POLYMATH SOLUTIONS TO THE CHEMICAL ENGINEERING DEMONSTRATION PROBLEM SET

Mathematical Software - Sessions 16 and 116*

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INTRODUCTION

These solutions are for a set of representative numerical problems in chemical engineering developed for Session 16 and 116 at the ASEE Chemical Engineering Summer School held at the University of Colorado in Boulder, CO from July 27 - August 1, 2002. The problems in this set are intended to utilize the basic numerical methods in problems which are appropriate to a variety of chemical engineering subject areas.

The package used to solve each problem is the POLYMATH Numerical Computation Package Version 5.1 which is widely used in Chemical Engineering. Inexpensive educational site licenses and academic evaluation copies of the software are available from the CACHE Corporation** with information at http://www.che.utexas.edu/cache/polymath.html. More details on POLYMATH and on-line purchasing options for individual copies are found at http://www.polymath-software.com.

The POLYMATH Numerical Computation Package has four companion programs.

- SIMULTANEOUS DIFFERENTIAL EQUATIONS
- SIMULTANEOUS ALGEBRAIC EQUATIONS
- SIMULTANEOUS LINEAR EQUATIONS
- CURVE FITTING AND REGRESSION

POLYMATH is a proven computational system which has been specifically created for educational use by Mordechai Shacham and Michael B. Cutlip. The latest version runs on all Windows™ operating systems. The various POLYMATH programs allow the user to apply effective numerical analysis techniques during interactive problem solving on personal computers. Results are presented graphically for easy understanding and for incorporation into papers and reports. Students with a need to solve numerical problems will appreciate the efficiency and speed of problem solution. With POLYMATH, the user is able to focus complete attention to the problem rather that spending valuable time in learning how to use or reuse the software.

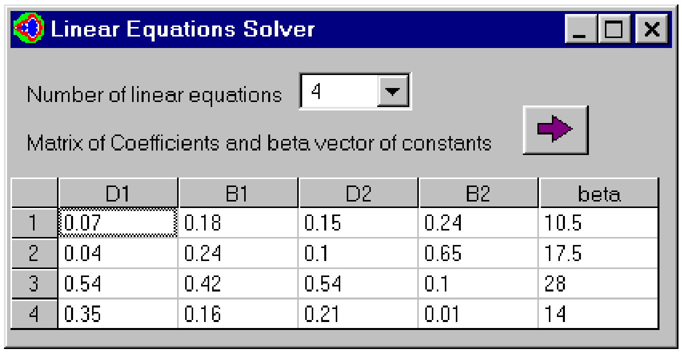
NOTE - The box around the references to the solution files at the end of each problem can be clicked to launch POLYMATH with the particular problem solution ready to be solved. If this is not available, then the problem solution files can be executed from the Polymath Solution Files directory.

*The Ch. E. Summer School was sponsored by the Chemical Engineering Division of the American Society for Engineering Education.

**A non-profit educational corporation supported by most North American chemical engineering departments and many chemical corporation. CACHE stands for computer aides for chemical engineering.

Problem 1D Solution - Steady State Material Balances on a Separation Train

(a) The coefficients and the constants in the problem given as Equation Set (D-1) can be directly introduced into the POLYMATH *Linear Equation Solver* in matrix form as shown



	D1	B1	D2	B2	beta
1	0.07	0.18	0.15	0.24	10.5
2	0.04	0.24	0.1	0.65	17.5
3	0.54	0.42	0.54	0.1	28
4	0.35	0.16	0.21	0.01	14

The solution is

```
[1] D1 =  26.25
[2] B1 =  17.5
[3] D2 =  8.75
[4] B2 =  17.5
```

and the equations are

```
[1] 0.07·D1 + 0.18·B1 + 0.15·D2 + 0.24·B2 = 10.5
[2] 0.04·D1 + 0.24·B1 + 0.1·D2 + 0.65·B2 = 17.5
[3] 0.54·D1 + 0.42·B1 + 0.54·D2 + 0.1·B2 = 28
[4] 0.35·D1 + 0.16·B1 + 0.21·D2 + 0.01·B2 = 14
```

in which these flow rates have units of mol/min.

(b) The overall balances and individual component balances on distillation column #2 given as Equation Set (D-2) can be solved algebraically to give $X_{Dx} = 0.114$, $X_{Ds} = 0.120$, $X_{Dt} = 0.492$ and $X_{Db} = 0.274$. Similarly, the overall balance and individual component balances on distillation column #3 presented as Equation Set (D-3) yield $X_{Bx} = 0.210$, $X_{Bs} = 0.4667$, $X_{Bt} = 0.2467$ and $X_{Bb} = 0.0767$.

(a&b) A combined solution is possible for all equation sets using the POLYMATH *Simultaneous Algebraic Equation Solver*. This program will solve nonlinear equations and explicit algebraic equations. The linear equations of Equation Set (D-1) of the problem must be entered as nonlinear equations where the function is equal to zero at the solution. Thus, the POLYMATH equations for this combined solution can be expressed as:

Nonlinear equations

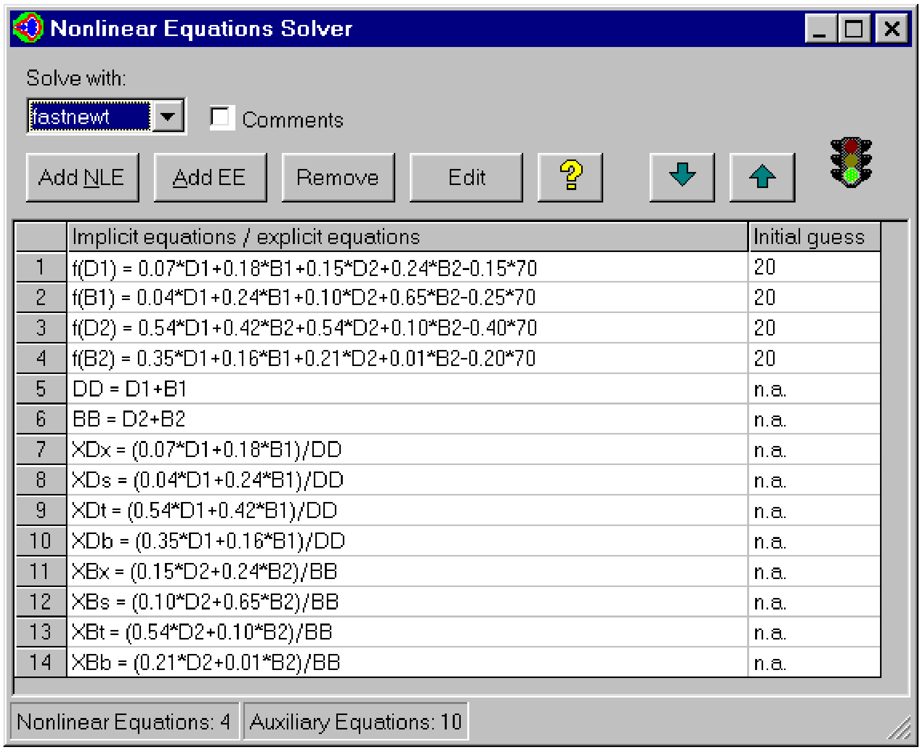
```
[1] f(D1) = 0.07*D1+0.18*B1+0.15*D2+0.24*B2-0.15*70 = 0
[2] f(B1) = 0.04*D1+0.24*B1+0.10*D2+0.65*B2-0.25*70 = 0
[3] f(D2) = 0.54*D1+0.42*B2+0.54*D2+0.10*B2-0.40*70 = 0
[4] f(B2) = 0.35*D1+0.16*B1+0.21*D2+0.01*B2-0.20*70 = 0
```

Explicit equations

```
[1] DD = D1+B1
[2] BB = D2+B2
[3] XDx = (0.07*D1+0.18*B1)/DD
[4] XDs = (0.04*D1+0.24*B1)/DD
[5] XDt = (0.54*D1+0.42*B1)/DD
[6] XDb = (0.35*D1+0.16*B1)/DD
```

[7] XBx = (0.15*D2+0.24*B2)/BB
[8] XBs = (0.10*D2+0.65*B2)/BB
[9] XBt = (0.54*D2+0.10*B2)/BB
[10] XBb = (0.21*D2+0.01*B2)/BB

The nonlinear equations (really only linear equations in this example) need to have "initial guesses" for the solutions entered into POLYMATH. A screen display is given below.



The Polymath solution output file yields the following results:

Variable	Value	f(x)	Ini Guess
D1	26.25	1.121E-09	20
B1	17.5	-1.965E-09	20
D2	8.75	4.112E-09	20
B2	17.5	-9.819E-10	20
DD	43.75		
BB	26.25		
XDx	0.114		
XDs	0.12		
XDt	0.492		
XDb	0.274		
XBx	0.21		
XBs	0.4666667		
XBt	0.2466667		
XBb	0.0766667		

The POLYMATH problem solution file for this problem is D01.pol. An alternate solution where all three equation sets are solved simultaneously is given in D01alt.pol.

Problem 2D Solution - Molar Volume and Compressibility Factor from Van Der Waals Equation

Equation (D4) can not be rearranged into a form where V can be explicitly expressed as a function of T and P. However, it can easily be solved numerically using techniques for nonlinear equations. In order to solve Equation (D4) using the POLYMATH *Simultaneous Algebraic Equation Solver*, it must be rewritten in the form

$$f(V) = \left(P + \frac{a}{V^2}\right)(V - b) - RT \qquad \textbf{PD-(1)}$$

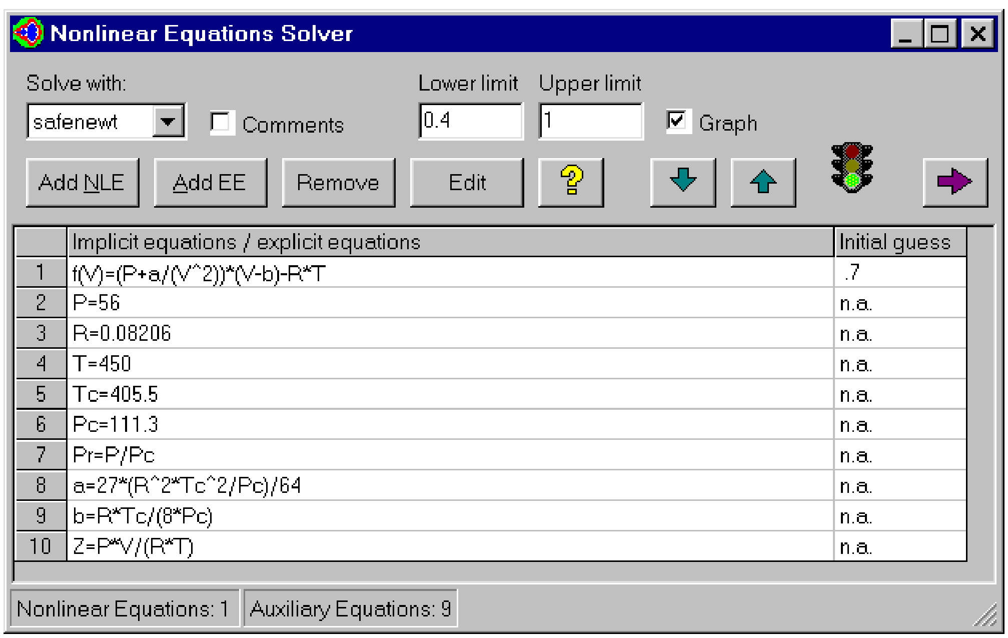
where the solution is obtained when the function is close to zero, $f(V) \approx 0$. Additional explicit equations and data can be entered into the POLYMATH program in direct algebraic form. The POLYMATH program will reorder these equations as necessary in order to allow sequential calculation.

The POLYMATH equation set for this problem is given by

Nonlinear equations
[1] f(V) = (P+a/(V^2))*(V-b)-R*T = 0

Explicit equations
[1] P = 56
[2] R = 0.08206
[3] T = 450
[4] Tc = 405.5
[5] Pc = 111.3
[6] Pr = P/Pc
[7] a = 27*(R^2*Tc^2/Pc)/64
[8] b = R*Tc/(8*Pc)
[9] Z = P*V/(R*T)

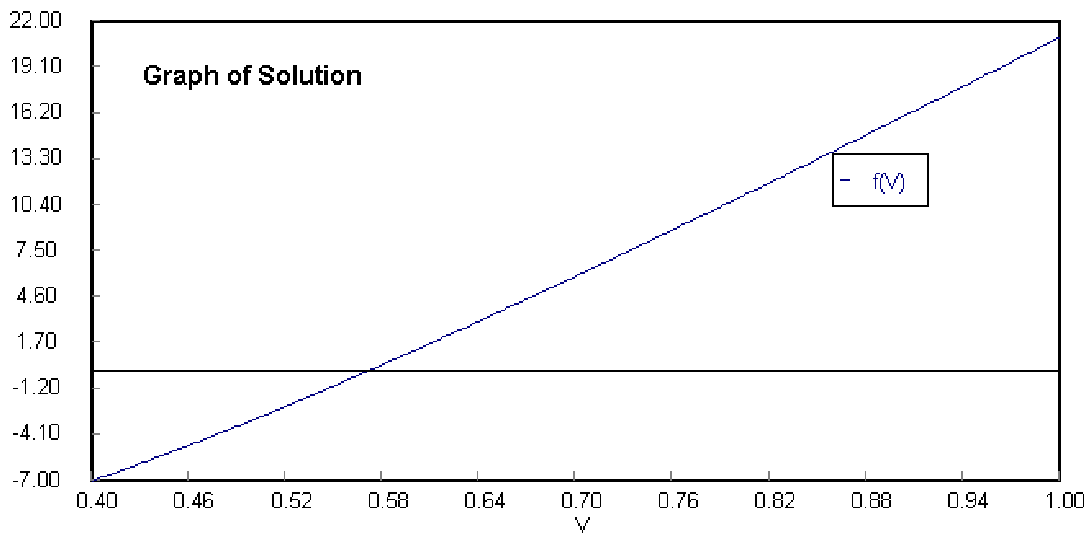
The POLYMATH input display for this problem is given below.



In order to solve a single nonlinear equation with POLYMATH, an interval for the expected solution variable, V

in this case, must be entered into the program. This interval can usually be found by consideration of the physical nature of the problem.

(a) For part (a) of this problem, the volume calculated from the ideal gas law as $V = 0.66$ liter/g-mol can be a basis for specifying the required solution interval. An interval for the expected solution for V can be entered as between 0.4 as the lower limit and 1.0 as the higher limit. The POLYMATH solution, which is given in Figure PD-(1) for $T = 450$ K and $P = 56$ atm, yields $V = 0.5749$ liter/gmol where the compressibility factor is $Z = 0.8718$.



NLE Solution

Variable	Value	f(x)	Ini Guess
V	0.5748919	6.395E-13	0.7
P	56		
R	0.08206		
T	450		
Tc	405.5		
Pc	111.3		
Pr	0.5031447		
a	4.1969459		
b	0.0373712		
Z	0.8718268		

Figure PD-1 Plot of f(V) versus V for van der Waals Equation and Solution Summary Table for Problem 2(a).

(b) Solution for the additional pressure values can be accomplished by changing the equations in the POLYMATH program for P and P_r to

```
Pr=1
P=Pr*Pc
```

Additionally, the bounds on the molar volume V may need to be altered to obtain an interval where there is a solution. Subsequent program execution for the various P_r's is required.

(c) The calculated molar volumes and compressibility factors are summarized in Table PD-(1). These calculated results indicate that there is a minimum in the compressibility factor Z at approximately $P_r = 2$. The compressibility factor then starts to increase and reaches $Z = 2.783$ for $P_r = 20$.

Table PD-1 Compressibility Factor for Gaseous Ammonia at 450 K

***P*(atm)**	P_r	V	Z
56	0.503	.574892	0.871827
111.3	1.0	.233509	0.703808
222.6	2.0	.0772676	0.465777
445.2	4.0	.0606543	0.731261
1113.0	10.0	.0508753	1.53341
2226.0	20.0	.046175	2.78348

A graph can be prepared using the POLYMATH Data Table Program to yield Figure PD-(2).

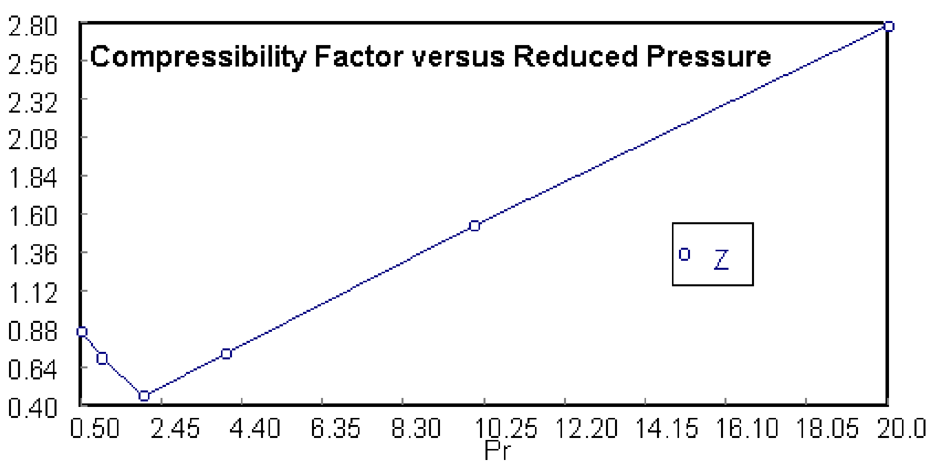


Figure PD-2 Compressibility Factor versus Reduced Pressure

The POLYMATH problem solution files for this problem are D02a.pol and D02b.pol.

Problem 3D Solution - Three Phase Equilibrium - Bubble Point

This problem contains simultaneous nonlinear algebraic equations and also explicit algebraic equations. Equations (9) and (10) can be written for each of the two components which result in four nonlinear equations. Equations (11) and (12) can also be written as nonlinear equations. Note that the entry of a nonlinear equation into the POLYMATH *Simultaneous Algebraic Equation Solver*, it must be rewritten in the form where the right hand side expression should be zero at the solution.

f(x) = an expression

The argument x in the above equation can be any variable in the problem, and this variable does not need to be in the particular expression. This argument just served to identify the name of a problem variable to the POLYMATH software.

There are many ways to arrange the nonlinear and explicit algebraic equations in this problem. The following POLYMATH Report presents the results from one such Problem 3 solution that uses the default solution algorithm and reasonable initial estimates of the solution.

NLES Solution

Variable	Value	f(x)	Ini Guess
x11	0.0226982	8.538E-10	0
x12	0.6867476	7.962E-10	1
x21	0.9773018	-5.656E-11	1
x22	0.3132524	8.117E-10	0
t	88.53783	-1.558E-08	100
beta	0.7329991	0	0.8
p1	357.05029		
p2	498.65881		
A	1.7		
B	0.7		
gamma11	33.36649		
gamma21	1.0046055		
gamma12	1.1028207		
gamma22	3.1342223		
k11	15.675678		
k21	0.6591518		
k12	0.5181085		
k22	2.0564573		
z1	0.2		
z2	0.8		
y1	0.3558097		
y2	0.6441903		

NLES Report (fastnewt)

Nonlinear equations

```
[1] f(x11) = x11*(beta+(1-beta)*k11/k12)-z1 = 0
[2] f(x12) = x12*k12-x11*k11 = 0
[3] f(x21) = x21*(beta+(1-beta)*k21/k22)-z2 = 0
[4] f(x22) = x22*k22-x21*k21 = 0
[5] f(t) = x11-y1+x21-y2 = 0
[6] f(beta) = (x11-x12)+(x21-x22) = 0
```

Explicit equations

```
[1] p1 = 10^(7.62231-1417.9/(191.15+t))
[2] p2 = 10^(8.10765-1750.29/(235+t))
[3] A = 1.7
[4] B = 0.7
[5] gamma11 = 10^(A*x21*x21/((A*x11/B+x21)^2))
```

```
[6]  gamma21 = 10^(B*x11*x11/((x11+B*x21/A)^2))
[7]  gamma12 = 10^(A*x22*x22/((A*x12/B+x22)^2))
[8]  gamma22 = 10^(B*x12*x12/((x12+B*x22/A)^2))
[9]  k11 = gamma11*p1/760
[10] k21 = gamma21*p2/760
[11] k12 = gamma12*p1/760
[12] k22 = gamma22*p2/760
[13] z1 = 0.2
[14] z2 = 0.8
[15] y1 = k11*x11
[16] y2 = k21*x21
```

Comments

```
[1]  f(x11) = x11*(beta+(1-beta)*k11/k12)-z1
     Rearrangement of Equation (9) for component i = 1
[2]  f(x12) = x12*k12-x11*k11
     Rearrangement of Equation (10) for component i = 1
[3]  f(x21) = x21*(beta+(1-beta)*k21/k22)-z2
     Rearrangement of Equation (9) for component i = 2
[4]  f(x22) = x22*k22-x21*k21
     Rearrangement of Equation (10) for component i = 2
[5]  f(t) = x11-y1+x21-y2
     Rearrangement of Equation (11)
[6]  f(beta) = (x11-x12)+(x21-x22)
     Rearrangement of Equation (12)
[7]  p1 = 10^(7.62231-1417.9/(191.15+t))
     Antoine equation for component i = 1
[8]  p2 = 10^(8.10765-1750.29/(235+t))
     Antoine equation for component i = 2
[9]  A = 1.7
     Numerator constant in Equation (15)
[10] B = 0.7
     Numerator constant in Equation (16)
[11] gamma11 = 10^(A*x21*x21/((A*x11/B+x21)^2))
     Equation (15) for component i =1 in liquid phase j = 1
[12] gamma21 = 10^(B*x11*x11/((x11+B*x21/A)^2))
     Equation (16) for component i =2 in liquid phase j = 1
[13] gamma12 = 10^(A*x22*x22/((A*x12/B+x22)^2))
     Equation (15) for component i =1 in liquid phase j = 2
[14] gamma22 = 10^(B*x12*x12/((x12+B*x22/A)^2))
     Equation (16) for component i =1 in liquid phase j = 2
[15] k11 = gamma11*p1/760
     Equation (13) for component i = 1 in liquid phase j = 1
[16] k21 = gamma21*p2/760
     Equation (13) for component i = 2 in liquid phase j = 1
[17] k12 = gamma12*p1/760
     Equation (13) for component i = 1 in liquid phase j = 2
[18] k22 = gamma22*p2/760
     Equation (13) for component i = 2 in liquid phase j = 2
[19] z1 = 0.2
     Mole fraction of component i = 1 in feed
[20] z2 = 0.8
     Mole fraction of component i = 2 in feed
[21] y1 = k11*x11
     Equation (10) for mole fraction of i = 1 in vapor phase
[22] y2 = k21*x21
     Equation (10) for mole fraction of i = 2 in vapor phase
```

The POLYMATH problem solution file for this problem is D03.pol.

Problem 4D Solution - Terminal Velocity of Falling Particles

(a) For conditions similar to those of this problem, the Reynolds number will not exceed 1000 so that only Equations (D-18) and (D-19) need to be applied. The logic which selects the proper equation based on the value of *Re* can be employed using the "if... then... else..." statement within the POLYMATH *Simultaneous Algebraic Equation Solver.*

$$C_D = \text{if}(\ \text{Re} < 0.1) \quad \text{then} \quad (24/Re) \quad \text{else} \quad (24 \times (1 + 0.14 Re^{0.7})) \qquad \textbf{PD-(2)}$$

Equation (D17) should be rearranged in order to avoid possible division by zero and negative square roots as it is entered into the form of a nonlinear equation for POLYMATH.

$$f(v_t) = v_t^2(3C_D\rho) - 4g(\rho_p - \rho)D_p \qquad \textbf{PD-(3)}$$

The following equation set can be solved by POLYMATH.

```
Nonlinear equations
[1] f(vt) = vt^2*(3*CD*rho)-4*g*(rhop-rho)*Dp = 0

Explicit equations
[1] rho = 994.6
[2] g = 9.80665
[3] rhop = 1800
[4] Dp = 0.208e-3
[5] vis = 8.931e-4
[6] Re = Dp*vt*rho/vis
[7] CD = if (Re<0.1) then (24/Re) else (24*(1+0.14*Re^0.7)/Re)
```

Specifying $v_{t,\,min} = 0.0001$ and $v_{t,\,max} = 0.05$ leads to the results summarized below from the POLYMATH Report.

Variable	Value	f(x)	Ini Guess
vt	0.0157816	2.665E-15	0.02505
rho	994.6		
g	9.80665		
rhop	1800		
Dp	2.08E-04		
vis	8.931E-04		
Re	3.6556385		
CD	8.8426582		

(b) The terminal velocity in the centrifugal separator can be calculated by replacing the *g* in Equation PD-(3) by 30*g*. Introduction of this change to the equation set gives the following results:

Variable	Value	f(x)	Ini Guess
vt	0.2060215	2.842E-13	0.02505
rho	994.6		
g	294.1995		
rhop	1800		
Dp	2.08E-04		
vis	8.931E-04		
Re	47.722612		
CD	1.5566185		

The POLYMATH problem solution files for this problem are D04a.pol and D04b.pol.

Problem 5D Solution - Reaction Equilibrium for Multiple Gas Phase Reactions

The Equation Set (D-22) can be entered into the POLYMATH *Simultaneous Algebraic Equation Solver,* but the nonlinear equilibrium expressions must be written as functions which are equal to zero at the solution. A simple transformation of the equilibrium expressions of Equation Set (D-22) to the required functional form yields

$$f(C_D) = \frac{C_C C_D}{C_A C_B} - K_{C1}$$
$$f(C_X) = \frac{C_X C_Y}{C_B C_C} - K_{C2} \qquad \textbf{PD-(4)}$$
$$f(C_Z) = \frac{C_Z}{C_A C_X} - K_{C3}$$

The above equation set may be difficult to solve because the division by unknowns may make most solution algorithms diverge.

Expediting the Solution of Nonlinear Equations

An additional simple transformation of the nonlinear function can make many functions much less nonlinear and easier to solve by simply eliminating division by the unknowns. In this case, the Equation Set PD-(4) can be modified to

$$f(C_D) = C_C C_D - K_{C1} C_A C_B$$
$$f(C_X) = C_X C_Y - K_{C2} C_B C_C \qquad \textbf{PD-(5)}$$
$$f(C_Z) = C_Z - K_{C3} C_A C_X$$

The POLYMATH Report file utilizing Equation Set PD-(5) with the initial conditions for part (a) of $C_D = C_X = C_Z = 0$ is given below.

NLES Solution

Variable	Value	f(x)	Ini Guess
CD	0.7053344	3.577E-13	0
CX	0.1777924	3.588E-13	0
CZ	0.3739766	-2.287E-13	0
KC1	1.06		
CY	0.551769		
KC2	2.63		
KC3	5		
CA0	1.5		
CB0	1.5		
CC	0.1535654		
CA	0.420689		
CB	0.2428966		

NLES Report (safenewt)

Nonlinear equations

[1] f(CD) = CC*CD-KC1*CA*CB = 0
[2] f(CX) = CX*CY-KC2*CB*CC = 0
[3] f(CZ) = CZ-KC3*CA*CX = 0

Explicit equations

[1] KC1 = 1.06

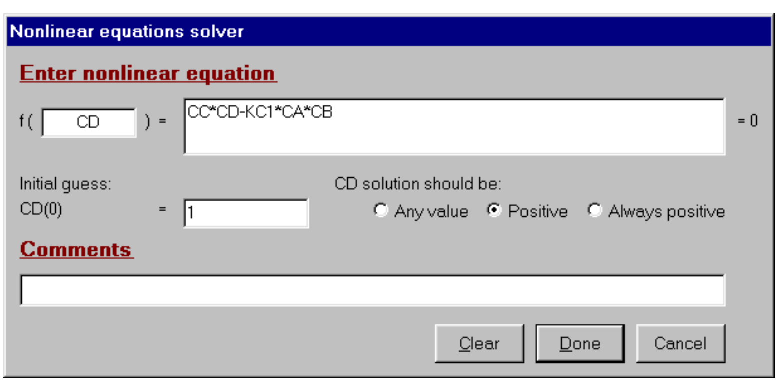
```
[2] CY = CX+CZ
[3] KC2 = 2.63
[4] KC3 = 5
[5] CA0 = 1.5
[6] CB0 = 1.5
[7] CC = CD-CY
[8] CA = CA0-CD-CZ
[9] CB = CB0-CD-CY
```

(a), (b) and (c) The POLYMATH solutions are summarized in Table PD-(2) for the three sets of initial conditions. Note that the initial conditions for problem part (a) converged to all positive concentrations. However the initial conditions for parts (b) and (c) converged to some negative values for some of the concentrations. Thus a "reality check" on Table PD-(2) for physical feasibility reveals that the negative concentrations in parts (b) and (c) are the basis for rejecting these solutions as not representing a physically valid situation.

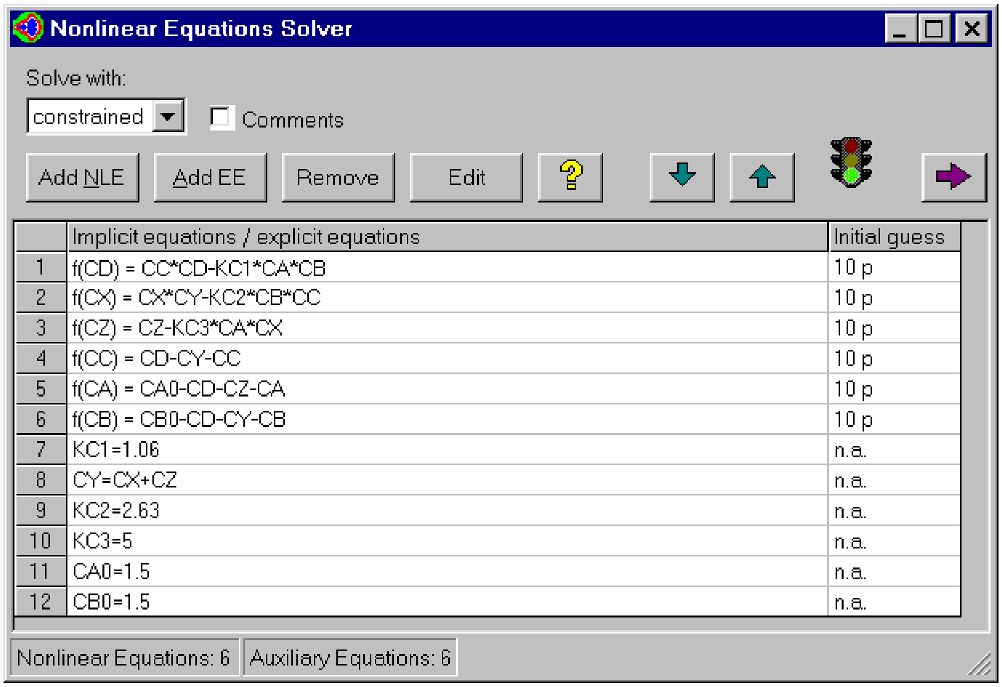
Table PD-2 POLYMATH Solutions of the Chemical Equilibrium Problem

Variable	Part (a)	Part (b)	Part (c)
C_D	0.7053	0.05556	1.070
C_X	0.1778	0.5972	-0.3227
C_Z	0.3740	1.082	1.131
C_A	0.4207	0.3624	-0.7006
C_B	0.2429	-0.2348	-0.3779
C_C	0.1536	-1.624	0.2623
C_Y	0.5518	1.679	0.8078

Alternate Constrained Solution The POLYMATH *Simultaneous Algebraic Equation Solver* also offers a selection of algorithms for solving the nonlinear equations. For this example, the constrained algorithm selection allows selected variables to be either (1) be positive or negative at solution, (2) positive at the solution, or (3) positive during iterations and at the solution. The specification of a positive solution is shown below in the input box for variable CD.



In this problem, it is also helpful to express the other gas concentrations as nonlinear equations so that the constraints will allow all gas concentrations to be positive at the problem solution. The POLYMATH input display that allows this alternate solution is shown below for the initial conditions of part (c).



	Implicit equations / explicit equations	Initial guess
1	f(CD) = CC*CD-KC1*CA*CB	10 p
2	f(CX) = CX*CY-KC2*CB*CC	10 p
3	f(CZ) = CZ-KC3*CA*CX	10 p
4	f(CC) = CD-CY-CC	10 p
5	f(CA) = CA0-CD-CZ-CA	10 p
6	f(CB) = CB0-CD-CY-CB	10 p
7	KC1=1.06	n.a.
8	CY=CX+CZ	n.a.
9	KC2=2.63	n.a.
10	KC3=5	n.a.
11	CA0=1.5	n.a.
12	CB0=1.5	n.a.

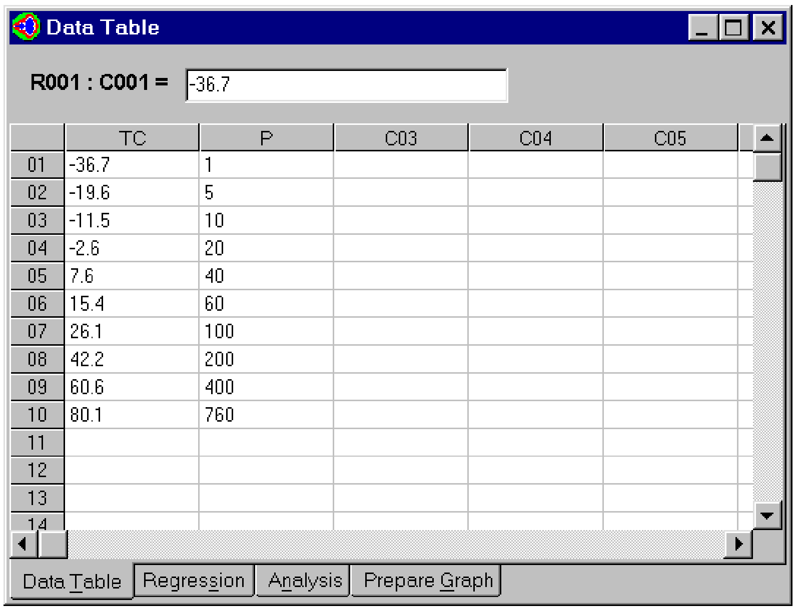
The results of all three sets of initial conditions with this alternate treatment are equivalent to the original problem solution of part (a) indicating the value of constrained solutions to sets of nonlinear equations.

Variable	Value	f(x)	Ini Guess
CD	0.7053344	0	10
CX	0.1777924	0	10
CZ	0.3739766	0	10
CC	0.1535654	-5.551E-17	10
CA	0.420689	0	10
CB	0.2428966	-2.776E-17	10
KC1	1.06		
CY	0.551769		
KC2	2.63		
KC3	5		
CA0	1.5		
CB0	1.5		

The POLYMATH problem solution files for this problem are D05a.pol, D05b.pol, D05c.pol, D05b(alt).pol, and D05c(alt).pol.

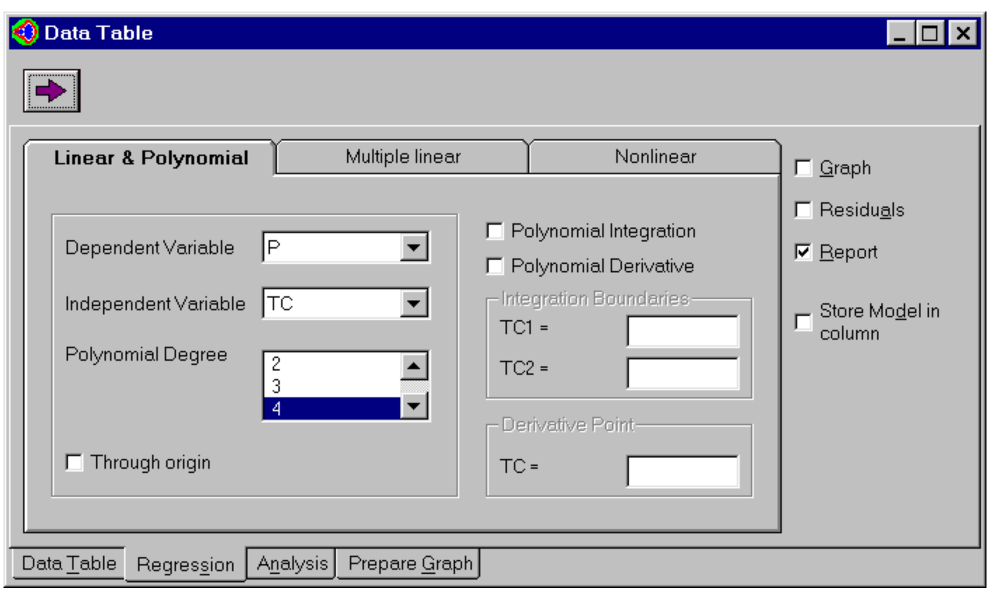
Problem 6D Solution - Vapor Pressure Data Representation by Polynomials and Equations

(a) Data Regression with a Polynomial The POLYMATH *Polynomial, Multiple Linear and Nonlinear Regression Program* can be used to solve this problem by first entering the data in a similar manner to using a spreadsheet. Let us denote the column of temperature data in °C as *TC* and the column of pressure data as *P*. This POLYMATH Data Table worksheet is reproduced below where the first two columns of data have been entered with appropriate titles.



	TC	P	C03	C04	C05
01	-36.7	1			
02	-19.6	5			
03	-11.5	10			
04	-2.6	20			
05	7.6	40			
06	15.4	60			
07	26.1	100			
08	42.2	200			
09	60.6	400			
10	80.1	760			
11					
12					
13					
14					

The Regression tab at the bottom of the POLYMATH Data Table allows a polynomial regression option with the dependent variable column P and the independent variable column TC. This corresponds directly to Equation (D23).



The resulting POLYMATH Report give the details of the polynomial regression including the variance.

POLYMATH Results

Problem 6 - Vapor Pressure Data Representation by Polynomials and Equations

Linear Regression Report

Model: P = a0 + a1*TC + a2*TC^2 + a3*TC^3 + a4*TC^4

Variable	Value	95% confidence
a0	24.678757	0.7872334
a1	1.6061958	0.0544632
a2	0.0360443	0.0010089
a3	4.131E-04	4.005E-05
a4	3.963E-06	4.514E-07

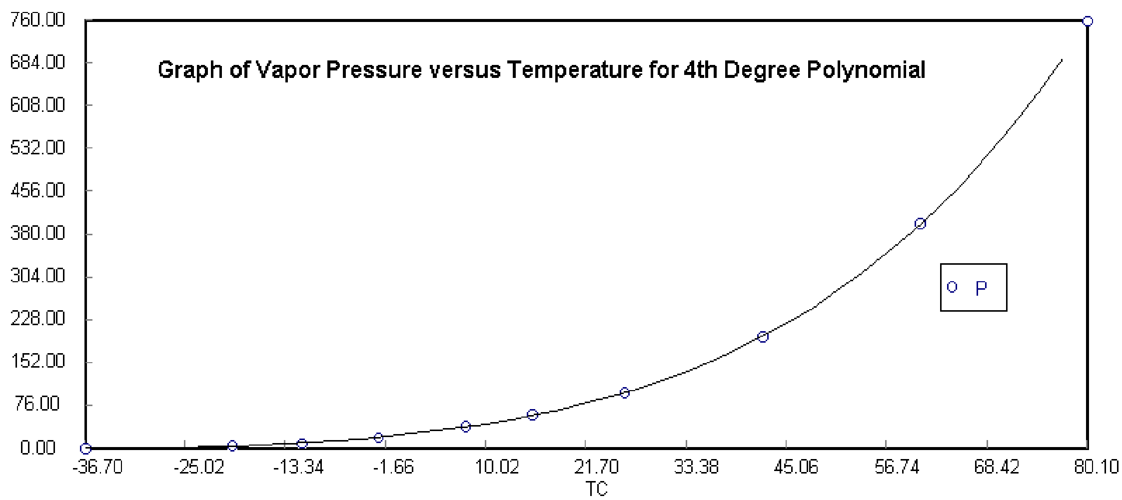
General

```
Order of polynomial = 4
Regression including free parameter
Number of observations = 10
```

Statistics

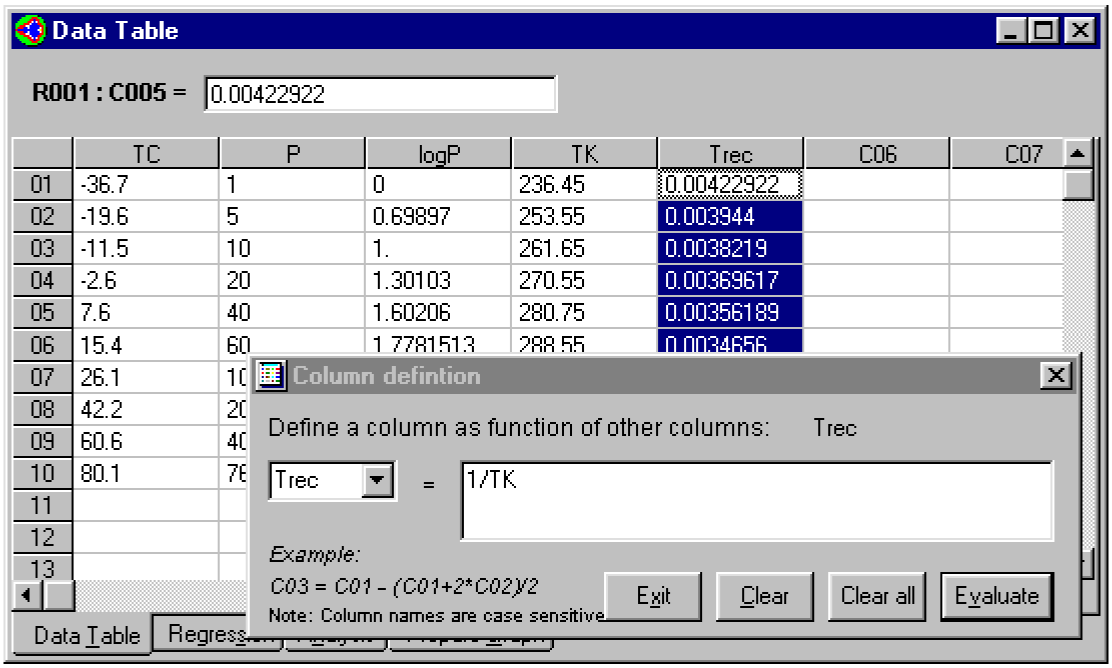
```
R^2 =        0.9999963
R^2adj =  0.9999934
Rmsd =  0.1410532
Variance =  0.3979203
```

A POLYMATH plot of this resulting polynomial is given below.

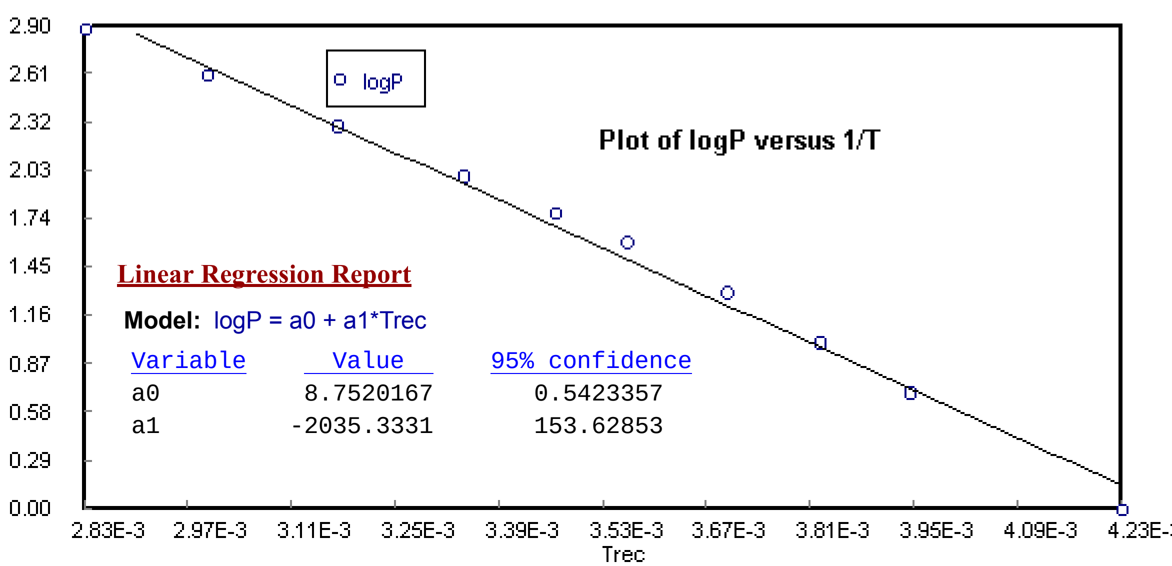


Successive polynomial regressions indicate that the polynomial with the minimum variance is the 4th degree.

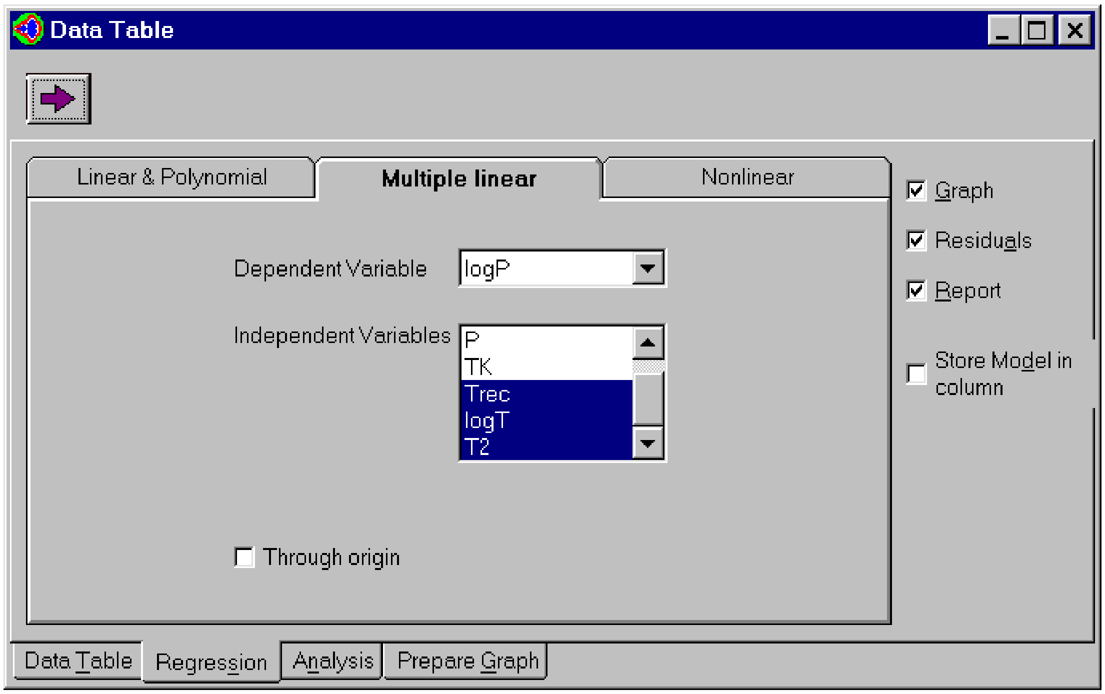
(b) Regression with Clausius-Clapeyron Equation Data regression with the Clausius-Clapeyron expression, Equation (D24), can be accomplished by three additional transformed variables (columns) in the POLYMATH Data Table used for part (a). Additional columns can be defined by the relationships: logP = log(P), TK= T + 273.15, and Trec = 1/TK as indicated below.



A request for linear regression (polynomial with 1st degree) when the dependent variable column is logP and the independent variable column is Trec yields the following plot and numerical results from POLYMATH.



(c) Riedel Equation Data Correlation The Riedel equation correlation requires two additional columns for transformed variables, $\log T = \log(TK)$ and $T2 = TK \times TK$. The Multiple linear option from the Regression tab with *T*rec, log*T*, and *T2* as the independent variables and log*P* as the dependent variable can be selected as shown below.



The resulting Polymath Report yields the following results.

POLYMATH Results

Problem D6(c) - Vapor Pressure Data Representation by Polynomials and Equations

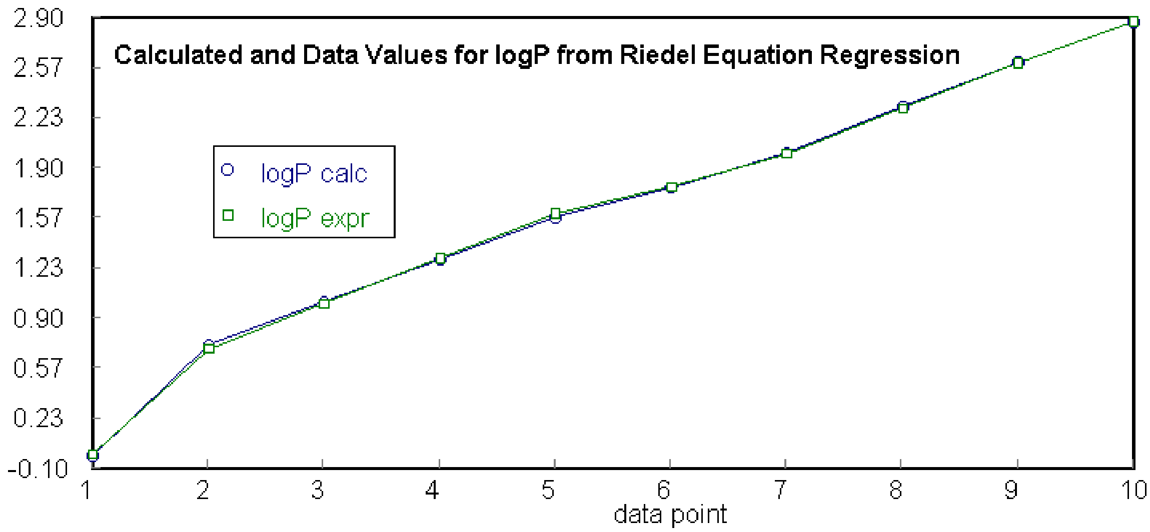
Multiple linear regression

Model: logP = a0 + a1*Trec + a2*logT + a3*T2

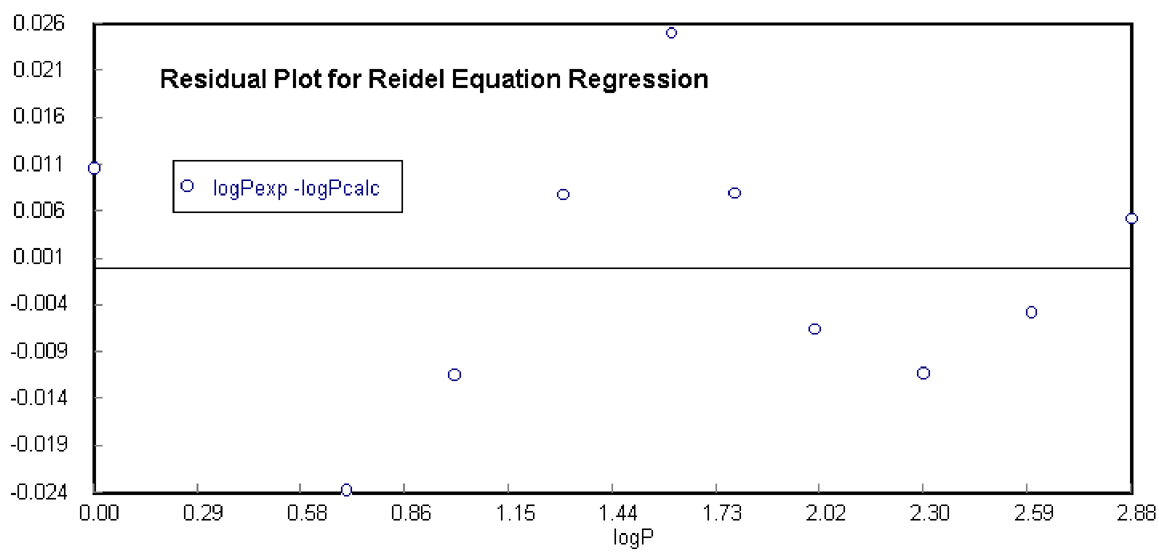
Variable	Value	95% confidence
a0	216.72144	156.41354
a1	-9318.66	4857.1966
a2	-75.748179	58.427175
a3	4.445E-05	5.001E-05

The Graph plot shows that there is a fairly good agreement between the experimental and calculated values of

$\log(P)$.

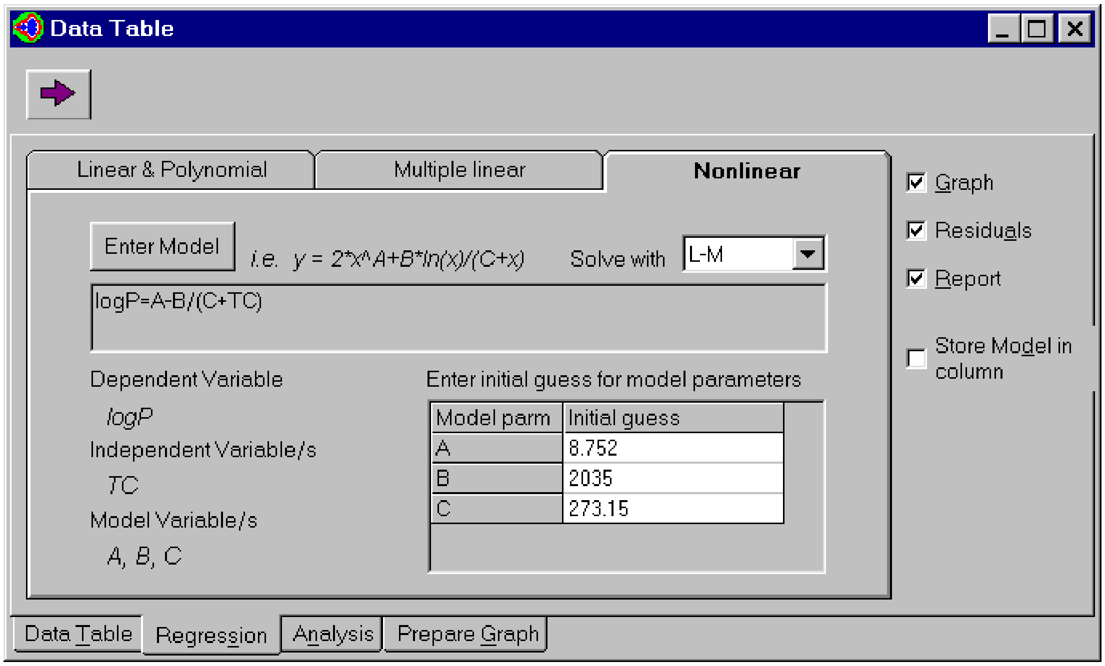


The Residual plot showing the error distribution given in is more random than for either the polynomial or the Clapeyron equation.



(d) Nonlinear Regression with the Antoine Equation This expression, Equation (D26), cannot be linearized and so it must be regressed with nonlinear regression option of the POLYMATH *Polynomial, Multiple Linear and Nonlinear Regression Program*. With this option, the user must supply initial estimates. In this case, it is helpful to use the initial estimates for A and B which were determined in part (b) and use the estimate for C as 273.15. Direct entry of Equation (D26) with the initial guesses for the parameters is accomplished using the Nonlinear tab of the

Regression options in the POLYMATH Data Table.



The POLYMATH Report of the regression gives more statistical information as shown below.

Nonlinear regression (L-M)

Model: logP = A-B/(C+TC)

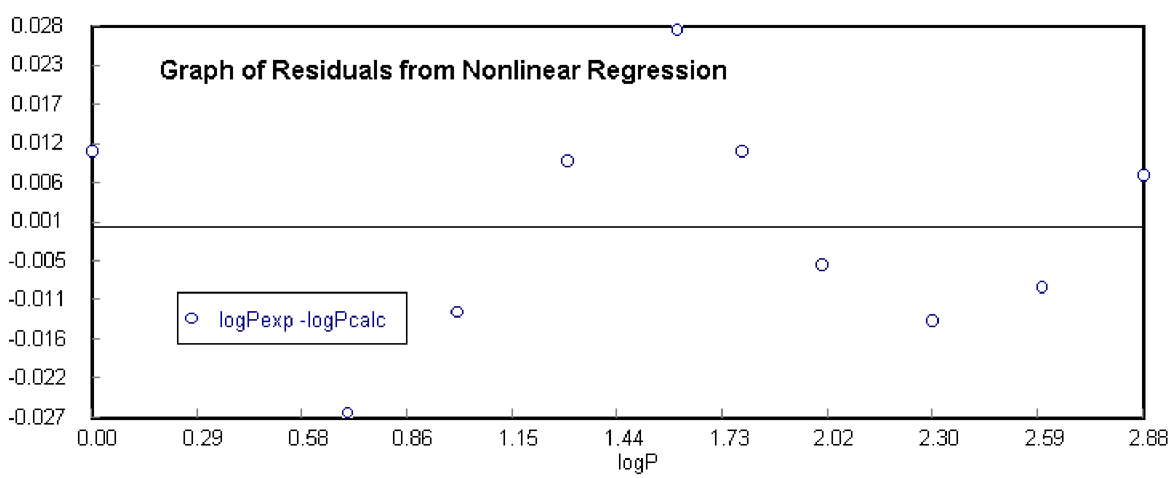
Variable	Ini guess	Value	95% confidence
A	8.752	5.7673466	0.1520845
B	2035	677.09401	48.159076
C	273.15	153.88537	5.6870913

Nonlinear regression settings
Max # iterations = 64

Precision
R^2 = 0.9996879
R^2adj = 0.9995987
Rmsd = 0.0047228
Variance = 3.186E-04

General
Sample size = 10
Model vars = 3
Indep vars = 1
Iterations = 24

A graph of the residuals from the regressed equation can be used to verify that the errors are approximately randomly distributed.

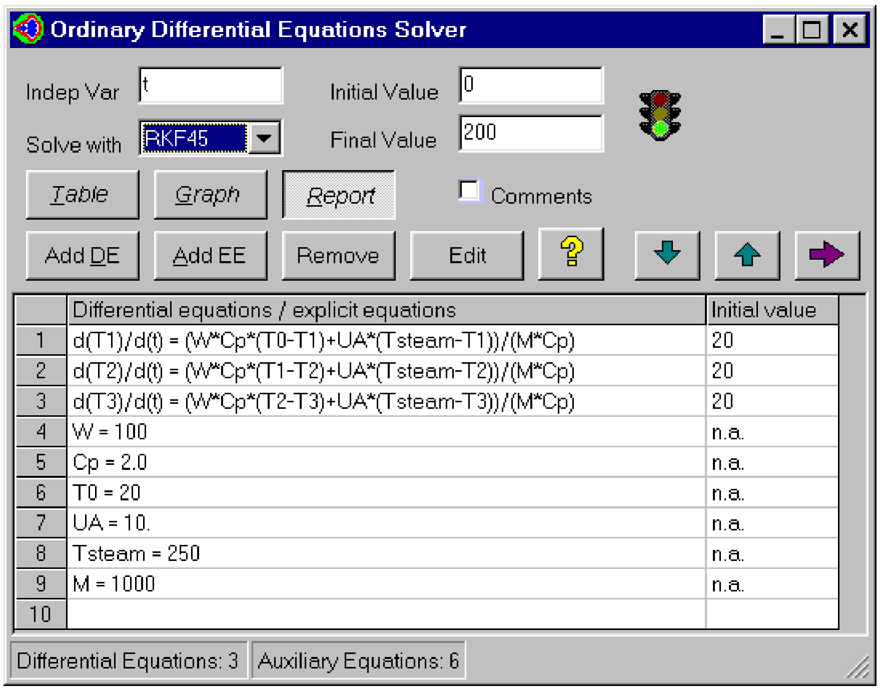



The POLYMATH problem solution files for this problem are D06a.pol and D06bcd.pol.

Problem 7D Solution - Unsteady State Heat Exchange in a Series of Agitated Tanks

Equations (D-29) to (D-31), together with the numerical data and initial values given in the problem statement, can be entered into the POLYMATH *Simultaneous Differential Equation Solver*. The initial startup is from a temperature of 20°C in all three tanks, thus this is the appropriate initial condition for each tank temperature. The final value or steady state value can be determined by solving the differential equations to steady state by giving a large time interval for the numerical solution. Alternately one could set the time derivatives to zero, and solve the resulting algebraic equations. In this case, it is easiest just to numerically solve the differential equations to large value of t where steady state is achieved.

The POLYMATH differential equation input display with the input of the appropriate equations is shown below where the final value of t is large enough to reach steady state.



The POLYMATH Report provides an overview of the problem solution as given below.

Problem D7 - Unsteady State Heat Exchange in a Series of Agitated Tanks

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	200	200
T1	20	20	30.952381	30.952381
T2	20	20	41.38322	41.38322
T3	20	20	51.31735	51.31735
W	100	100	100	100
Cp	2	2	2	2
T0	20	20	20	20
UA	10	10	10	10
Tsteam	250	250	250	250
M	1000	1000	1000	1000

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(T1)/d(t) = (W*Cp*(T0-T1)+UA*(Tsteam-T1))/(M*Cp)
[2] d(T2)/d(t) = (W*Cp*(T1-T2)+UA*(Tsteam-T2))/(M*Cp)
[3] d(T3)/d(t) = (W*Cp*(T2-T3)+UA*(Tsteam-T3))/(M*Cp)

Explicit equations as entered by the user

[1] W = 100
[2] Cp = 2.0
[3] T0 = 20
[4] UA = 10.
[5] Tsteam = 250
[6] M = 1000

The time to reach steady state is usually considered to be the time to reach 99% of the final steady state value for the variable which is increasing and responds the most slowly. For this problem, T_3 increases the most slowly, and the steady state value is found to be 51.317°C. In POLYMATH, this can be easily done by displaying the output in tabular form for T_1, T_2, and T_3 so that the approach to steady state can accurately be observed. Thus the time must be determined when T_3 reaches 0.99(51.317) or 50.804 °C. The POLYMATH Data Table output from the *Differential Equation Solver* is useful in determining this time as illustrated in the table which is partly reproduced below.

ODE Results: RKF45, Solution #5

R001 : C001 =

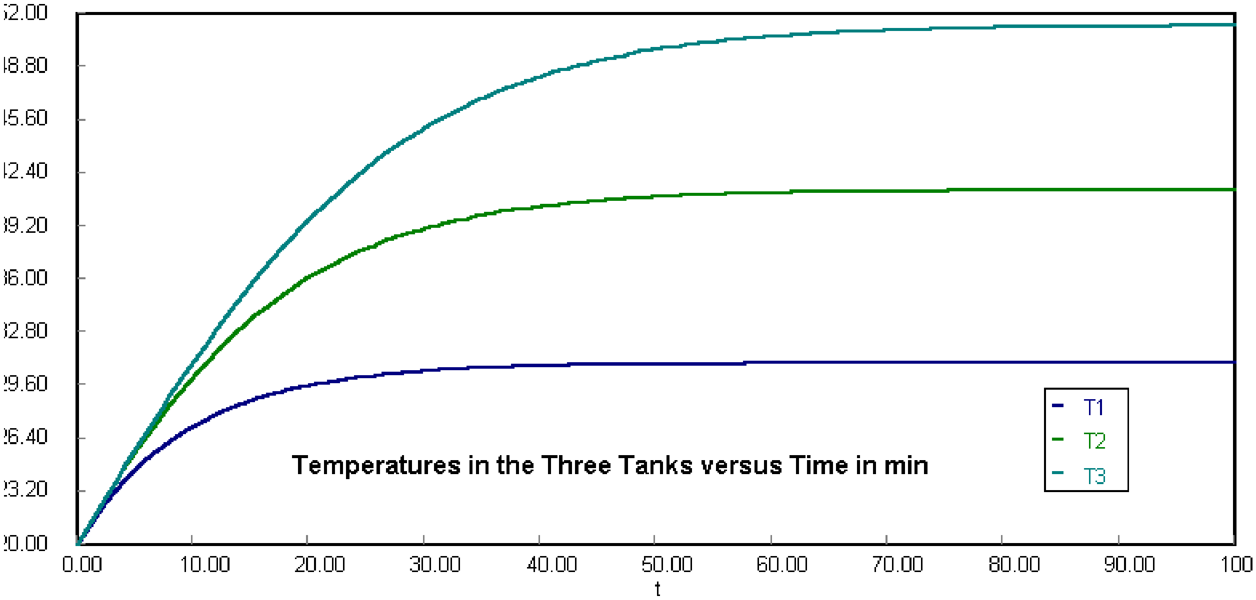
	t	T1	T2	T3	W	Cp	T0
25	50.549872	30.898132	41.003081	49.933737	100	2	20
26	52.149872	30.906522	41.05453	50.095705	100	2	20
27	55.349872	30.919609	41.137844	50.367492	100	2	20
28	56.949872	30.924677	41.171358	50.480841	100	2	20
29	58.549872	30.928961	41.200374	50.581249	100	2	20
30	60.149872	30.932583	41.225483	50.6701	100	2	20
31	63.349872	30.938233	41.26597	50.818015	100	2	20
32	64.949872	30.940421	41.282189	50.879224	100	2	20
33	66.549872	30.94227	41.296195	50.933184	100	2	20
34	68.149872	30.943834	41.308286	50.980714	100	2	20
35	71.349872	30.946273	41.327716	51.059334	100	2	20
36	72.949872	30.947218	41.335473	51.091662	100	2	20
37	74.549872	30.948016	41.342159	51.120051	100	2	20
38	76.149872	30.948691	41.347918	51.144961	100	2	20

Data Table | Regression | Analysis | Prepare Graph

Thus the time to reach steady state for T3 is approximately 63.3 minutes as estimated from the above table.

The temperatures in the three tanks can be easily plotted using the POLYMATH Graph option from the main

Differential Equation display.



Alternate Solution The POLYMATH "if... then... else..." statement can be used in this solution to calculate the time to reach 99% of the steady state temperature for T3. This involves creating a new differential equation for variable, named "ts" for example, which follows the time variable until T3 reaches 99% of the steady state temperature, and then the differential change of this variable is set to zero for all larger times. The following statement can be entered into the POLYMATH to provide this differential equation.

```
d(ts)/d(t) = if (T3<50.804) then (1) else (0)
```

Part of the POLYMATH Report for this alternate solution is shown below where the ts (steady state time) is calculated to be 83.00

Variable	initial value	minimal value	maximal value	final value
t	0	0	200	200
T1	20	20	30.952381	30.952381
T2	20	20	41.38322	41.38322
T3	20	20	51.31735	51.31735
ts	20	20	83.004524	83.004524


The POLYMATH problem solution files for this problem are D07.pol and D07(alt).pol.

Problem 8D Solution - Diffusion with Chemical Reaction in a One Dimensional Slab

Solving Higher Order Ordinary Differential Equations

POLYMATH, like most mathematical software packages, can solve only systems of first order ordinary differential equations (ODE's). Fortunately, the solution of an n-th order ODE can be accomplished by expressing the equation with a series of simultaneous first order differential equations. This is the approach that is typically used for the integration of higher order ODE's.

(a) Equation (D32) is a second order ODE, but it can be converted into a system of first order equations by substituting new variables for the higher order derivatives. In this particular case, a new variable *y* can be defined which represent the first derivation of C_A with respect to z. Thus Equation (D32) can be written as the equation set

$$\frac{dC_A}{dz} = y$$
$$\frac{dy}{dz} = \frac{k}{D_{AB}}C_A \qquad \textbf{PD-(6)}$$

This set of first order ODE's can be entered into the *POLYMATH Simultaneous Differential Equation Solver* for solution, but initial conditions for both C_A and *y* are needed. Since the initial condition of *y* is not known, an iterative method (also referred to as a shooting method) can be used to find the correct initial value for *y* which will yield the boundary condition given by Equation (D33).

Shooting Method-Trial and Error

The shooting method is used to achieve the solution of a boundary value problem to one of an iterative solution of an initial value problem. Known initial values are utilized while unknown initial values are optimized to achieve the corresponding boundary conditions. Either "trial and error" or variable optimization techniques are used to achieve convergence on the boundary conditions.

For this problem, a first "trial and error" value for the initial condition of *y*, for example y_0 = -150, is used to carry out the integration and calculate the error for the boundary condition designated by ε. Thus the difference between the calculated and desired final value of *y* at z = L is given by

$$\varepsilon(y_0) = y_{f,\,calc} - y_{f,\,desired} \qquad \textbf{PD-(7)}$$

Note that for this example, $y_{f,desired}$ = 0 and thus $\varepsilon(y_0) = y_{f,calc}$ only because this desired boundary condition is zero.

The equations as entered in the POLYMATH Simultaneous Differential Equation Solver for an initial "trial and error" solution are shown in Figure PD-(3). The calculation of err in the POLYMATH equation set which corresponds to Equation PD-(7) is only valid at the end of the ODE solution. Repeated reruns of this POLYMATH equation set with different initial conditions for *y* can be used in a "trial and error" mode to converge upon the desired boundary condition for y_0 where $\varepsilon(y_0)$ or err ≅ 0. Some results are summarized in Table PD-(3) for various values of y_0. The

Table PD-3 Trial Boundary Conditions for Equation Set PD-(6)

y_0 (z = 0)	-120.	-130.	-140.	-150.
$y_{f,calc}$ (z = L)	17.23	2.764	-11.70	-26.16
$\varepsilon(y_0)$	17.23	2.764	-11.70	-26.16

desired initial value for y_0 lies between -130 and -140. This "trial and error" approach can be continued to obtain a

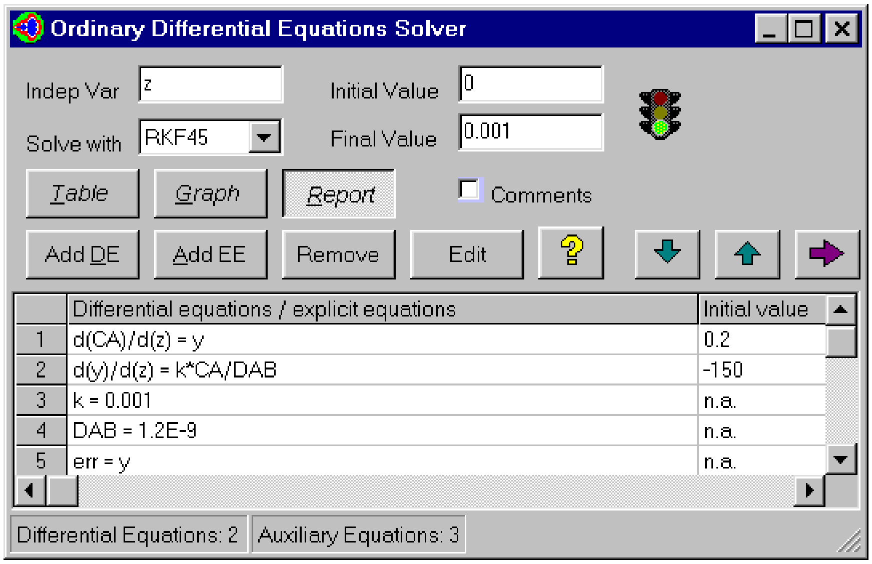


Figure PD-3 POLYMATH Equation Entry

more accurate value for y_0, or an optimization technique can be applied.

Newton's Method for Boundary Condition Convergence

A very useful method for optimizing the proper initial condition is to consider this determination to be a problem in finding the zero of a function. In the notation of this problem, the variable to be optimized is y_0 and the objective function is $\varepsilon(y_0)$ which is defined by Equation PD-(7).

Newton's method, an effective method for optimizing a single variable, can be applied here to minimize the above objective function. According to this method, an improved estimate for y_0 can be calculated using the equation

$$y_{0,\,new} = y_0 - \varepsilon(y_0)/\varepsilon'(y_0) \qquad \textbf{PD-(8)}$$

where $\varepsilon'(y_0)$ is the derivative of ε at $y = y_0$. The derivative, $\varepsilon'(y_0)$, can be estimated using a finite difference approximation

$$\varepsilon'(y_0) \cong \frac{\varepsilon(y_0 + \delta y_0) - \varepsilon(y_0)}{\delta y_0} \qquad \textbf{PD-(9)}$$

where δy_0 is a small increment in the value of y_0. It is very convenient that $\varepsilon(y_0 + \delta y_0)$ can be calculated *simultaneously with the numerical ODE solution* for $\varepsilon(y_0)$ thereby allowing calculation of $\varepsilon'(y_0)$ from Equation PD-(9) and a *new estimate* for y_0 from Equation PD-(8).

Using $\delta = 0.0001$ for this example, the POLYMATH equation set for carrying out the first step in Newton's method procedure is given by

	Differential equations / explicit equations	Initial value
1	d(CA)/d(z) = y	0.2
2	d(y)/d(z) = k*CA/DAB	-130
3	d(CA1)/d(z) = y1	0.2
4	d(y1)/d(z) = k*CA1/DAB	-130.013
5	k = 0.001	n.a.
6	DAB = 1.2E-9	n.a.
7	err = y-0	n.a.
8	err1 = y1-0	n.a.
9	y0 = -130	n.a.
10	L = .001	n.a.
11	delta = 0.0001	n.a.
12	CAanal = 0.2*cosh(L*(k/DAB)^.5*(1-z/L))/(cosh(L*(k/DAB)^.5))	n.a.
13	derr = (err1-err)/(delta*y0)	n.a.
14	ynew = y0-err/derr	n.a.

This set of equations yields the results POLYMATH Report give below where the new estimate for y_0 is the final value of the POLYMATH variable `ynew` or -131.911. Another iteration of Newton's method can be obtained by starting with the new estimate and modifying the initial conditions for `y` and `y1` and the value of `y0` in the POLYMATH equation set. The second iteration indicates that the `err` is approximately 3.e-4 and that `ynew` is unchanged indicating that convergence has been obtained. For the value of y0 = -131.911, the numerical and analytical solutions are equal to at least six significant digits.

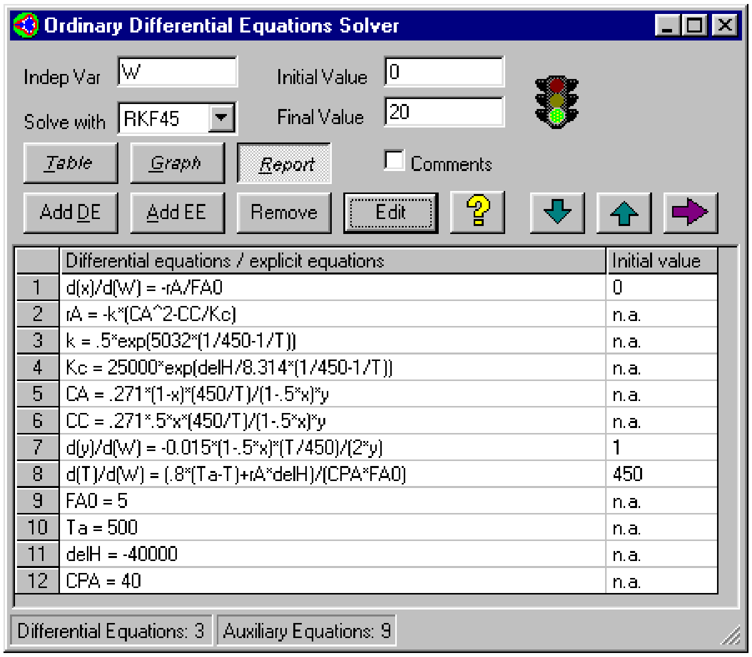
Calculated values of the DEQ variables (FIRST ITERATION)

Variable	initial value	minimal value	maximal value	final value
z	0	0	0.001	0.001
CA	0.2	0.1404279	0.2	0.1404606
y	-130	-130	2.7643829	2.7643829
CA1	0.2	0.1404135	0.2	0.1404457
y1	-130.013	-130.013	2.7455795	2.7455795
k	0.001	0.001	0.001	0.001
DAB	1.2E-09	1.2E-09	1.2E-09	1.2E-09
err	-130	-130	2.7643829	2.7643829
err1	-130.013	-130.013	2.7455795	2.7455795
y0	-130	-130	-130	-130
L	0.001	0.001	0.001	0.001
delta	1.0E-04	1.0E-04	1.0E-04	1.0E-04
CAanal	0.2	0.1382726	0.2	0.1382726
derr	1	1	1.4464177	1.4464177
ynew	-5.227E-11	-131.91119	-5.227E-11	-131.91119

The POLYMATH problem solution files for this problem are D08a1.pol, D08a2.pol, and D08a3.pol.

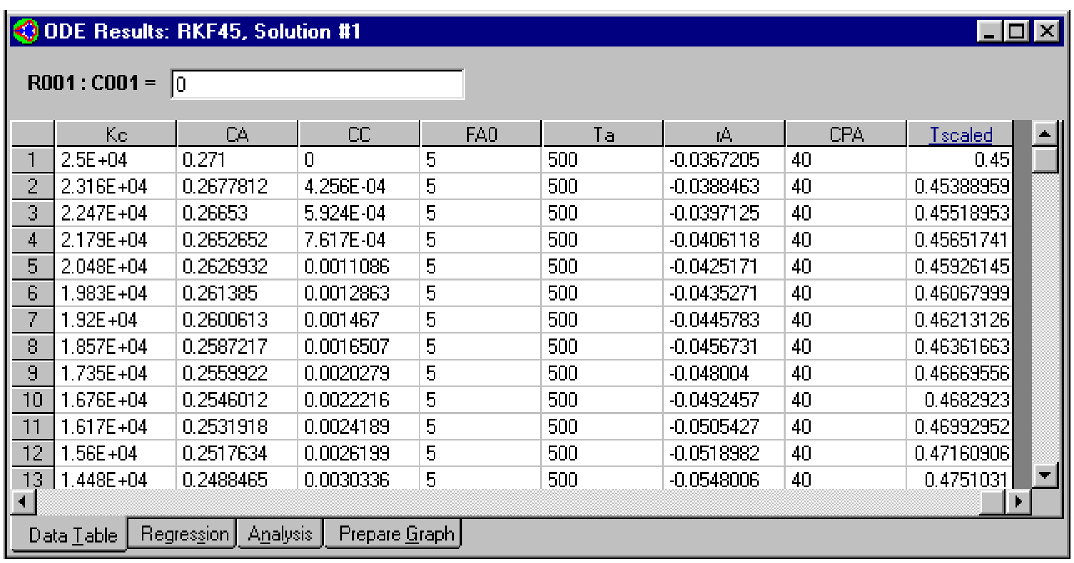
Problem 9D Solution - Reversible, Exothermic, Gas Phase Reaction in a Catalytic Reactor

Introduction of the given equations and the numerical values of the parameter provided in the problem statement into the *POLYMATH Simultaneous Differential Equation Solver* is shown below.



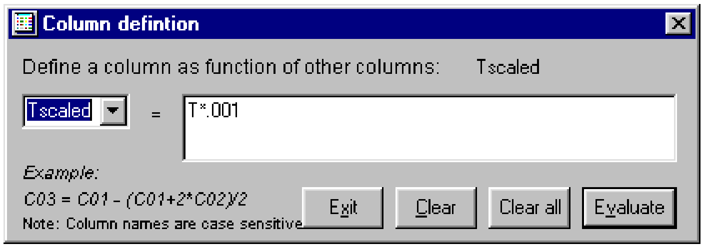
	Differential equations / explicit equations	Initial value
1	d(x)/d(W) = -rA/FA0	0
2	rA = -k*(CA^2-CC/Kc)	n.a.
3	k = .5*exp(5032*(1/450-1/T))	n.a.
4	Kc = 25000*exp(delH/8.314*(1/450-1/T))	n.a.
5	CA = .271*(1-x)*(450/T)/(1-.5*x)*y	n.a.
6	CC = .271*.5*x*(450/T)/(1-.5*x)*y	n.a.
7	d(y)/d(W) = -0.015*(1-.5*x)*(T/450)/(2*y)	1
8	d(T)/d(W) = (.8*(Ta-T)+rA*delH)/(CPA*FA0)	450
9	FA0 = 5	n.a.
10	Ta = 500	n.a.
11	delH = -40000	n.a.
12	CPA = 40	n.a.

(a) The requested plot for the conversion (X), reduced pressure (y) and temperature ($T \times 10^{-3}$) can be accomplished by requesting the POLYMATH Table during the problem solution that is partially shown below The scaled

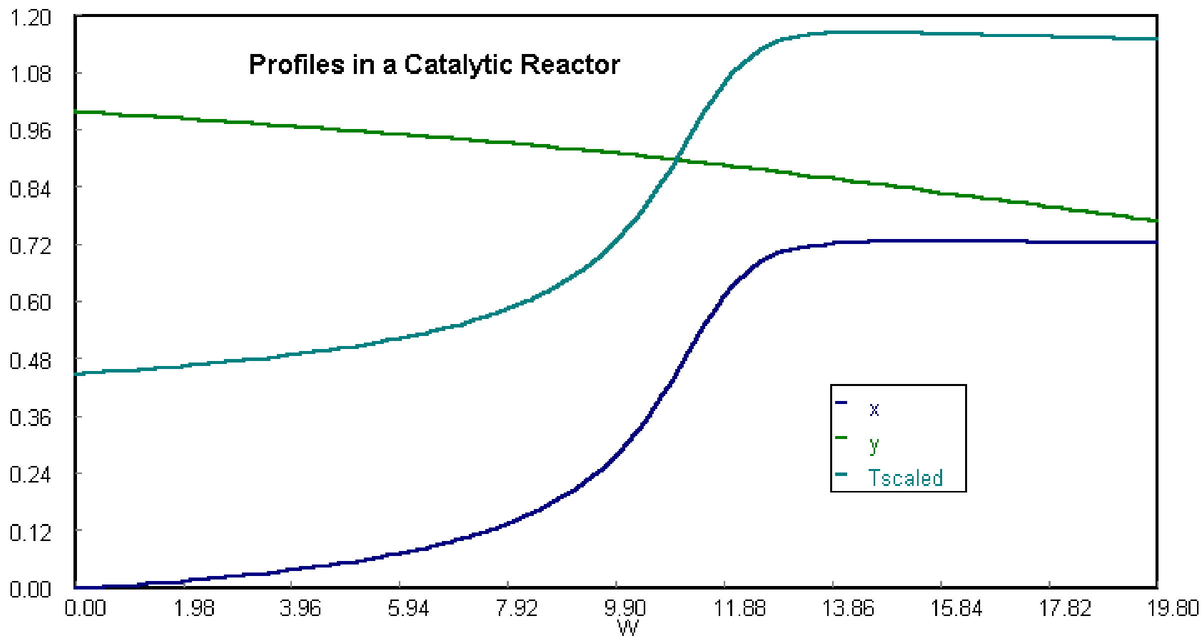


	Kc	CA	CC	FA0	Ta	rA	CPA	Tscaled
1	2.5E+04	0.271	0	5	500	-0.0367205	40	0.45
2	2.316E+04	0.2677812	4.256E-04	5	500	-0.0388463	40	0.45388959
3	2.247E+04	0.26653	5.924E-04	5	500	-0.0397125	40	0.45518953
4	2.179E+04	0.2652652	7.617E-04	5	500	-0.0406118	40	0.45651741
5	2.048E+04	0.2626932	0.0011086	5	500	-0.0425171	40	0.45926145
6	1.983E+04	0.261385	0.0012863	5	500	-0.0435271	40	0.46067999
7	1.92E+04	0.2600613	0.001467	5	500	-0.0445783	40	0.46213126
8	1.857E+04	0.2587217	0.0016507	5	500	-0.0456731	40	0.46361663
9	1.735E+04	0.2559922	0.0020279	5	500	-0.048004	40	0.46669556
10	1.676E+04	0.2546012	0.0022216	5	500	-0.0492457	40	0.4682923
11	1.617E+04	0.2531918	0.0024189	5	500	-0.0505427	40	0.46992952
12	1.56E+04	0.2517634	0.0026199	5	500	-0.0518982	40	0.47160906
13	1.448E+04	0.2488465	0.0030336	5	500	-0.0548006	40	0.4751031

temperature variable is calculated by adding a column to the solution Data Table.as defined below.

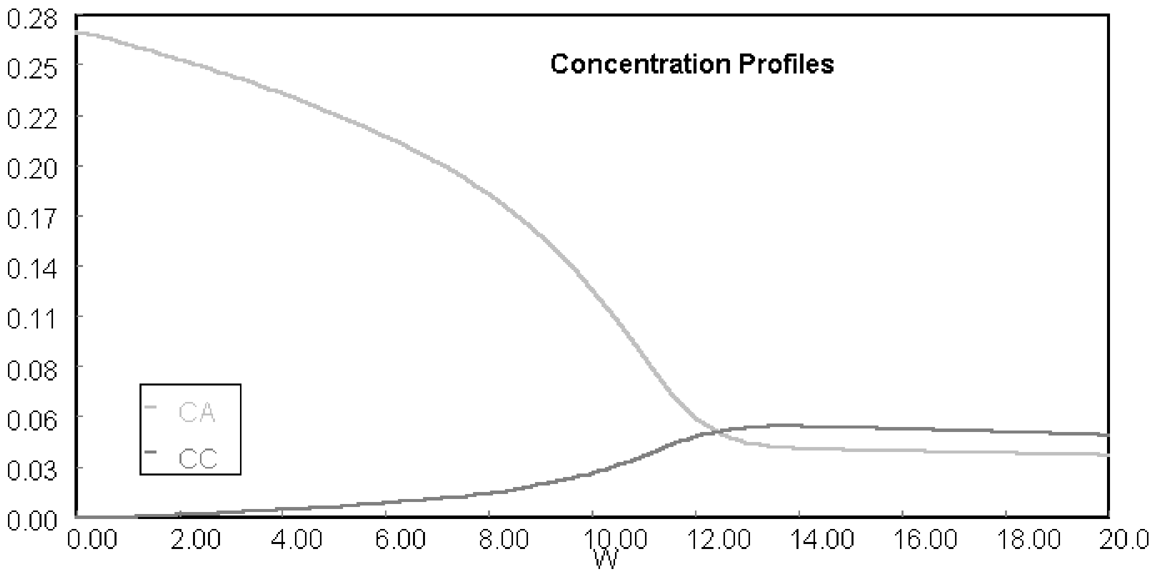


The resulting plot indicates that there is a rapid increase in conversion and temperature within the reactor at approximately the midpoint of the catalyst bed. The bed pressure drop is enhanced by the increased temperature and reduced pressure even though the number of moles is decreasing.



(b) The dramatic increase in conversion and temperature is due to the exothermic reaction rapidly accelerating due to the increasing temperature even though the reactant concentration falling. Equilibrium is rapidly achieved after this hot spot is achieved with the temperature and conversion only reducing slightly due to the external heat transfer which tends to slightly cool the reactor as the reacting mixture continues toward the reactor exit.

(c) The concentration profiles reflect the net effects of reaction rate and changes in temperature and pressure within the reactor.



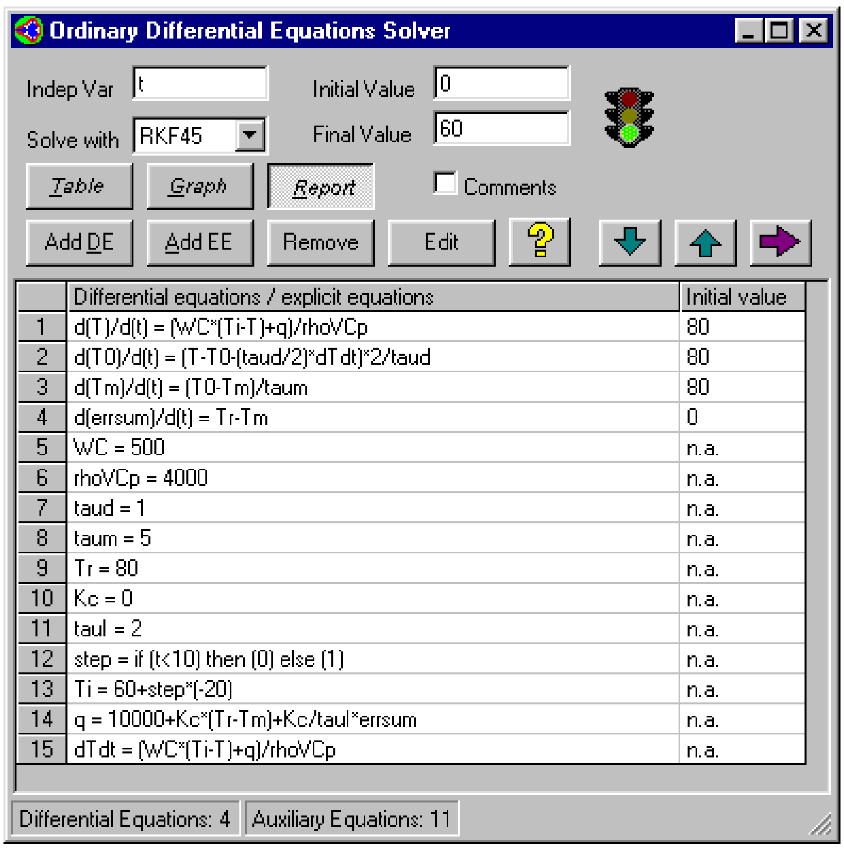
The POLYMATH problem solution files for this problem are D09.pol and D09a.pol.

Problem 10D Solution - Dynamics of a Heated Tank with PI Temperature Control

This problem requires the solution of Equations (D-46) and (D-48) through (D-53) which can be accomplished with the POLYMATH *Simultaneous Differential Equation Solver*. The step change in the inlet temperature can be introduced at $t = 10$ by using the POLYMATH "if... then... else..." statement to provide the logic for a variable to change at a particular value of t. The generation of a step change at $t = 10$, for example, is accomplished by the following POLYMATH program statement

```
step=if (t<10) then (0) else (1)
```

(a) Open Loop Performance The step down of 20°C in the inlet temperature at $t = 10$ is implemented below in the equation set for the case where $K_c = 0$ which gives the open loop response.



A plot of the temperatures T, T_0 and T_m as generated by POLYMATH is given in Figure PD-(4) which also verifies the steady state operation for $t < 10$ min as there is no change in any of the temperature values.

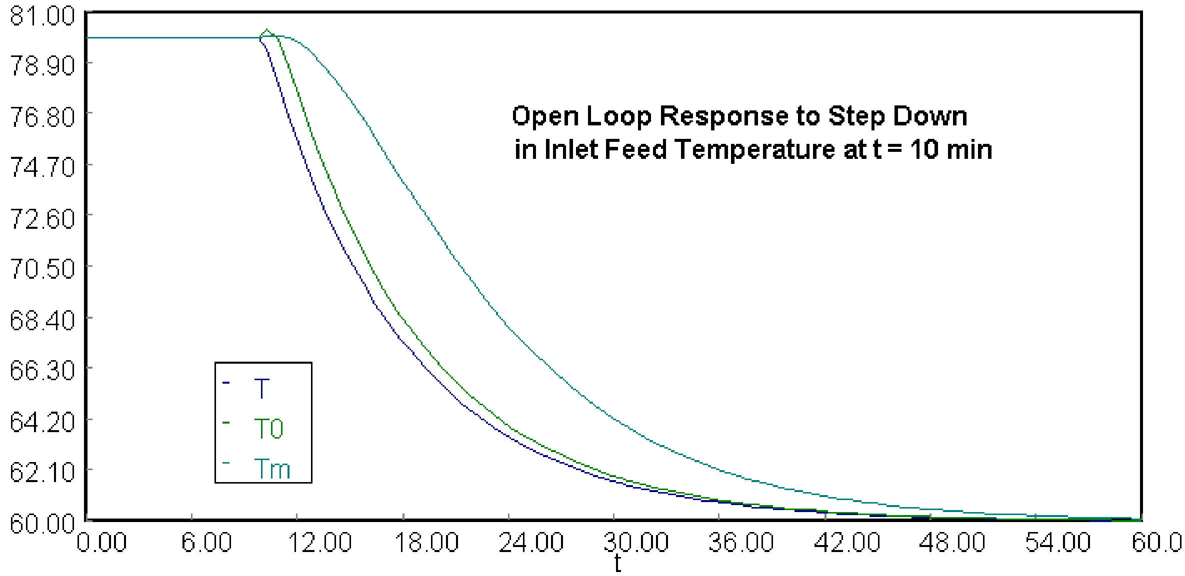


Figure PD-4 Open Loop Response to Step Down in Inlet Feed Temperature at t = 10 min.

(b) Closed Loop Performance The closed loop performance of the PI controller requires the change of K_c from zero in part (a) to the baseline proportional gain of 50. This simple change results in the temperature transients shown in Figure PD-(5).

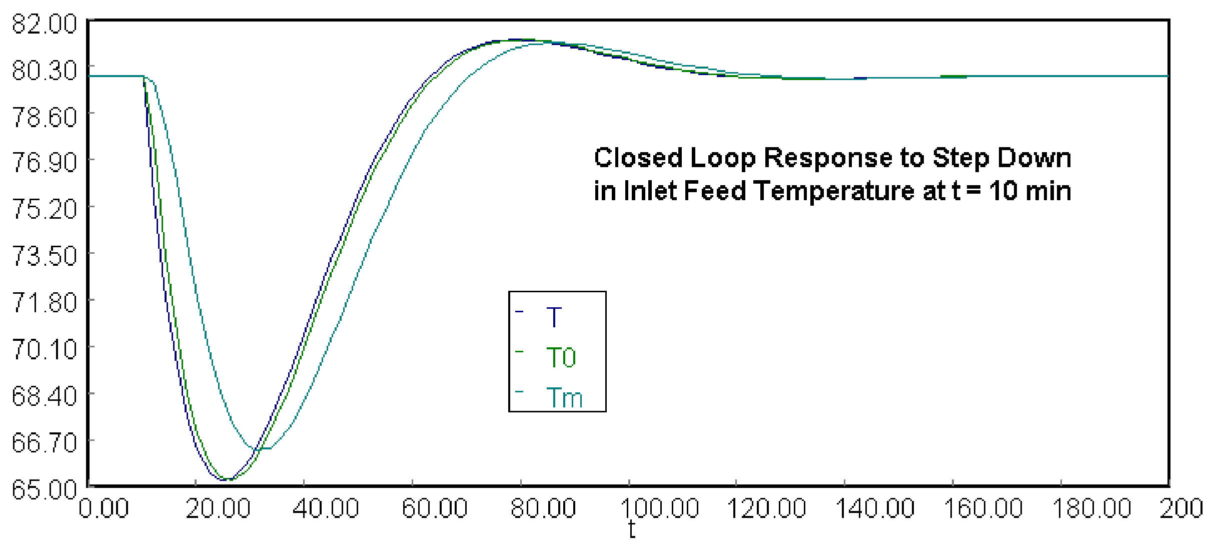


Figure PD-5 Closed Loop Response to Step Down in Inlet Feed Temperature at t = 10 min

(c) Closed Loop Performance for K_c = 500 The increase of a factor of 10 in the proportional gain from the baseline case gives the unstable result plotted in Figure PD-(6). This is clearly an undesirable result.

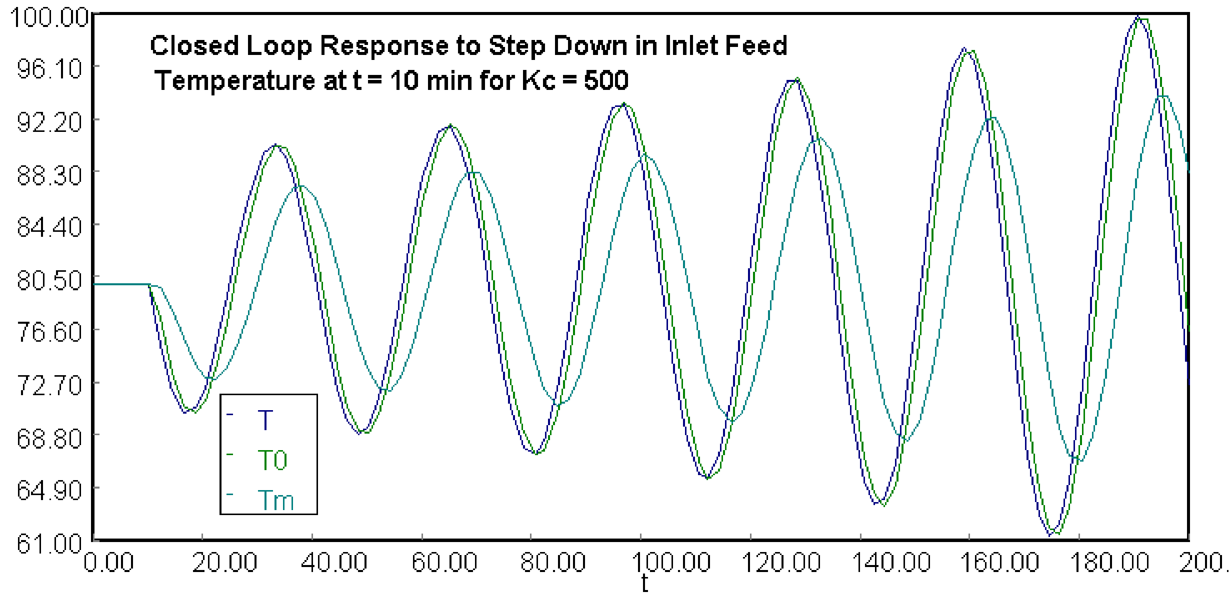


Figure PD-6 Closed Loop Response to Step Down in Inlet Feed Temperature at t = 10 min for K_c = 500.

(d) Closed Loop Performance for Only Proportional Control The removal of the integral control action gives the stable result plotted in Figure PD-(7). Note that there is offset from the set point when the system returns to steady state operation. This is always the case for only proportional control, and the use of integral control allows the offset to be eliminated.

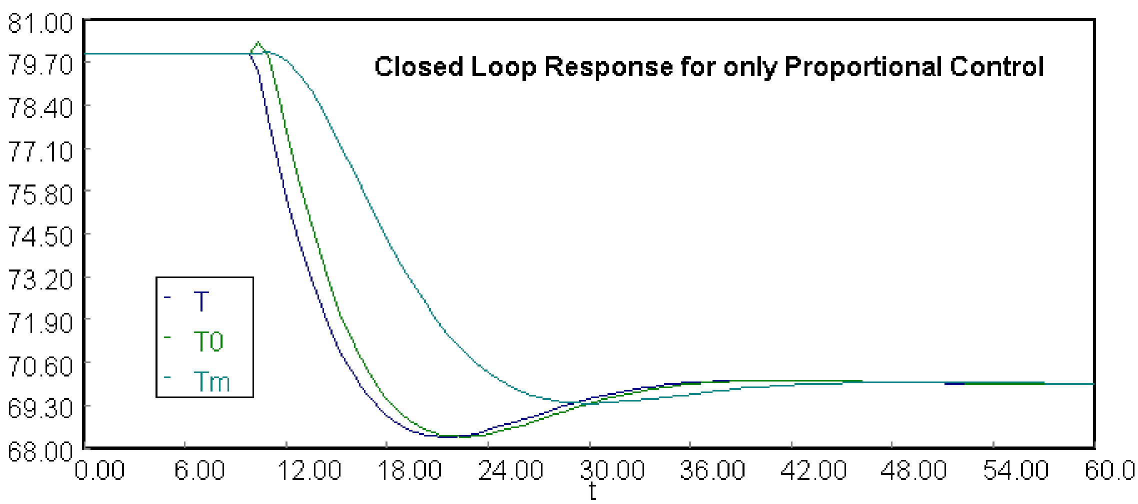


Figure PD-7 Closed Loop Response for only Proportional Control.

(e) Closed Loop Performance with Limits on q There are many times in control when limits must be established. In this example, the limits on q can be achieved by a POLYMATH "if... then... else..." statement which is indicated on the complete POLYMATH Report given below.

Problem 10(e) - Closed Loop Response for only Proportional Control with Limits on q

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	200	200
T	80	80	98.38435	89.088128
T0	80	79.42612	98.382229	89.090896
Tm	80	79.944186	92.31428	89.093176
errsum	0	0	211.07106	211.07106
WC	500	500	500	500
Ti	60	60	60	60
rhoVCp	4000	4000	4000	4000
taud	1	1	1	1
taum	5	5	5	5
Kc	5000	5000	5000	5000
tauI	2	2	2	2
step	0	0	1	1
Tr	80	80	90	90
q	10000	-1587.6249	6.028E+04	1.453E+04
qlim	10000	0	2.6E+04	1.453E+04
dTdt	0	-3.9572635	4	-0.0024859

ODE Report (RKF45)

Differential equations as entered by the user

```
[1]  d(T)/d(t) = (WC*(Ti-T)+qlim)/rhoVCp
[2]  d(T0)/d(t) = (T-T0-(taud/2)*dTdt)*2/taud
[3]  d(Tm)/d(t) = (T0-Tm)/taum
[4]  d(errsum)/d(t) = Tr-Tm
```

Explicit equations as entered by the user

```
[1]  WC = 500
[2]  Ti = 60
[3]  rhoVCp = 4000
[4]  taud = 1
[5]  taum = 5
[6]  Kc = 5000
[7]  tauI = 2
[8]  step = if (t<10) then (0) else (1)
[9]  Tr = 80+step*(10)
[10]  q = 10000+Kc*(Tr-Tm)
[11]  qlim = if(q<0)then(0)else(if(q>=2.6*10000)then(2.6*10000)else (q))
[12]  dTdt = (WC*(Ti-T)+qlim)/rhoVCp
```

Independent variable

variable name : t
initial value : 0
final value : 200

The values of q and q_{lim} plotted in Figure PD-(8) indicate that this proportional controller has wide oscillations before settling to a steady state, and the limits imposed on q_{lim} are evident. The corresponding plots of the system temperatures are presented in Figure PD-(9).

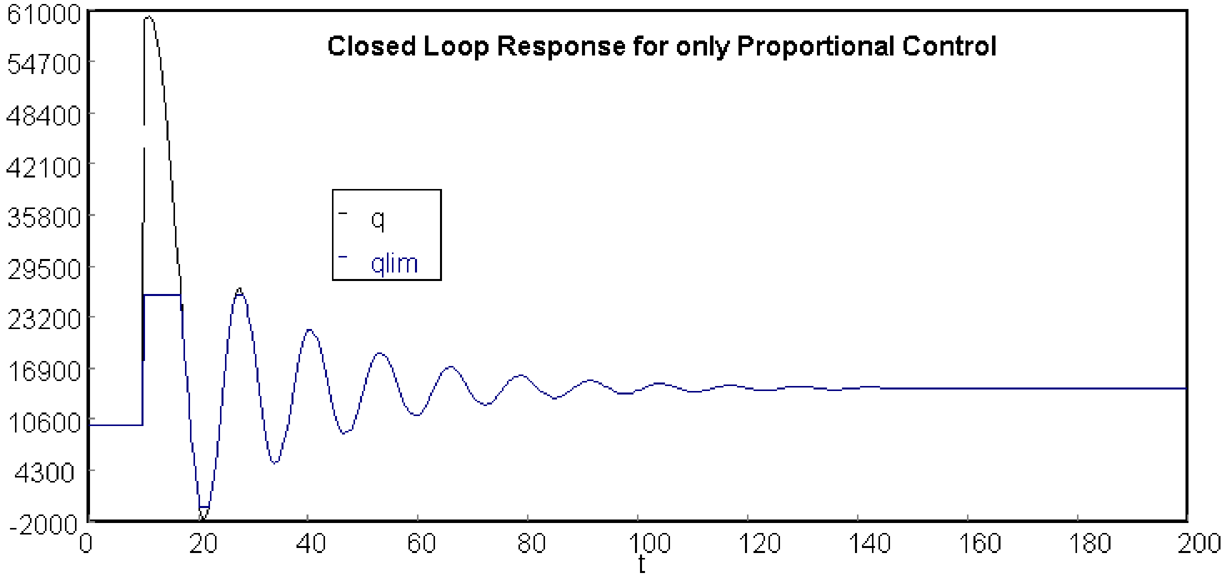


Figure PD-8 Closed Loop Response for only Proportional Control with Limits on q.

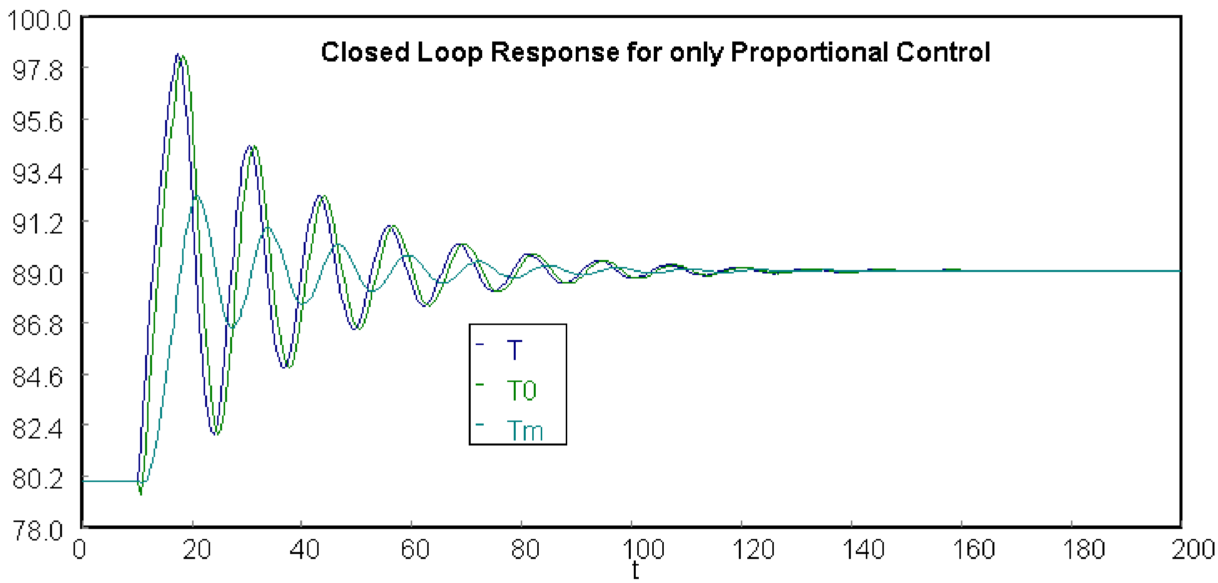


Figure PD-9 Closed Loop Response for only Proportional Control with Limits on q.

The POLYMATH problem solution files for this problem are D10a.pol, D10b.pol, D10c.pol, D10d.pol, and D10e.pol.

Problem 11D Solution - Binary Batch Distillation

This problem requires the simultaneous solution of Equation (D54) while the temperature is calculated from the bubble point considerations implicit in Equation (D56). A system of equations comprising of differential and implicit algebraic equations is called "differential algebraic" or a DAE system. There are several numerical methods for solving DAE systems. Most problem solving software packages including POLYMATH do not have the specific capability for DAE systems.

Approach 1 The first approach will be to use the *controlled integration technique* proposed by Shacham, et al. Using this method, the nonlinear Equation (D56) is rewritten with an error term given by

$$\varepsilon = 1 - k_1 x_1 - k_2 x_2 \qquad \textbf{PD-(10)}$$

where the ε calculated from this equation provides the basis for keeping the temperature of the distillation at the bubble point. This is accomplished by changing the temperature in proportion to the error in an analogous manner to a proportion controller action. Thus this can be represented by another differential equation

$$\frac{dT}{dx_2} = K_c \varepsilon \qquad \textbf{PD-(11)}$$

where a proper choice of the proportionality constant K_c will keep the error below a desired error tolerance.

The calculation of K_c is a simple trial and error procedure for most problems. At the beginning K_c is set to a small value (say $K_c = 1$), and the system is integrated. If ε is too large, then K_c must be increased and the integration repeated. This trial and error procedure is continued until ε becomes smaller than a desired error tolerance throughout the entire integration interval.

The temperature at the initial point is not specified in the problem, but it is necessary to start the problem solution at the bubble point of the initial mixture. This separate calculation can be carried out on Equation (D56) for $x_1 = 0.6$ and $x_2 = 0.4$ and the Antoine Equation (D55) using the POLYMATH *Simultaneous Algebraic Equation Solver*. The POLYMATH Report is as follows.

Problem 11a1 - Initial Bubble Point... for Binary Batch Distillation

NLE Solution

Variable	Value	f(x)	Ini Guess
Tbp	95.585087	2.654E-08	90
xA	0.6		
PA	1196.2189		
PB	485.67158		
xB	0.4		
yA	0.7869861		
yB	0.2130139		

NLE Report (safenewt)

Nonlinear equations

[1] f(Tbp) = xA*PA+xB*PB-760*1.2 = 0

Explicit equations

[1] xA = 0.6
[2] PA = 10^(6.90565-1211.033/(Tbp+220.79))
[3] PB = 10^(6.95464-1344.8/(219.482+Tbp))
[4] xB = 1-xA

[5] yA = xA*PA/(760*1.2)
[6] yB = xB*PB/(760*1.2)

where the resulting initial temperature is found to be $T_0 = 95.5851$.

The system of equations for the batch distillation can then be solved with the POLYMATH *Simultaneous Differential Equation Solver* for $K_c = 0.5 \times 10^6$ to yield the following POLYMATH Report.

Problem 11 - DAE Equations for Binary Batch Distillation

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
x2	0.4	0.4	0.8	0.8
T	95.5851	95.5851	108.56926	108.56926
L	100	14.045555	100	14.045555
k2	0.5325348	0.5325348	0.7857526	0.7857526
Kc	5.0E+05	5.0E+05	5.0E+05	5.0E+05
x1	0.6	0.2	0.6	0.2
k1	1.311644	1.311644	1.8566024	1.8566024
err	-3.646E-07	-3.646E-07	7.798E-05	7.747E-05

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(T)/d(x2) = Kc*err
[2] d(L)/d(x2) = L/(k2*x2-x2)

Explicit equations as entered by the user
[1] k2 = 10^(6.95464-1344.8/(T+219.482))/(760*1.2)
[2] Kc = 0.5e6
[3] x1 = 1-x2
[4] k1 = 10^(6.90565-1211.033/(T+220.79))/(760*1.2)
[5] err = (1-k1*x1-k2*x2)

Independent variable
variable name : x2
initial value : 0.4
final value : 0.8

The final values from the Report indicate that 14.05 mol of liquid remain in the column when the concentration of the toluene reaches 80%. During the distillation the temperature increases from $95.6°C$ to $108.6°C$. The error calculated from Equation PD-(10) increases from about -3.6×10^{-7} to 7.75×10^{-5} during the numerical solution, but it is still small enough for the solution to be considered as accurate.

Approach 2 A different approach for solving this problem can be used because Equation (D56) can be differentiated with respect to x_2 to yield

$$\frac{dT}{dx_2} = \frac{(k_2 - k_1)}{\ln(10)\left[x_1 k_1 \frac{-B_1}{(C_1 + T)^2} + x_2 k_2 \frac{-B_2}{(C_2 + T)^2}\right]} \qquad \text{PD-(12)}$$

Thus Equation PD-(12) can provide the bubble point temperature during the simultaneous integration with Equation (D54). The Report from the POLYMATH *Simultaneous Differential Equation Solver* is given below.

Problem 11- Approach 2 - Differential Equations for Binary Batch Distillation

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
x2	0.4	0.4	0.8	0.8
L	100	14.041632	100	14.041632
T	95.5851	95.5851	108.57208	108.57208
k2	0.5325348	0.5325348	0.7856879	0.7856879
k1	1.311644	1.311644	1.856466	1.856466
x1	0.6	0.2001465	0.6	0.2001465

ODE Report (RKF45)

Differential equations as entered by the user

```
[1] d(L)/d(x2) = L/(k2*x2-x2)
[2] d(T)/d(x2) = (k2-k1)/(ln(10)*(x1*k1*(-1211.033)/(220.79+T)^2+x2*k2*(-
    1344.8)/(219.482+T)^2))
```

Explicit equations as entered by the user

```
[1] k2 = 10^(6.95464-1344.8/(T+219.482))/(760*1.2)
[2] k1 = 10^(6.90565-1211.033/(T+220.79))/(760*1.2)
[3] x1 = 1-x2
```

Independent variable

```
variable name : x2
initial value : 0.4
final value : 0.8
```

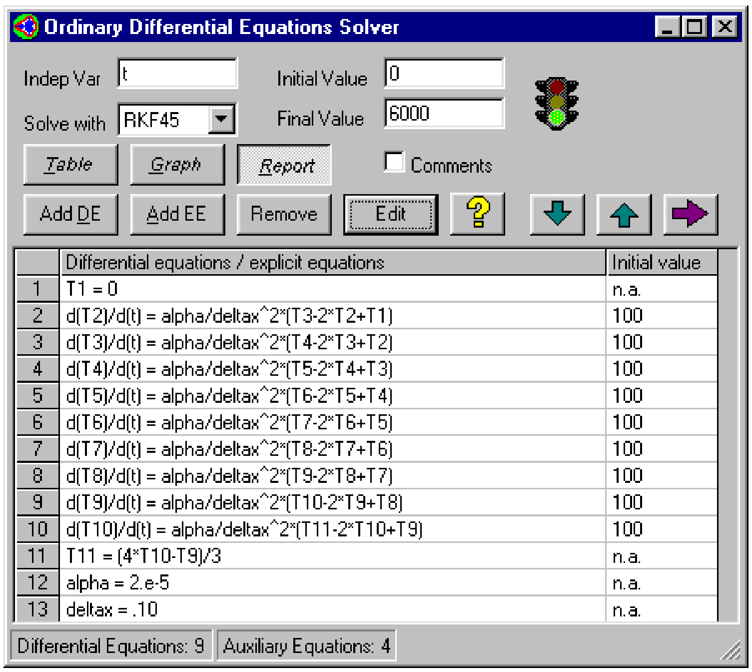
The above POLYMATH solution, **Approach 2**, gives essentially the same results as those determined in **Approach 1**.

The POLYMATH problem solution files for this problem are D11a1.pol, D11a2.pol, and D11a3.pol.

Problem 12D Solution - Unsteady-state Heat Conduction in a Slab

The appropriate equations for this solution are presented in the problem statement.

(a) The problem then requires the solution of Equations (D-62), (D-63), and (D-65) which results in nine simultaneous ordinary differential equations and two explicit algebraic equation for the 11 temperature nodes. This set of equations can be entered into the POLYMATH *Simultaneous Differential Equation Solver*. The equation set as entered into POLYMATH is given below.



The plots of the temperatures in the first four sections, node points 2 … 5, are shown in Figure PD-(10). The transients in temperatures show an approach to steady state. The numerical results are compared to the hand calculations of a finite difference solution by Geankoplis[1](pp. 471–3) at the time of 6000 s in Table PD-(4). These results

Table PD-4 Results for Unsteady-State Heat Transfer in One-Dimensional Slab at t = 6000 s

Distance from Slab Surface in m	Geankoplis[1] Δx = 0.20 m *n*	*T* in °C	Method of Lines (a) Δx = 0.10 m *n*	*T* in °C	Method of Lines (b) Δx = 0.05 m *n*	*T* in °C
0	1	0.0	1	0.0	1	0.0
0.2	2	31.25	3	31.71	5	31.68
0.4	3	58.59	5	58.49	9	58.47
0.6	4	78.13	7	77.46	13	77.49
0.8	5	89.84	9	88.22	17	88.29
1.0	6	93.75	11	91.66	21	91.72

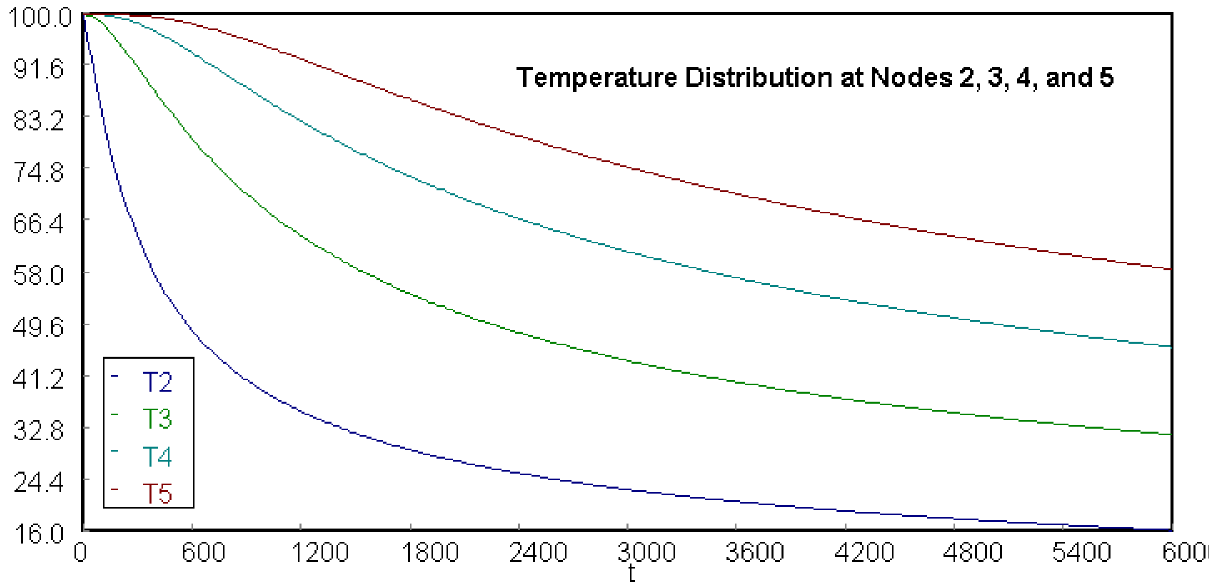


Figure PD-10 Temperature Profiles for Unsteady-State Heat Conduction in a One-Dimensional Slab

indicate that there is general agreement regarding the problem solution, but differences between the temperatures at the nodes increase as the nodes approach the insulated boundary of the slab.

(b) The accuracy of the numerical solution can be investigated by doubling the number of sections for the numerical method of lines solution. This just involves adding an additional 10 equations given by the relationship in Equation (D62) and modifying Equation (D65) to calculate T_{21}. The results for this change in the POLYMATH equation set are also summarized in Table PD-(4). Here the numerical solution is only slightly changed from the previous solution in part (a), which gives reassurance to the first choice of 10 sections for this problem. The temperature profiles are virtually unchanged.

(c) The calculation of T_1 at node 1 is required by the convection boundary condition for this case, and Equation (D68) can be entered into the equation set used in part (a) along with an equation for the ambient temperature T_0. This equation set should indicate a somewhat slower response of the temperatures within the slab because of the additional resistance to heat transfer.

A comparison with the approximate hand calculations by Geankoplis[1] is summarized in Table PD-(5). In this case, the simplified hand calculations give results that have some error relative to the numerical method of lines solutions, which are in good agreement with each other.

Table PD-5 Unsteady-State Heat Transfer with Convection in One-Dimensional Slab at t = 1500 s

Distance from Slab Surface in m	**Geankoplis[1]** Δx = 0.20 m		**Method of Lines (a)** Δx = 0.10 m		**Method of Lines (b)** Δx = 0.05 m	
	n	***T* in °C**	***n***	***T* in °C**	***n***	***T* in °C**
0	1	64.07	1	64.40	1	64.99
0.2	2	89.07	3	88.13	5	88.77
0.4	3	98.44	5	97.38	9	97.73
0.6	4	100.00	7	99.61	13	99.72
0.8	5	100.00	9	99.96	17	99.98
1.0	6	100.00	11	100.00	21	100.00

The POLYMATH problem solution files for this problem are D12a.pol, D12b.pol, D12c1.pol, and D12c2.pol.

REFERENCES

1. Geankoplis, C. J. *Transport Processes and Unit Operations*, 3rd ed. Englewood Cliffs, NJ: Prentice Hall, 1993.