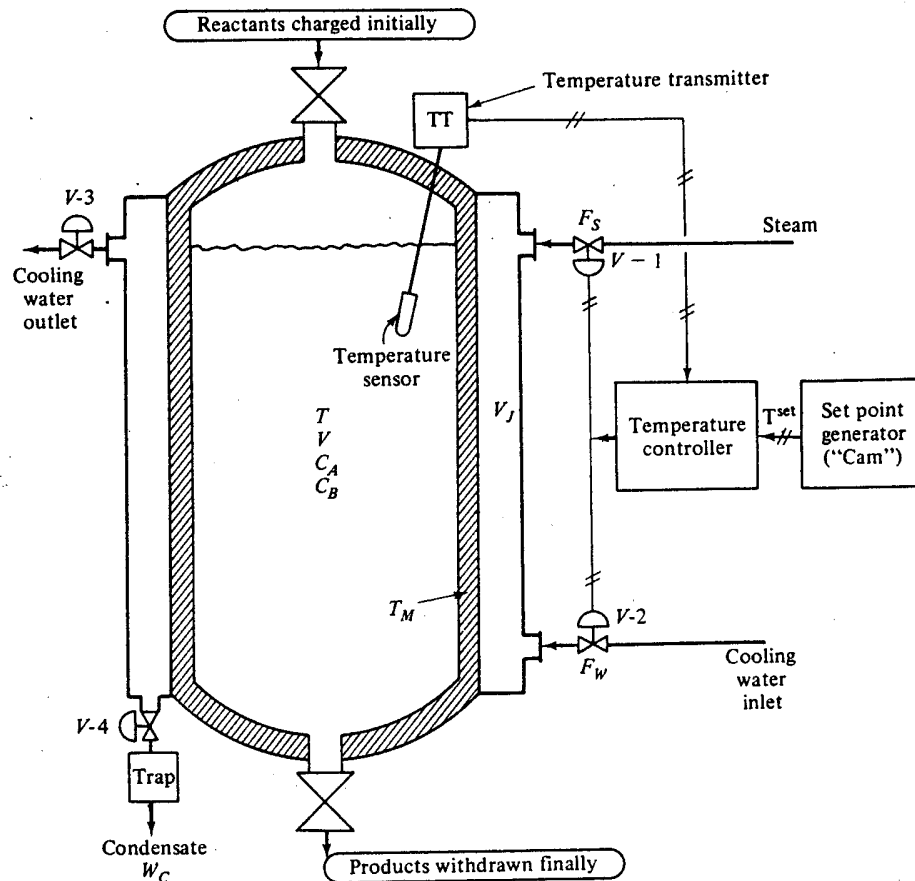
Control of steam heating of a batch reactor.

### 11.3 Course Usage

Reaction Engineering and Process Dynamics and Control

### 11.4 Problem Statement

The exothermic liquid-phase reaction  $A \rightarrow B \rightarrow C$  is carried out in a batch reactor. The batch reactor is sketched below which is taken from Luyben<sup>5</sup>.



Reactant is charged into the vessel first, and then steam is fed into the jacket to bring the reaction mass up to the



desired temperature. The equations representing the operation of the reactor are the following:

$$\frac{dC_A}{dt} = -k_1 C_A \quad (\text{A57})$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \quad (\text{A58})$$

$$\frac{dT}{dt} = \frac{-\lambda_1}{\rho C_p} k_1 C_A - \frac{\lambda_2}{\rho C_p} k_2 C_B - \frac{Q_M}{V \rho C_p} \quad (\text{A59})$$

$$Q_M = h_i A_i (T - T_M) \quad (\text{A60})$$

$$\frac{dT_M}{dt} = \frac{Q_M - Q_J}{V_M \rho_M C_M} \quad (\text{A61})$$

The definitions of the variables and constants, their numerical value or initial value (whenever applicable) are shown in Tables (A6) and (A7).

**Table A6** Variable Definitions and Numerical Values

Name	Initial value	Description
$C_A$	$C_A(0)=0.8$	Concentration of A (mol/cu. ft.)
$C_B$	$C_B(0)=0$	Concentration of B (mol/cu. ft.)
$T$	$T(0)=80$	Temperature in the reactor vessel ( $^{\circ}$ F)
$Q_m$		Heat transferred through the metal wall (Btu/min)
$T_m$	$T_m(0)=80$	Temperature of the metal wall ( $^{\circ}$ F)
$\rho_s$	$\rho_s(0)=0.0803$	Density of the steam in the jacket (lb/cu. ft.)
$T_j$	$T_j(0)=259$	Temperature in the heating/cooling jacket( $^{\circ}$ F)
$\epsilon$		Steam density deviation for controlled integration
$P_j$		Steam pressure inside the jacket (psi)
$w_s$		Steam mass flow rate (lb/min)
$Q_j$		Heat transferred to the jacket (Btu/min)
$w_c$		Condensate mass flow rate (lb/min)
$d\rho_s/dt$		Steam density derivative (for controlled integration)
$P_{tt}$		Output pneumatic signal from temp. transmitter (psi)
$P_1$		Controller output pressure (psi)
$P_c$		Controller adjusted output pressure (psi)
$p^{set}$	$p^{set}(0)=12.6$	Set point signal (psi)

**Table A6** Variable Definitions and Numerical Values

$x_1$		Steam valve - fraction open
$x_s$		Steam valve - fraction open (adjusted)
$k_1$		Reaction rate coefficient for A $\rightarrow$ B (1/min)
$k_2$		Reaction rate coefficient for B $\rightarrow$ C (1/min)

**Table A7** Constant Definitions and Numerical Values

Name	Definition	Description
$\lambda_1$	$\lambda_1 = -40000$	Heat of reaction for A $\rightarrow$ B (Btu/mol)
$\lambda_2$	$\lambda_2 = -50000$	Heat of reaction for B $\rightarrow$ C (Btu/mol)
$A_{vp}$	$A_{vp} = -8744.4$	Vapor pressure equation coefficient
$B_{vp}$	$B_{vp} = 15.7$	Vapor pressure equation coefficient
$\rho$	$\rho = 50$	Density of reacting mass (lb/cu.ft.)
$V$	$V = 42.4$	Volume of reaction vessel (cu. ft.)
$\rho_m$	$\rho_m = 512$	Density of metal wall (lb/cu.ft.)
$Cp_m$	$Cp_m = 0.12$	Specific heat of metal wall (Btu/lb.- cu. ft.)
$V_m$	$V_m = 9.42$	Volume of metal wall (cu. ft.)
$V_j$	$V_j = 18.83$	Total volume of the jacket (cu. ft.)
$h_i$	$h_i = 160$	Inside heat transfer coefficient. (Btu/hr-deg. F-sq. ft.)
$A_0$	$A_0 = 56.5$	Jacket's total heat transfer area (sq. ft.)
$h_{os}$	$h_{os} = 1000$	Jacket's heat transfer coeff. (with steam, Btu/hr-deg. F-sq. ft.)
$H_s - h_c$	$H_s - h_c = 939$	Steam's heat of condensation (Btu/lb)
$K_c$	$K_c = 7000$	Proportional gain for controlled integration

The equations representing the heating jacket are the following:

$$V \frac{d\rho_s}{dt} = w_s - w_c \quad (\text{A62})$$

$$\rho_s = \frac{144}{1545} \frac{MP_J}{T_J + 460} \quad (\text{A63})$$

$$P_J = \exp\left(\frac{A_{vp}}{T_J + 460} + B_{vp}\right) \quad (\text{A64})$$

$$Q_J = -h_{os}A_o(T_J - T_M) \quad (\text{A65})$$

$$w_c = -\frac{Q_J}{H_s + h_c} \quad (\text{A66})$$

The reaction rate coefficients  $k_1$  and  $k_2$  change with temperature according to the equations:

$$k_1 = 729.5488 \exp\left(\frac{-15000}{1.99(T + 460)}\right) \quad (\text{A67})$$

$$k_2 = 6567.587 \exp\left(\frac{-20000}{1.99(T + 460)}\right) \quad (\text{A68})$$

The equations representing the temperature transmitter, the feedback controller and the fractional opening of the steam valve are the following:

$$P_{tt} = 3 + (T - 50) \frac{12}{200} \quad (\text{A69})$$

$$P_c = 7 + K_c(P^{set} - P_{tt}) \quad (\text{A70})$$

$$x_s = \frac{P_c - 9}{6} \quad (\text{A71})$$

$$w_s = 112x_s \sqrt{35 - P_j} \quad (\text{A72})$$

The temperature and pressure in the steam jacket are specified in implicit relationships. If the controlled integration method is used to solve for the jacket's temperature the following equations should be included:

$$\frac{d\rho_s}{dt} = \frac{w_s - w_c}{18.83} \quad (\text{A73})$$

$$\frac{dT_j}{dt} = K_c \left( \varepsilon + \frac{1}{10} \frac{d\rho_s}{dt} \right) \quad (\text{A74})$$

$$\varepsilon = \rho_s - \frac{18(144)P_j}{1545(T_j + 460)} \quad (\text{A75})$$

## A12. UNSTEADY-STATE MASS TRANSFER IN A SLAB

### 12.1 Numerical Methods

Unsteady-state mass transfer in a one-dimensional slab having only one face exposed and an initial concentration profile.

### 12.2 Concepts Utilized

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

### 12.3 Course Usage

Mass Transfer, Mathematical Methods

### 12.4 Problem Statement\*

A slab of material with a thickness of 0.004 m has one surface suddenly exposed to a solution containing component  $A$  with  $C_{A0} = 6 \times 10^{-3}$  kg-mol/m<sup>3</sup> while the other surface is supported by an insulated solid allowing no mass transport. There is an initial linear concentration profile of component  $A$  within the slab from  $C_A = 1 \times 10^{-3}$  kg-mol/m<sup>3</sup> at the solution side to  $C_A = 2 \times 10^{-3}$  kg-mol/m<sup>3</sup> at the solid side. The diffusivity  $D_{AB} = 1 \times 10^{-9}$  m<sup>2</sup>/s. The distribution coefficient relating between the concentration in the solution adjacent to the slab  $C_{ALi}$  and the concentration in the solid slab at the surface  $C_{Ai}$  is defined by

$$K = \frac{C_{ALi}}{C_{Ai}} \quad (\text{A76})$$

where  $K = 1.5$ . The convective mass transfer coefficient at the slab surface can be considered as infinite.

The unsteady-state diffusion of component  $A$  within the slab is described by the partial differential equation

$$\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial x^2} \quad (\text{A77})$$

The initial condition of the concentration profile for  $C_A$  is known to be linear at  $t = 0$ . Since the differential equation is second order in  $C_A$ , two boundary conditions are needed. Utilization of the distribution coefficient at the slab surface gives

$$C_{Ai} \Big|_{x=0} = \frac{C_{A0}}{K} \quad (\text{A78})$$

and the no diffusional flux condition at the insulated slab boundary gives

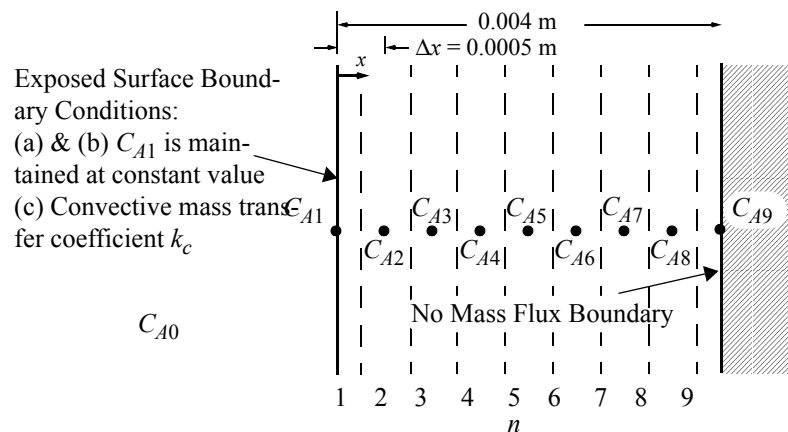
$$\frac{\partial C_A}{\partial x} \Big|_{x=0.004} = 0 \quad (\text{A79})$$

\* Adapted from Geankoplis<sup>3</sup>, pp. 471–473.

- Calculate the concentrations within the slab after 2500 s. Utilize the numerical method of lines with an interval between nodes of 0.0005 m.
- Compare the results obtained with those reported by Geankoplis<sup>3</sup>, p. 473, and summarized in Table (A9).
- Plot the concentrations versus time to 20000 s at  $x = 0.001, 0.002, 0.003,$  and  $0.004$  m.
- Repeat part (a) with an interval between nodes of 0.00025. Compare results with those of part (a).
- Repeat parts (a) and (c) for the case where mass transfer is present at the slab surface. The external mass transfer coefficient is  $k_c = 1.0 \times 10^{-6}$  m/s.

### The Numerical Method of Lines

The method of lines (MOL) is a general technique for the solution of partial differential equations that has been introduced in Problem (D12). This method utilizes ordinary differential equations for the time derivative and finite differences on the spatial derivatives. The finite difference elements for this problem are shown in Figure (A6), where the interior of the slab has been divided into  $N = 8$  intervals involving  $N + 1 = 9$  nodes.



**Figure A6** Unsteady-State Mass Transfer in a One-Dimensional Slab

Equation (A77) can be written using a central difference formula for the second derivative and replacing the partial time derivatives with ordinary derivatives

$$\frac{dC_{A_n}}{dt} = \frac{D_{AB}}{(\Delta x)^2} (C_{A_{n+1}} - 2C_{A_n} + C_{A_{n-1}}) \quad \text{for } (2 \leq n \leq 8) \quad (\text{A80})$$

### ***Boundary Condition for Exposed Surface***

The general surface boundary condition is obtained from a mass balance at the interface, which equates the mass transfer to the surface via the mass transfer coefficient to the mass transfer away from the surface due to diffusion within the slab. Thus at any time for mass transfer normal to the slab surface in the  $x$  direction,

$$k_c(C_{A0} - KC_{A1}) = -D_{AB} \frac{\partial C_A}{\partial x} \Big|_{x=0} \quad (\text{A81})$$

where  $k_c$  is the external mass transfer coefficient in m/s and the partition coefficient  $K$  is used to have the liquid phase concentration driving force.

The derivative on the right side of Equation (81) can be written in finite difference form using a second-order three-point forward difference expression at node 1.

$$\frac{\partial C_A}{\partial x} \Big|_{x=0} = \frac{(-C_{A3} + 4C_{A2} - 3C_{A1})}{2\Delta x} \quad (\text{A82})$$

Thus substitution of Equation (A82) into Equation (A81) yields

$$k_c(C_{A0} - KC_{A1}) = -D_{AB} \frac{(-C_{A3} + 4C_{A2} - 3C_{A1})}{2\Delta x} \quad (\text{A83})$$

The preceding equation can be directly solved for  $C_{A1}$  to give

$$C_{A1} = \frac{2k_c C_{A0} \Delta x - D_{AB} C_{A3} + 4D_{AB} C_{A2}}{3D_{AB} + 2k_c K \Delta x} \quad (\text{A84})$$

which is the general result. For good mass transfer to the surface where  $k_c \rightarrow \infty$  in Equation (A84), the expression for  $C_{A1}$  is given by

$$C_{A1} = \frac{C_{A0}}{K} \quad (\text{A85})$$

### ***Boundary Condition for Insulated Surface (No Mass Flux)***

The mass flux is zero at the insulated surface; thus from Fick's law

$$\frac{\partial C_A}{\partial x} \Big|_{x=0.004} = 0 \quad (\text{A86})$$

Utilizing the second-order approximation for the three-point forward difference for the preceding derivative yields

$$\frac{\partial C_{A9}}{\partial x} = \frac{3C_{A9} - 4C_{A8} + C_{A7}}{2\Delta x} = 0 \quad (\text{A87})$$

which can be solved for  $C_{A9}$  to yield

$$C_{A9} = \frac{4C_{A8} - C_{A7}}{3} \quad (\text{A88})$$

### ***Initial Concentration Profile***

The initial profile is known to be linear, so the initial concentrations at the various nodes can be calculated as summa-

rized in Table (A8).

**Table A8** Initial Concentration Profile in Slab

$x$ in m	$C_A$	node $n$
0	$1.0 \times 10^{-3}$	1
0.0005	$1.125 \times 10^{-3}$	2
0.001	$1.25 \times 10^{-3}$	3
0.0015	$1.375 \times 10^{-3}$	4
0.002	$1.5 \times 10^{-3}$	5
0.0025	$1.625 \times 10^{-3}$	6
0.003	$1.75 \times 10^{-3}$	7
0.0035	$1.825 \times 10^{-3}$	8
0.004	$2.0 \times 10^{-3}$	9

### 12.5 Solution (Partial)

(a), (b), & (c) The problem is solved by the numerical solution of Equations (A80), (A85), and (A88), which results in seven simultaneous ordinary differential equations and two explicit algebraic equations for the nine concentration nodes. Note that the equations for nodes 1 and 9 need to use logical statements to satisfy the boundary conditions.

The concentration variables at  $t = 2500$  are summarized in Table (A9) where a comparison with the approximate hand calculations by Geankoplis<sup>3</sup> shows reasonable agreement.

**Table A9** Results for Unsteady-state Mass Transfer in One-Dimensional Slab at  $t = 2500$  s

Distance from Slab Surface in m	$n$	Geankoplis <sup>3</sup> $\Delta x = 0.001$ m	Method of Lines (a) $\Delta x = 0.0005$ m	
		$C_A$ in kg-mol/m <sup>3</sup>	$n$	$C_A$ in kg-mol/m <sup>3</sup>
0	1	0.004	1	0.004
0.001	2	0.003188	3	0.003169
0.002	3	0.002500	5	0.002509
0.003	4	0.002095	7	0.002108
0.004	5	0.001906	9	0.001977

The calculated concentration profiles for  $C_A$  at nodes 3, 5, 7, and 9 to  $t = 20000$  s are presented in Figure (A7), where the dynamics of the interior points show the effects of the initial concentration profile.



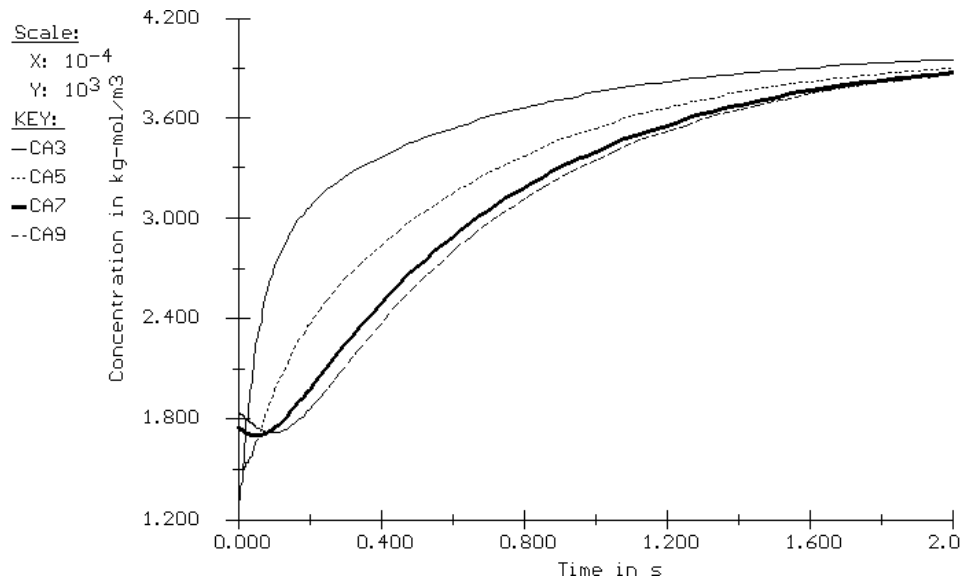


Figure A7 Calculated Concentration Profiles for  $C_A$  at Selected Node Points

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