

MATHCAD SOLUTIONS TO THE CHEMICAL ENGINEERING PROBLEM SET

Mathematical Software Session

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INTRODUCTION

This document contains Mathcad solutions for a set of chemical engineering problems developed for the Use of Mathematical Software Packages in Chemical Engineering Education Session at the ASEE Chemical Engineering Summer School held in Snowbird, Utah on August 13, 1997. The problems chosen are representative of numerical problems that are typically found in most chemical engineering undergraduate courses.

Mathcad is a commercial software package developed by MathSoft, Inc. It is widely used by engineers, scientists and mathematicians in universities as well as industry. Mathcad allows for the integration of equations, text and graphics in a WYSIWYG interface. It has built into it a wide variety of numerical routines to solve problems including simultaneous nonlinear equations, systems of ordinary differential equations, numerical integration and differentiation, regression and curve fitting as well as many other powerful features. Complete details of Mathcad's features, system requirements and academic pricing can be found on the MathSoft Web site (www.mathsoft.com). The solutions presented here are available at the Chemical Engineering Mathcad Users' Group Web site (<ftp://ftp.umecheme.maine.edu/mathcad/asee>).

Mathcad Solution to Problem 1

Mathcad uses a structure called a solve block to solve non-linear equations. The solve block starts with a *Given* statement and ends with a *Find* which includes the variables to be solved for. Mathcad requires an initial guess of the solution before the start of the solve block. Note that Mathcad allows for dimensional variables with automatic units conversion and the final solution can be expressed in any desired units.

The equation to be solved is the van der Waals equation:

$$\left(P + \frac{a}{V^2}\right) \cdot (V - b) = R \cdot T$$

Define the constants to be used in the calculations (units included).

$$R := 0.08206 \cdot \frac{\text{atm} \cdot \text{liter}}{\text{mole} \cdot \text{K}}$$

For ammonia:

$$T_c := 405.5 \cdot \text{K}$$

$$P_c := 111.3 \cdot \text{atm}$$

$$a := \frac{27}{64} \cdot \left(\frac{R^2 \cdot T_c^2}{P_c} \right)$$

$$a = 4.197 \cdot \frac{\text{atm} \cdot \text{liter}^2}{\text{mole}^2}$$

$$b := \frac{R \cdot T_c}{8 \cdot P_c}$$

$$b = 0.037 \cdot \frac{\text{liter}}{\text{mole}}$$

a) Specify T and P:

$$P := 56 \cdot \text{atm}$$

$$T := 450 \cdot \text{K}$$

Solve for the molar volume using a solve block

Initial guess of V using Ideal Gas Law:

$$V := \frac{R \cdot T}{P}$$

$$V = 0.659 \cdot \frac{\text{liter}}{\text{mole}}$$

Given

Start of Solve Block

$$\left(P + \frac{a}{V^2}\right) \cdot (V - b) = R \cdot T$$

Equation to be solved

$$V := \text{Find}(V)$$

$$V = 0.575 \cdot \frac{\text{liter}}{\text{mole}}$$

End of Solve Block

$$Z := \frac{P \cdot V}{R \cdot T}$$

$$Z = 0.872$$

In the Find statement above, Mathcad solves for the value of the unknown variable but does not change the value of the variable (V). Therefore, the value of the solution of the equation is assigned to the variable (V) so that it can be used in subsequent calculations (e.g., calculation of the compressibility factor (Z)).

b) Reformulate solution in terms of P_r . One powerful feature of Mathcad is the ability to define a function using a solve block. The argument of the function is one of the variables in the equation being solved and the value of the function is the solution of the equation. In this case the molar volume is defined as a function of the reduced pressure. The structure of the solve block is essentially the same as in part a).

Initial guess for volume: $V := 0.6 \cdot \frac{\text{liter}}{\text{mole}}$

Given

$$\left(P_r \cdot P_c + \frac{a}{V^2} \right) \cdot (V - b) = R \cdot T$$

$$V(P_r) := \text{Find}(V) \qquad Z(P_r) := \frac{P_r \cdot P_c \cdot V(P_r)}{R \cdot T}$$

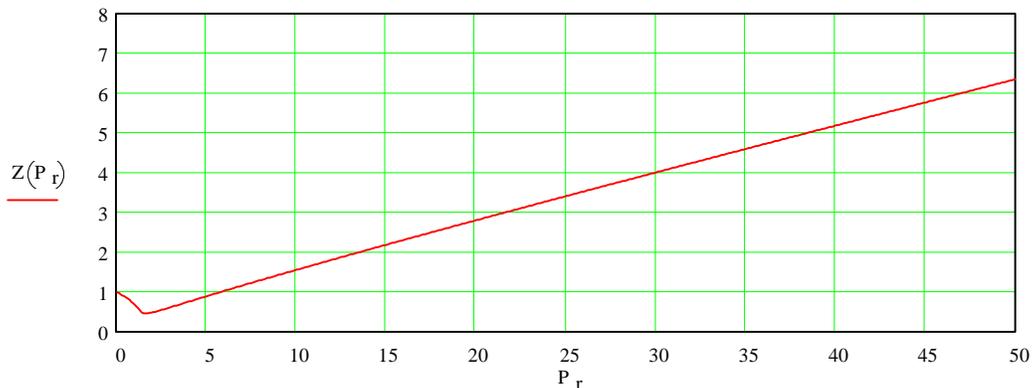
$i := 1..5$ The variable i here is called a *range variable* and takes on a range of values, in this case 1, 2, ..., 5. This is similar to an index variable in a counted loop. P_r is an array of values specified in the problem statement.

$$P_{r_i} := \frac{V(P_{r_i})}{\text{liter} \cdot \text{mole}^{-1}} \cdot Z(P_{r_i})$$

| | | |
|----|-------|-------|
| 1 | | 0.704 |
| 2 | 0.234 | 0.466 |
| 4 | 0.077 | 0.731 |
| 10 | 0.061 | 1.533 |
| 20 | 0.051 | 2.783 |
| | 0.046 | |

c) The reduced pressure can be defined as a range variable and the molar volume can then be plotted as a function of reduced pressure.

$P_r := 0.1, 0.2.. 50$



Mathcad Solution to Problem 2

There are two approaches to solving this problem in Mathcad. The first is to simply include all of the equations in a Solve Block and solve for the unknown variables. This simplifies the formulation of the numerical problem because the problem does not need to be rewritten in matrix form. In the second method, the problem is broken up into a problem requiring the solution of 4 simultaneous linear equations followed by a series of simple algebraic equations.

First method solving all of the equations in a solve block

Defined feed rate and mole fractions.

$$\begin{array}{lllll} F := 70 & x_{FX} := 0.15 & x_{FS} := 0.25 & x_{FT} := 0.4 & x_{FB} := 0.2 \\ & x_{D1X} := 0.07 & x_{D1S} := 0.04 & x_{D1T} := 0.54 & x_{D1B} := 0.35 \\ & x_{B1X} := 0.18 & x_{B1S} := 0.24 & x_{B1T} := 0.42 & x_{B1B} := 0.16 \\ & x_{D2X} := 0.15 & x_{D2S} := 0.10 & x_{D2T} := 0.54 & x_{D2B} := 0.21 \\ & x_{B2X} := 0.24 & x_{B2S} := 0.65 & x_{B2T} := 0.10 & x_{B2B} := 0.01 \end{array}$$

Guess values of flow rates
and mole fractions:

$$\begin{array}{llll} D := \frac{F}{2} & D_1 := \frac{D}{2} & B_1 := \frac{D}{2} & \\ B := \frac{F}{2} & D_2 := \frac{B}{2} & B_2 := \frac{B}{2} & \\ x_{DX} := 0.25 & x_{DS} := 0.25 & x_{DT} := 0.25 & x_{DB} := 0.25 \\ x_{BX} := 0.25 & x_{BS} := 0.25 & x_{BT} := 0.25 & x_{BB} := 0.25 \end{array}$$

Given

Component balances over entire system

$$x_{FX} \cdot F = x_{D1X} \cdot D_1 + x_{B1X} \cdot B_1 + x_{D2X} \cdot D_2 + x_{B2X} \cdot B_2$$

$$x_{FS} \cdot F = x_{D1S} \cdot D_1 + x_{B1S} \cdot B_1 + x_{D2S} \cdot D_2 + x_{B2S} \cdot B_2$$

$$x_{FT} \cdot F = x_{D1T} \cdot D_1 + x_{B1T} \cdot B_1 + x_{D2T} \cdot D_2 + x_{B2T} \cdot B_2$$

$$x_{FB} \cdot F = x_{D1B} \cdot D_1 + x_{B1B} \cdot B_1 + x_{D2B} \cdot D_2 + x_{B2B} \cdot B_2$$

Overall Balances on columns #2 and #3

$$D = D_1 + B_1 \quad B = D_2 + B_2$$

Component balances over column #2

$$x_{DX} \cdot D = x_{D1X} \cdot D_1 + x_{B1X} \cdot B_1$$

$$x_{DS} \cdot D = x_{D1S} \cdot D_1 + x_{B1S} \cdot B_1$$

$$x_{DT} \cdot D = x_{D1T} \cdot D_1 + x_{B1T} \cdot B_1$$

$$x_{DB} \cdot D = x_{D1B} \cdot D_1 + x_{B1B} \cdot B_1$$

Component balances over column #3

$$x_{BX} \cdot B = x_{D2X} \cdot D_2 + x_{B2X} \cdot B_2$$

$$x_{BS} \cdot B = x_{D2S} \cdot D_2 + x_{B2S} \cdot B_2$$

$$x_{BT} \cdot B = x_{D2T} \cdot D_2 + x_{B2T} \cdot B_2$$

$$x_{BB} \cdot B = x_{D2B} \cdot D_2 + x_{B2B} \cdot B_2$$

$$\begin{bmatrix} D \\ B \\ D_1 \\ B_1 \\ D_2 \\ B_2 \\ x_{DX} \\ x_{DS} \\ x_{DXT} \\ x_{DXB} \\ x_{BX} \\ x_{BS} \\ x_{BT} \\ x_{BB} \end{bmatrix} := \text{Find}(D, B, D_1, B_1, D_2, B_2, x_{DX}, x_{DS}, x_{DT}, x_{DB}, x_{BX}, x_{BS}, x_{BT}, x_{BB})$$

Answer

$$\begin{array}{r}
 D = 43.75 \quad x_{DX} = 0.114 \quad x_{DS} = 0.12 \quad x_{DT} = 0.25 \quad x_{DB} = 0.25 \quad D_1 = 26.25 \\
 B_1 = 17.5 \\
 \\
 B = 26.25 \quad x_{BX} = 0.21 \quad x_{BS} = 0.467 \quad x_{BT} = 0.247 \quad x_{BB} = 0.077 \quad D_2 = 8.75 \\
 B_2 = 17.5
 \end{array}$$

The second method starts with the solution the component balances over the entire process. This yields a system of four linear equations in four unknowns. The problem is formulated in matrix form and is solved by matrix inversion.

$$A := \begin{bmatrix} x_{D1X} & x_{B1X} & x_{D2X} & x_{B2X} \\ x_{D1S} & x_{B1S} & x_{D2S} & x_{B2S} \\ x_{D1T} & x_{B1T} & x_{D2T} & x_{B2T} \\ x_{D1B} & x_{B1B} & x_{D2B} & x_{B2B} \end{bmatrix} \quad b := \begin{bmatrix} x_{FX} \cdot F \\ x_{FS} \cdot F \\ x_{FT} \cdot F \\ x_{FB} \cdot F \end{bmatrix} \quad \begin{bmatrix} D_1 \\ B_1 \\ D_2 \\ B_2 \end{bmatrix} := A^{-1} \cdot b$$

The remaining total and component balances yield a series of simple algebraic equations.

$$\begin{array}{ll}
 D := D_1 + B_1 & B := D_2 + B_2 \\
 x_{DX} := \frac{x_{D1X} \cdot D_1 + x_{B1X} \cdot B_1}{D} & x_{BX} := \frac{x_{D2X} \cdot D_2 + x_{B2X} \cdot B_2}{B} \\
 x_{DS} := \frac{x_{D1S} \cdot D_1 + x_{B1S} \cdot B_1}{D} & x_{BS} := \frac{x_{D2S} \cdot D_2 + x_{B2S} \cdot B_2}{B} \\
 x_{DT} := \frac{x_{D1T} \cdot D_1 + x_{B1T} \cdot B_1}{D} & x_{BT} := \frac{x_{D2T} \cdot D_2 + x_{B2T} \cdot B_2}{B} \\
 x_{DB} := \frac{x_{D1B} \cdot D_1 + x_{B1B} \cdot B_1}{D} & x_{BB} := \frac{x_{D2B} \cdot D_2 + x_{B2B} \cdot B_2}{B}
 \end{array}$$

Answer

$$\begin{array}{r}
 D = 43.75 \quad x_{DX} = 0.114 \quad x_{DS} = 0.12 \quad x_{DT} = 0.492 \quad x_{DB} = 0.274 \quad D_1 = 26.25 \\
 B_1 = 17.5 \\
 \\
 B = 26.25 \quad x_{BX} = 0.21 \quad x_{BS} = 0.467 \quad x_{BT} = 0.247 \quad x_{BB} = 0.077 \quad D_2 = 8.75 \\
 B_2 = 17.5
 \end{array}$$

Mathcad Solution to Problem 3

There are a variety of ways to solve this problem in Mathcad. To fit a polynomial, the Mathcad function, *linfit*, can be used to fit any linear combination of arbitrary functions in the form $y = a_0 + a_1 \cdot f_1(x) + a_2 \cdot f_2(x) + \dots + a_n \cdot f_n(x)$. Mathcad gives as the result the vector *a*, the coefficients of the linear combination.

Both the Clausius-Clapeyron and Antoine equations can be rewritten in a form so that linear regression can be used. Otherwise, a non-linear least-squares technique could be applied.

a) To fit an *n*th order polynomial, an vector containing the *n*+1 functions is used in the *linfit* function. The function also requires the vectors containing the data. To calculate the variance of the error, the Mathcad function *var* is used. This example shows the calculation for the polynomial that gave the smallest variance. The variance for other polynomials is shown in a table below.

Define vectors T and P containing the data:

Define the vector of functions, F(x), to be fit:

$$F(x) := \begin{bmatrix} 1 \\ x \\ x^2 \\ x^3 \\ x^4 \\ x^5 \end{bmatrix}$$

$$T := \begin{bmatrix} -36.7 \\ -19.6 \\ -11.5 \\ -2.6 \\ 7.6 \\ 15.4 \\ 26.1 \\ 42.2 \\ 60.6 \\ 80.1 \end{bmatrix} \quad P := \begin{bmatrix} 1 \\ 5 \\ 10 \\ 20 \\ 40 \\ 60 \\ 100 \\ 200 \\ 400 \\ 760 \end{bmatrix}$$

Use the *last* function to count the number of data points, *ndata*, and the number of terms in the function array. Note that Mathcad starts vectors and matrices with index 0 as the default. The *last* function actually gives the index of the last term in the vector.

$$ndata := last(T)$$

$$i := 0.. ndata$$

$$n := last(F(1))$$

$$c := linfit(T, P, F)$$

$$c = \begin{bmatrix} 24.754264 \\ 1.609017 \\ 0.035605 \\ 4.129782 \cdot 10^{-4} \\ 4.226066 \cdot 10^{-6} \\ -2.505099 \cdot 10^{-9} \end{bmatrix}$$

Results:

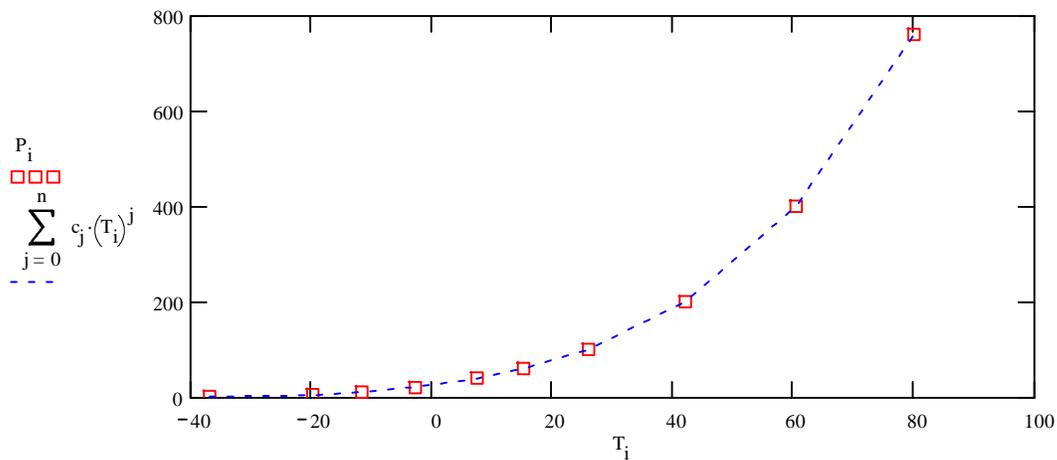
| Order | Variance |
|----------|---------------|
| 1 | 11,859 |
| 2 | 852 |
| 3 | 20 |
| 4 | 0.199 |
| 5 | 0.1944 |
| 6 | 0.1210 |

Calculate the errors and then the variance

$$error_i := P_i - \sum_{j=0}^n c_j \cdot (T_i)^j$$

$$var(error) = 0.194361$$

Plot the results for the polynomial fit



For the Clausius-Clapeyron and Antoine equations the equations can be rearranged into a form so that linear regression can be used. By multiplying by the denominator of the second term on the right hand side and rearranging algebraically, the following equations are obtained:

Clausius-Clapeyron: $\log(P) = A - B/(T+273.15)$

Antoine: $T \cdot \log(P) = A \cdot T - C \cdot \log(P) + [A \cdot C - B]$

For the Clausius-Clapeyron equation linear regression can be used by setting $y = \log(P)$ and $x = 1/(T+273.15)$. The slope = $-B$ and the intercept = A . Mathcad has slope and intercept functions for linear regression.

For the Antoine equation, least squares is used using a psuedo-inverse calculation.

b) Fitting the Clausius-Clapeyron equation.

$$x_i := \frac{1}{(T_i + 273.15)} \quad y_i := \log(P_i)$$

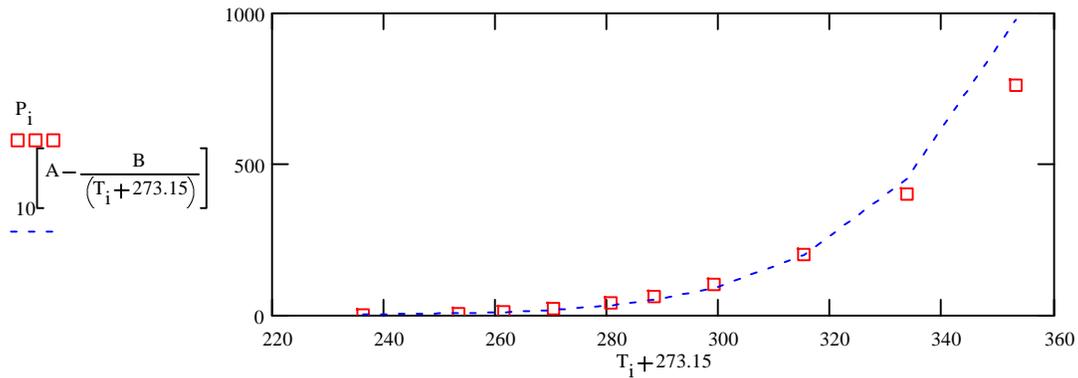
$$A := \text{intercept}(x, y) \quad A = 8.75201$$

$$B := -\text{slope}(x, y) \quad B = 2.035 \cdot 10^3$$

Calculate the errors and then the variance

$$\text{error}_i := \log(P_i) - \left(A - \frac{B}{T_i + 273.15} \right) \quad \text{var}(\text{error}) = 6.073244 \cdot 10^{-3}$$

Plot the results for the Clausius-Clapeyron equation



c) Fitting the Antoine equation

Define the matrix M with first column T_i , second column $-\log(P_i)$ and third column filled with 1's.

$$M_{i,0} := T_i \quad M_{i,1} := -\log(P_i) \quad M_{i,2} := 1$$

Define the vector b with columns $T_i \cdot \log(P_i)$. $b_i := T_i \cdot \log(P_i)$

Solve for the coefficients using a pseudo-inverse calculation. K is defined as the combination $A \cdot C - B$. A and C are found directly and B from the definition of K.

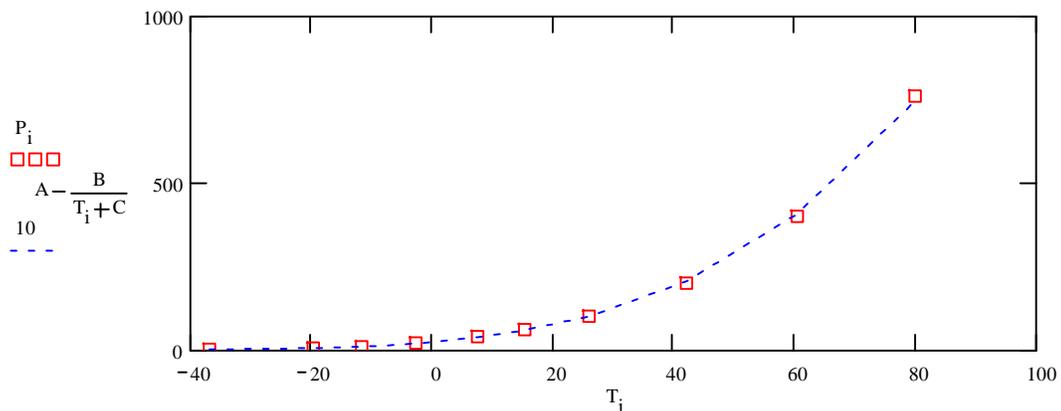
$$\begin{bmatrix} A \\ C \\ K \end{bmatrix} := (M^T \cdot M)^{-1} \cdot M^T \cdot b$$

B := A · C – K **Results:** A = 5.733 B = 665.423 C = 152.469

Calculate the errors and then the variance

$$\text{error}_i := \log(P_i) - \left(A - \frac{B}{T_i + C} \right) \quad \text{var}(\text{error}) = 2.26 \cdot 10^{-4}$$

Plot the results for the Antoine equation



Mathcad Solution to Problem 4

This problem can be solved directly using a Mathcad Solve Block. The Solve Block includes the equilibrium equations as well as the equations describing the stoichiometry. An initial guess must be made for the concentrations. Initial guesses will be used as given.

Given initial concentrations and equilibrium constants: $C_{A0} := 1.5$ $C_{B0} := 1.5$

$K_{C1} := 1.06$ $K_{C2} := 2.63$ $K_{C3} := 5$

a) First set of initial guesses: $C_D := 0$ $C_X := C_D$ $C_Z := C_D$

$C_A := \frac{C_{A0}}{2}$ $C_B := \frac{C_{B0}}{2}$ $C_C := \frac{C_{A0}}{2}$ $C_Y := 0$

Given

$$K_{C1} \cdot (C_A \cdot C_B) = C_C \cdot C_D \quad K_{C2} \cdot (C_B \cdot C_C) = C_X \cdot C_Y \quad K_{C3} \cdot (C_A \cdot C_X) = C_Z$$

$$C_A = C_{A0} - C_D - C_Z \quad C_B = C_{B0} - C_D - C_Y \quad C_C = C_D - C_Y \quad C_Y = C_X + C_Z$$

$$\text{Find}(C_A, C_B, C_C, C_D, C_X, C_Y, C_Z) = \begin{bmatrix} 0.4207 \\ 0.2429 \\ 0.1536 \\ 0.7053 \\ 0.1778 \\ 0.5518 \\ 0.374 \end{bmatrix}$$

b) Second set of initial guesses: $C_D := 1$ $C_X := C_D$ $C_Z := C_D$

Given

$$K_{C1} \cdot (C_A \cdot C_B) = C_C \cdot C_D \quad K_{C2} \cdot (C_B \cdot C_C) = C_X \cdot C_Y \quad K_{C3} \cdot (C_A \cdot C_X) = C_Z$$

$$C_A = C_{A0} - C_D - C_Z \quad C_B = C_{B0} - C_D - C_Y \quad C_C = C_D - C_Y \quad C_Y = C_X + C_Z$$

$$\text{Find}(C_A, C_B, C_C, C_D, C_X, C_Y, C_Z) = \begin{bmatrix} 0.4207 \\ 0.2429 \\ 0.1536 \\ 0.7053 \\ 0.1778 \\ 0.5518 \\ 0.374 \end{bmatrix}$$

c) Third set of initial guesses: $C_D := 10$ $C_X := C_D$ $C_Z := C_D$

Given

$$K_{C1} \cdot (C_A \cdot C_B) = C_C \cdot C_D \quad K_{C2} \cdot (C_B \cdot C_C) = C_X \cdot C_Y \quad K_{C3} \cdot (C_A \cdot C_X) = C_Z$$

$$C_A = C_{A0} - C_D - C_Z \quad C_B = C_{B0} - C_D - C_Y \quad C_C = C_D - C_Y \quad C_Y = C_X + C_Z$$

$$\text{Find}(C_A, C_B, C_C, C_D, C_X, C_Y, C_Z) = \begin{bmatrix} 0.4207 \\ 0.2429 \\ 0.1536 \\ 0.7053 \\ 0.1778 \\ 0.5518 \\ 0.374 \end{bmatrix}$$

Mathcad gives the same results for all sets of starting values.

Mathcad Solution to Problem 5

A Mathcad Solve Block will be used to solve the force balance for the terminal velocity, v_t . The drag coefficient can be defined using a Mathcad *if* function. The first argument in the *if* function is a conditional. The second argument is an expression that defines the value of the function if the conditional is true. The third argument is an expression that defines the value of the function if the conditional is false. In this case nested *if* functions are used for the three cases.

Define the drag coefficient, C_D , based on the value of the Reynolds number.

$$C_D(\text{Re}) := \text{if} \left[\text{Re} < 0.1, \frac{24}{\text{Re}}, \text{if} \left[\text{Re} < 1000, \frac{24}{\text{Re}} \cdot (1 + 0.14 \cdot \text{Re}^{0.7}), \text{if} \left(\text{Re} < 350000, 0.44, 0.19 - \frac{8 \cdot 10^4}{\text{Re}} \right) \right] \right]$$

a) Define the physical properties and dimensions of the system

Particle diameter and density $D_p := 0.208 \cdot 10^{-3} \cdot \text{m}$ $\rho_p := 1800 \cdot \frac{\text{kg}}{\text{m}^3}$

Fluid viscosity and density $\mu := 8.931 \cdot 10^{-4} \cdot \frac{\text{kg}}{\text{m} \cdot \text{sec}}$ $\rho := 994.6 \cdot \frac{\text{kg}}{\text{m}^3}$

Define the Reynolds number as a function of the terminal velocity:

$$\text{Re}(v_t) := \frac{D_p \cdot \rho \cdot v_t}{\mu}$$

Guess a starting value of the terminal velocity:

$$v_t := 1 \cdot \frac{\text{m}}{\text{sec}}$$

Given

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

$$v_t := \text{Find}(v_t)$$

Answer:

$$v_t = 0.016 \cdot \frac{\text{m}}{\text{sec}}$$

$$\text{Re}(v_t) = 3.656$$

Note that units have been included for all of the variables. The answer can be expressed in any set of units desired. Some examples are given below.

$$v_t = 0.052 \cdot \frac{\text{ft}}{\text{sec}}$$

$$v_t = 0.035 \cdot \frac{\text{mi}}{\text{hr}}$$

$$v_t = 15.782 \cdot \frac{\text{mm}}{\text{sec}}$$

$$v_t = 37.279 \cdot \frac{\text{in}}{\text{min}}$$

b) Mathcad has the gravitational acceleration predefined. For this case, g is redefined as 30g.

$$g := 30 \cdot g \quad \text{Guess:} \quad v_t := 1 \cdot \frac{\text{m}}{\text{sec}}$$

Given

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

$$v_t := \text{Find}(v_t)$$

Answer: $v_t = 0.206 \frac{\text{m}}{\text{sec}}$ $\text{Re}(v_t) = 47.723$

Mathcad Solution to Problem 6

Mathcad has built-in a variety of differential equation solvers. In this case, an adaptive Runge-Kutta method will be used since the solution varies slowly with time and all of the functions vary on the same time scale (i.e., they are not stiff).

System physical constants and properties $\text{kg} := 1$ $\text{min} := 1$ $\text{kJ} := 1$ $C := 1$

Mass of oil in each tank: $M := 1000 \cdot \text{kg}$

Oil mass flow rate: $W := 100 \cdot \frac{\text{kg}}{\text{min}}$ Oil heat capacity: $C_p := 2 \cdot \frac{\text{kJ}}{\text{kg} \cdot \text{C}}$

Temperature of entering oil: $T_0 := 20 \cdot \text{C}$

Steam temperature: $T_{\text{steam}} := 250 \cdot \text{C}$ Heat transfer coefficient: $UA := 10 \cdot \frac{\text{kJ}}{\text{min} \cdot \text{C}}$

Calculate the steady state temperature by setting derivatives to zero and solving remaining equations using a Mathcad Solve Block.

Initial guess for temperatures: $T_{1ss} := 20$ $T_{2ss} := 20$ $T_{3ss} := 30$

Given

$$\frac{W \cdot C_p \cdot (T_0 - T_{1ss}) + UA \cdot (T_{\text{steam}} - T_{1ss})}{M \cdot C_p} = 0$$

$$\frac{W \cdot C_p \cdot (T_{1ss} - T_{2ss}) + UA \cdot (T_{\text{steam}} - T_{2ss})}{M \cdot C_p} = 0$$

$$\frac{W \cdot C_p \cdot (T_{2ss} - T_{3ss}) + UA \cdot (T_{\text{steam}} - T_{3ss})}{M \cdot C_p} = 0$$

$$\begin{bmatrix} T_{1ss} \\ T_{2ss} \\ T_{3ss} \end{bmatrix} := \text{Find}(T_{1ss}, T_{2ss}, T_{3ss})$$

Steady state temperatures: $T_{1ss} = 30.952 \text{ }^\circ\text{C}$ $T_{2ss} = 41.383 \text{ }^\circ\text{C}$ $T_{3ss} = 51.317 \text{ }^\circ\text{C}$

For the solution of multiple ODEs Mathcad requires that the functions of the right hand side be defined in a vector of functions. The initial conditions are assigned to the vector variable to be solved for.

Initial conditions: $T := \begin{bmatrix} 20 \\ 20 \\ 20 \end{bmatrix}$

Function vector: $D(t, T) := \begin{bmatrix} \frac{W \cdot C_p \cdot (T_0 - T_1) + UA \cdot (T_{\text{steam}} - T_1)}{M \cdot C_p} \\ \frac{W \cdot C_p \cdot (T_1 - T_2) + UA \cdot (T_{\text{steam}} - T_2)}{M \cdot C_p} \\ \frac{W \cdot C_p \cdot (T_2 - T_3) + UA \cdot (T_{\text{steam}} - T_3)}{M \cdot C_p} \end{bmatrix}$

Set initial time, final time and size of time step in minutes. Calculate number of points calculated.

$t_0 := 0$ $t_{\text{final}} := 100$ $\Delta t := 1$ $n_{\text{points}} := \frac{t_{\text{final}} - t_0}{\Delta t} + 1$

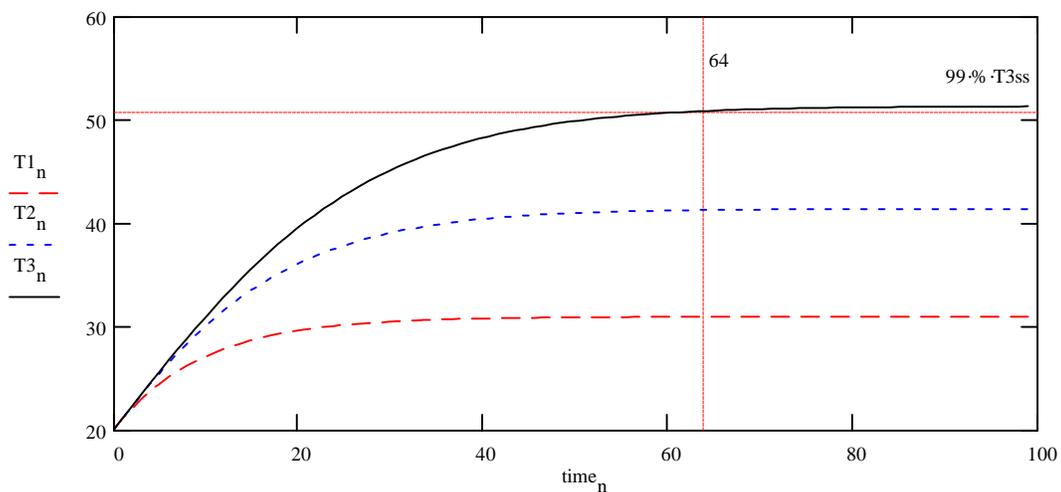
Solve the differential equations using the function *Rkadapt*.

$Z := \text{Rkadapt}(T, 0, t_{\text{final}}, n_{\text{points}}, D)$

The solution is stored in an array. The first column represents the time at each step. The remaining columns represent the solution vectors.

Assign columns of the solution array to vectors for clarity

$n := 1..n_{\text{points}}$ $\text{time}_n := Z_{n,1}$ $T1_n := Z_{n,2}$ $T2_n := Z_{n,3}$ $T3_n := Z_{n,4}$



99% of steady state value: $99\% \cdot T3_{\text{ss}} = 50.804$ Calculate value at 64 minutes: $T3_{\frac{64}{\Delta t}} = 50.777$

From the graph, T3 reaches 99% of steady state at approximately 64 minutes

Mathcad Solution to Problem 7

The solution to this problem will use Mathcad's ability to solve two point boundary value problems. The solution method has two parts. In the first part, Mathcad estimates the missing boundary conditions at the first point. These estimated values are then used in the standard ODE solvers to find the solution between the two boundary points. Check the Mathcad help files for more details on using this method.

Assign values to the physical properties and dimensions for the problem

Diffusivity $D_{AB} := 1.2 \cdot 10^{-9}$ Reaction rate constant $k := 10^{-3}$

Initial concentration: $C_{A0} := 0.2$ Slab depth: $L := 10^{-3}$

Set position of first and second point and step size: $z_1 := 0$ $z_2 := L$ $\Delta z := \frac{L}{100}$

Mathcad uses the *load* and *score* functions in estimating the missing initial conditions

Initial guess for vector of unknown initial conditions: $v_0 := 1$

Initial conditions (including guess vector): $\text{load}(z_1, v) := \begin{bmatrix} C_{A0} \\ v_0 \end{bmatrix}$

Vector of functions representing the right hand side of the differential equations:

$$D(z, C) := \begin{bmatrix} C_1 \\ \frac{k}{D_{AB}} \cdot C_0 \end{bmatrix}$$

Score function is a measure of the difference between the computed and given values at the end point.

$\text{score}(z_2, C) := C_1$

Function *sbval* calculates the missing initial conditions:

$C_1 := \text{sbval}(v, 0, L, D, \text{load}, \text{score})$ $C_1 := -131.911$

Now solve the differential equation using the estimated value of the initial conditions.

$C_0 := C_{A0}$

$z_0 := 0$ $z_{\text{end}} := L$ $\text{npoints} := \frac{L}{\Delta z} + 1$

$Y := \text{Rkadapt}(C, z_0, z_{\text{end}}, \text{npoints}, D)$

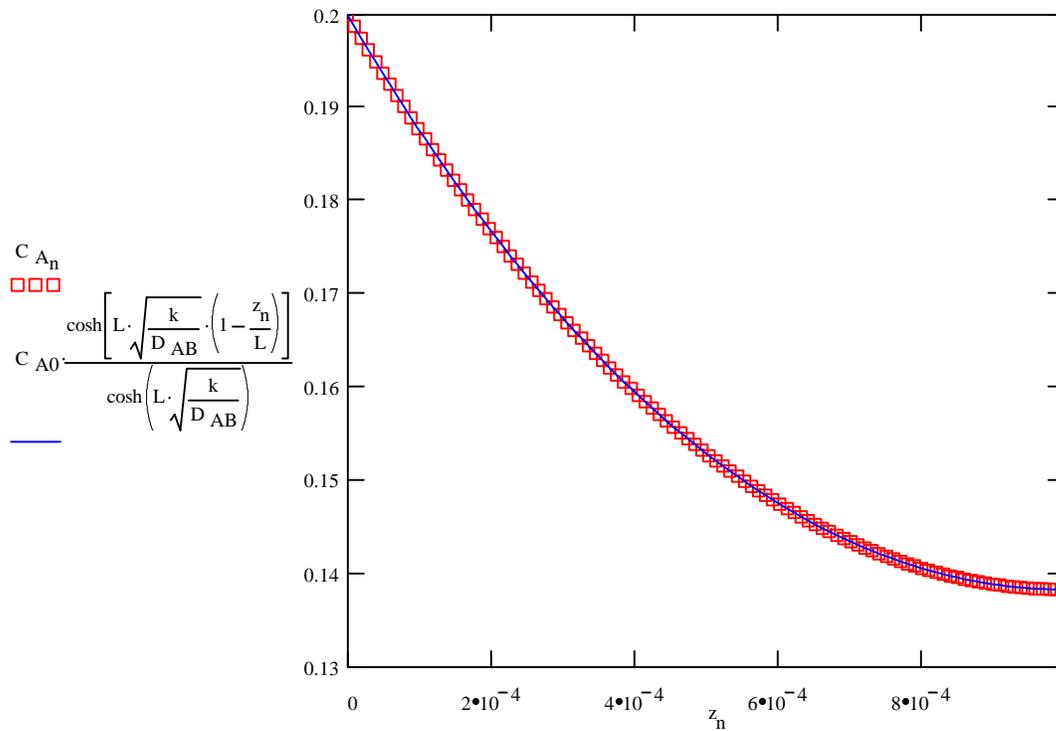
Assign columns of the solution array to vectors for clarity

$$n := 0..npoints \quad z_n := Y_{n,0} \quad C_{A_n} := Y_{n,1} \quad dC_{A_n} := Y_{n,2}$$

Verify boundary value at endpoint ($dC_A/dz = 0$)

$$dC_{A_{npoints}} = 2.787 \cdot 10^{-4} \quad \text{Close enough!}$$

Plot solution and compare with analytical solution



Numerical solution matches analytical solution very closely.

Mathcad Solution to Problem 8

This problem requires the simultaneous solution of a nonlinear equation (bubble point vapor composition) and an ordinary differential equation (unsteady state material balance). The ability to define a function using a Solve Block makes Mathcad a powerful tool in solving this problem.

The differential equation that describes the unsteady state material balance includes the k-value of component 2, k_2 . k_2 depends implicitly on the mole fraction of component 2, x_2 . A solve block will be used to define k_2 as a function of x_2 . The first step in doing this is to write the equilibrium temperature, T_{eq} , as a function of x_2 . The vapor mole fraction can then be defined as a function of x_2 assuming the liquid behaves as an ideal solution and the vapor as an ideal gas. k_2 can then be defined as the ratio y_2/x_2 .

mole := 1 mmHg := $\frac{\text{atm}}{760}$ C := K

Coefficients for Antoine equation

Benzene: $A_1 := 6.90565$ $B_1 := 1211.033 \cdot C$ $C_1 := 220.79 \cdot C$

Toluene: $A_2 := 6.95464$ $B_2 := 1344.8 \cdot C$ $C_2 := 219.482 \cdot C$

Antoine equation for vapor pressure

$$P_1(T) := 10^{A_1 - \frac{B_1}{T + C_1}} \cdot \text{mmHg} \qquad P_2(T) := 10^{A_2 - \frac{B_2}{T + C_2}} \cdot \text{mmHg}$$

Define the equilibrium temperature using a solve block

Set pressure to given value: $P := 1.2 \cdot \text{atm}$

Guess temperature for solve block $T := 90 \cdot C$

Given

$$(1 - x_2) \cdot P_1(T) + x_2 \cdot P_2(T) = P$$

$T_{eq}(x_2) := \text{Find}(T)$

Define vapor mole fraction assuming ideal gas: $y_2(x_2) := \frac{x_2 \cdot P_2(T_{eq}(x_2))}{P}$

Definition of k-value: $k_2(x_2) := \frac{y_2(x_2)}{x_2}$

Now solve the unsteady state material balance equation using the adaptive Runge-Kutta method

Initial condition: $L_0 := 100 \cdot \text{mole}$

Define the function on the right hand side of the differential equation:

$$D(x_2, L) := \frac{L}{x_2 \cdot (k_2(x_2) - 1)}$$

Set initial and final values $x_{2i} := 0.4$ $x_{2f} := 0.8$ $\Delta x_2 := 0.01$ $n_{\text{points}} := \frac{x_{2f} - x_{2i}}{\Delta x_2} + 1$

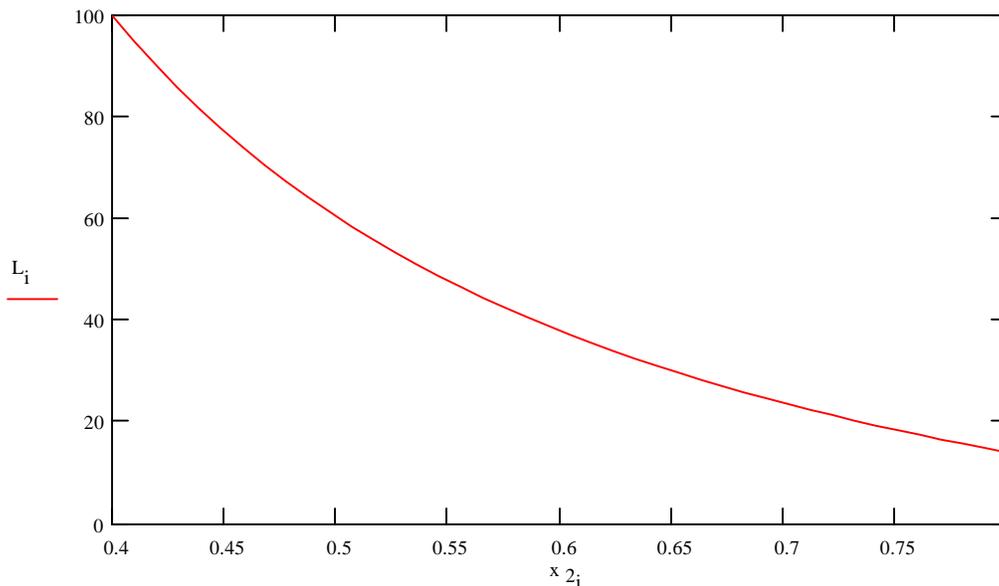
Solve the differential equation: $Z := \text{Rkadapt}(L, x_{2i}, x_{2f}, n_{\text{points}}, D)$

$i := 0.. n_{\text{points}}$ $L_i := Z_{i,1}$ $x_{2i} := Z_{i,0}$

Initial values: $L_0 = 100$ $T_{\text{eq}}(x_{2i}) = 95.585 \text{ }^\circ\text{C}$ $y_2(x_{2i}) = 0.213$ $k_2(x_{2i}) = 0.533$

Final conditions: $L_{n_{\text{points}}} = 14.042$ $T_{\text{eq}}(x_{2f}) = 108.572 \text{ }^\circ\text{C}$ $y_2(x_{2f}) = 0.629$ $k_2(x_{2f}) = 0.786$

Plot of mass of liquid remaining



Mathcad Solution to Problem 9

This problem involves the solution of 3 simultaneous ODEs and uses the adaptive Runge-Kutta Method built into Mathcad.

Define auxiliary units: $J := \text{joule}$ $\text{dm} := \frac{\text{m}}{10}$ $R := 8.314 \cdot \frac{J}{\text{mole} \cdot \text{K}}$

Physical properties and other parameters as given in the problem statement

Heat capacities: $C_{PA} := 40.0 \cdot \frac{J}{\text{mole} \cdot \text{K}}$ $C_{PB} := 80.0 \cdot \frac{J}{\text{mole} \cdot \text{K}}$

Heat of reaction: $\Delta H_R := -40000 \cdot \frac{J}{\text{mole}}$ Activation energy: $E_A := 41800 \cdot \frac{J}{\text{mole} \cdot \text{K}}$

Arrhenius constant at 450 K: $k_{450} := 0.5 \cdot \frac{\text{dm}^6}{\text{kg} \cdot \text{min} \cdot \text{mole}}$

Equilibrium constant at 450 K: $K_{C450} := 25000 \cdot \frac{\text{dm}^3}{\text{mole}}$

Heat transfer coefficient: $UA := 0.8 \cdot \frac{J}{\text{kg} \cdot \text{min} \cdot \text{K}}$ Coolant temperature: $T_a := 500 \cdot \text{K}$

Initial flow rate, concentration and pressure: $F_{A0} := 5.0 \cdot \frac{\text{mole}}{\text{min}}$ $C_{A0} := 0.271 \cdot \frac{\text{mole}}{\text{dm}^3}$ $P_0 := 10 \cdot \text{atm}$

Initial temperature and gas mole fraction of A: $T_0 := 450 \cdot \text{K}$ $y_{A0} := 1.0$

Constant used in calculating pressure drop: $\alpha := 0.015 \cdot \text{kg}^{-1}$

Kinetic rate expression: $k(T) := k_{450} \cdot \exp\left[\frac{E_A}{R} \cdot \left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$

Equilibrium expression: $K_C(T) := K_{C450} \cdot \exp\left[\frac{\Delta H_R}{R} \cdot \left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$

Concentrations expressed as a function of conversion, vapor mole fraction and temperature

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

Reaction rate expressed as a function of conversion, vapor mole fraction and temperature

$$r_A(X,y,T) := -k(T) \cdot \left(C_A(X,y,T)^2 - \frac{C_C(X,y,T)}{K_C(T)} \right)$$

Mathcad requires the unknown variables to be expressed as a vector. We will define the variables as follows: $X = x_0$, $y = x_1$ and $T = x_2$

Express the right hand side of the three differential equations as a vector of functions

$$D(W,x) := \begin{bmatrix} \frac{-r_A(x_0,x_1,x_2,T_0)}{F_{A0}} \\ -\alpha \frac{1 - 0.5 \cdot x_0 \cdot x_2 \cdot T_0}{2 \cdot x_1 \cdot T_0} \\ \frac{UA \cdot (T_a - x_2 \cdot T_0) + r_A(x_0,x_1,x_2,T_0) \cdot \Delta H_R}{F_{A0} \cdot C_{PA} \cdot T_0} \end{bmatrix}$$

Initial conditions: $x := \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}$

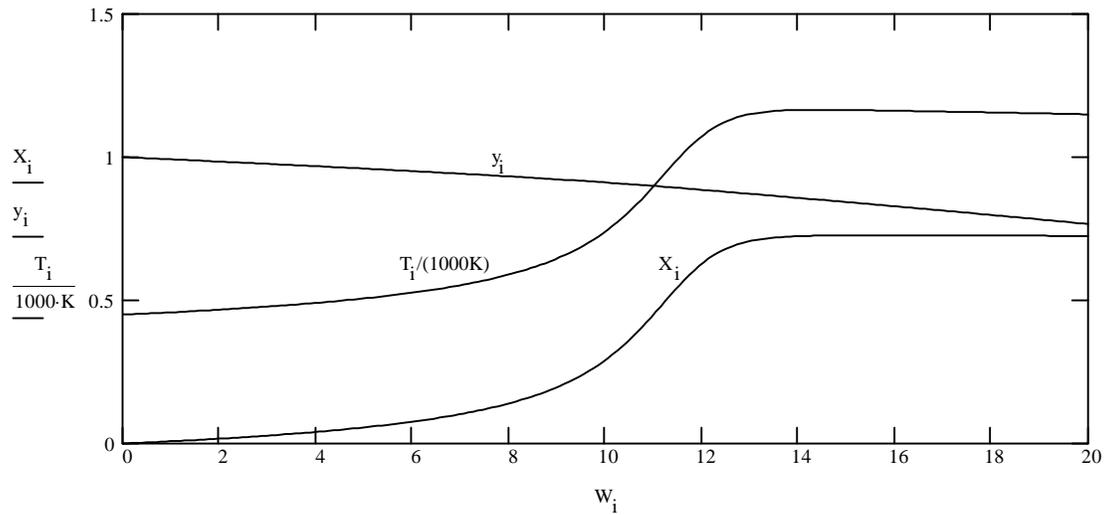
Initial and final weight of catalyst: $W_0 := 0$ $W_f := 20$ $\Delta W := 0.1$ $npoints := \frac{W_f - W_0}{\Delta W} + 1$

Solve the differential equations: $Z := \text{Rkadapt}(x, W_0, W_f, npoints, D)$

Assign columns of the solution array to vectors for clarity

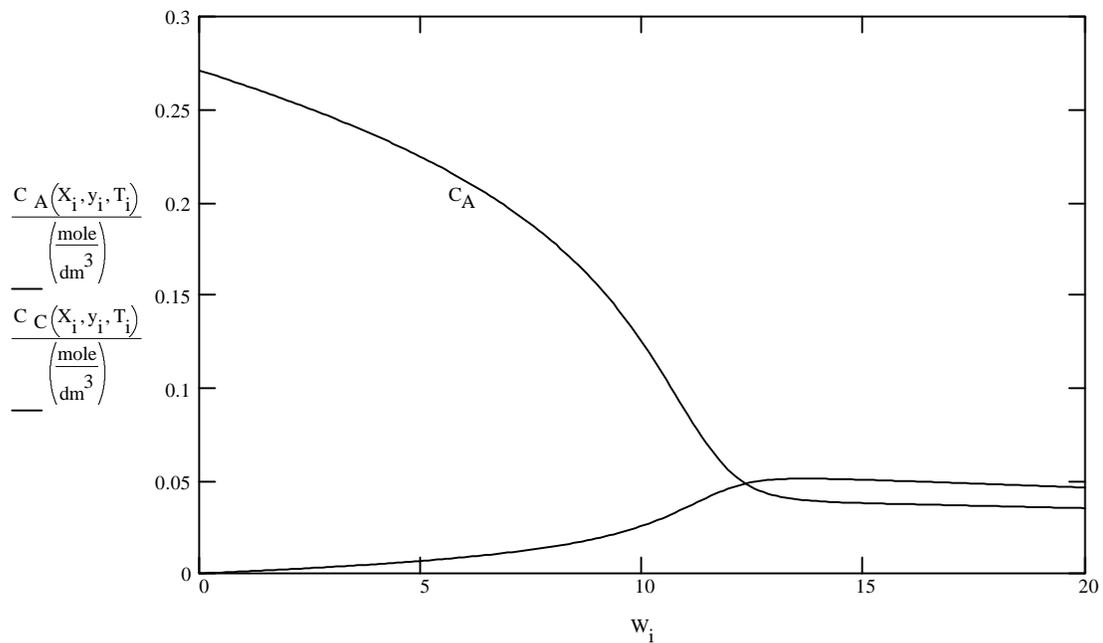
$i := 0..npoints$ $W_i := Z_{i,0}$ $X_i := Z_{i,1}$ $y_i := Z_{i,2}$ $T_i := Z_{i,3} \cdot T_0$

a) Plot the results



b) The "knee" in the curve represents the acceleration in reaction rate due to the rapid increase in temperature for the exothermic reaction.

c) Evaluate the concentration profiles using the calculated values of conversion, vapor mole fraction and temperature



Mathcad Solution to Problem 10

The solutions to this problem make use of the differential equation solver built into Mathcad

Define physical properties of the system as given in the problem statement.

$$\rho V C_p := 4000$$

$$W C_p := 500$$

$$\text{Inlet temperature: } T_{is} := 60$$

$$\text{Set point temperature: } T_r := 80$$

$$\text{Tank dead time } \tau_d := 1$$

$$\text{Thermocouple time constant: } \tau_m := 5$$

$$\text{Controller gain: } K_C := 2$$

$$\text{Controller integral time: } \tau_I := 2$$

$$\text{Calculate steady state heat input: } q_s := W C_p \cdot (T_r - T_{is})$$

$$\text{Define the heat input calculated by the controller: } q(T_m, e) := q_s + K_C \cdot (T_r - T_m) + \frac{K_C}{\tau_I} \cdot e$$

Mathcad requires the unknown variables to be expressed as a vector. We will define the variables as follows: $T = x_0$, $T_0 = x_1$, $T_m = x_2$, and $\text{errsum} = x_3$

a) Open Loop Performance

The step change in inlet temperature is represented in Mathcad by defining the inlet temperature as a function of time using an *if* function.

$$Ti(t) := \text{if}(t < 10, T_{is}, T_{is} - 20)$$

For open loop performance, set the controller gain to zero. $K_C := 0$

Define the vector of functions representing the right hand side of the ODEs

$$D(t, x) := \begin{bmatrix} \frac{W C_p \cdot (Ti(t) - x_0) + q(x_2, x_3)}{\rho V C_p} \\ x_0 - x_1 - \frac{\tau_d}{2} \cdot \left[\frac{W C_p \cdot (Ti(t) - x_0) + q(x_2, x_3)}{\rho V C_p} \right] \cdot \frac{2}{\tau_d} \\ \frac{x_1 - x_2}{\tau_m} \\ T_r - x_2 \end{bmatrix}$$

Initial conditions:

$$x := \begin{bmatrix} T_r \\ T_r \\ T_r \\ 0 \end{bmatrix}$$

Initial time: $t_0 := 0$

Final time: $t_f := 60$

Time step: $\Delta t := 0.1$

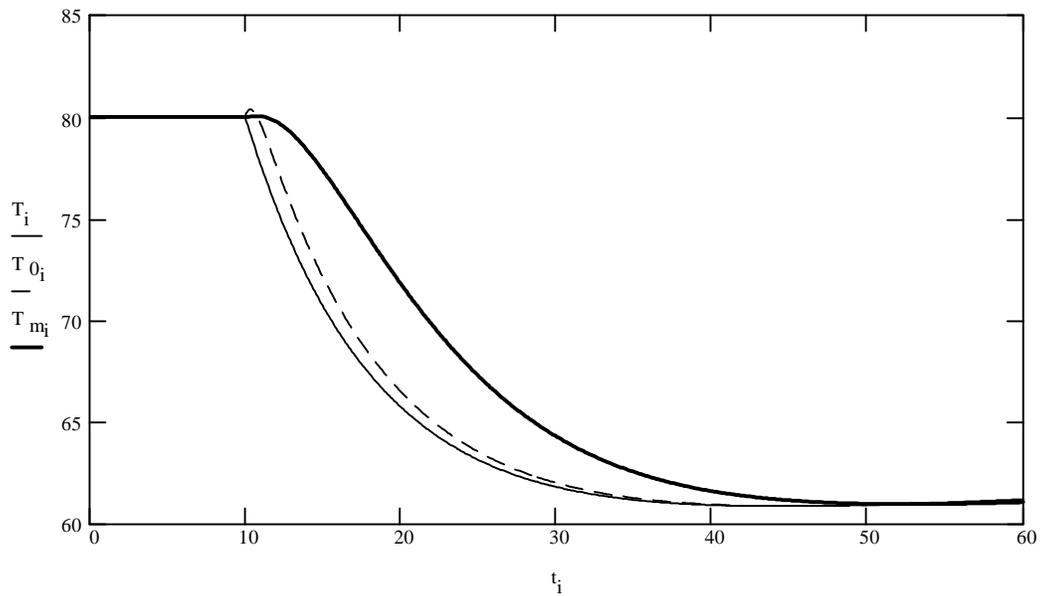
$npoints := \frac{t_f - t_0}{\Delta t} + 1$ $i := 1..npoints$

Solve the system of ODEs using the adaptive Runge-Kutta method

$$Z := \text{Rkadapt}(x, t_0, t_f, npoints, D)$$

Assign columns of the solution array to vectors for clarity

$$t_i := Z_{i,0} \quad T_i := Z_{i,1} \quad T_{0_i} := Z_{i,2} \quad T_{m_i} := Z_{i,3} \quad \text{errsum}_i := Z_{i,4}$$



b) Closed loop performance

Controller gain: Controller integral time:

$$K_C := 50$$

$$\tau_I := 2$$

$$q(T_m, e) := q_s + K_C \cdot (T_r - T_m) + \frac{K_C}{\tau_I} \cdot e$$

Define the vector of functions representing the right hand side of the ODEs

$$D(t, x) := \begin{bmatrix} \frac{WC_p \cdot (Ti(t) - x_0) + q(x_2, x_3)}{\rho VC_p} \\ x_0 - x_1 - \frac{\tau_d}{2} \cdot \left[\frac{WC_p \cdot (Ti(t) - x_0) + q(x_2, x_3)}{\rho VC_p} \right] \cdot \frac{2}{\tau_d} \\ \frac{x_1 - x_2}{\tau_m} \\ T_r - x_2 \end{bmatrix}$$

Initial conditions:

$$x := \begin{bmatrix} T_r \\ T_r \\ T_r \\ 0 \end{bmatrix}$$

Initial time: $t_0 := 0$

Final time: $t_f := 200$

Time step: $\Delta t := 0.1$

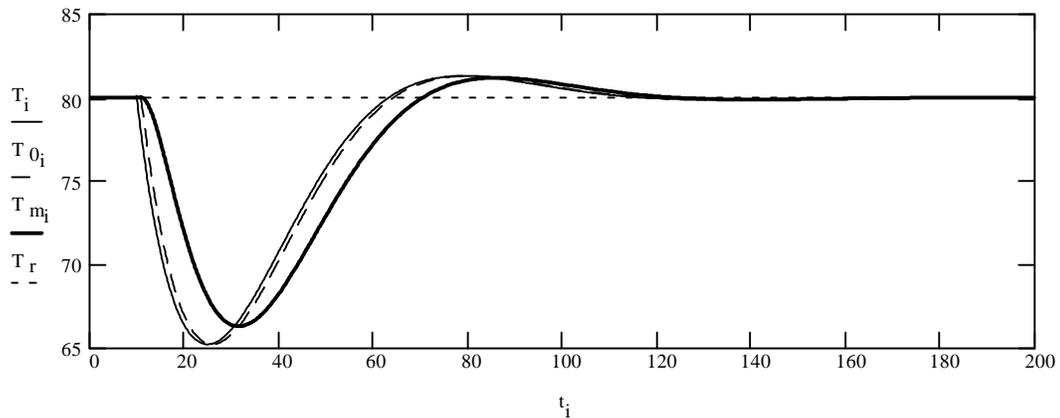
$npoints := \frac{t_f - t_0}{\Delta t} + 1$ $i := 1..npoints$

Solve the system of ODEs using the adaptive Runge-Kutta method

$$Z := Rkadapt(x, t_0, t_f, npoints, D)$$

Assign columns of the solution array to vectors for clarity

$$t_i := Z_{i,0} \quad T_i := Z_{i,1} \quad T_{0_i} := Z_{i,2} \quad T_{m_i} := Z_{i,3} \quad errsum_i := Z_{i,4}$$



c) Closed loop performance - increasing K_C to 500

Controller gain: Controller integral time:

$$K_C := 500$$

$$\tau_I := 2$$

$$q(T_m, e) := q_s + K_C \cdot (T_r - T_m) + \frac{K_C}{\tau_I} \cdot e$$

Define the vector of functions representing the right hand side of the ODEs

$$D(t, x) := \begin{bmatrix} \frac{WC_p \cdot (Ti(t) - x_0) + q(x_2, x_3)}{\rho VC_p} \\ x_0 - x_1 - \frac{\tau_d}{2} \cdot \left[\frac{WC_p \cdot (Ti(t) - x_0) + q(x_2, x_3)}{\rho VC_p} \right] \cdot \frac{2}{\tau_d} \\ \frac{x_1 - x_2}{\tau_m} \\ T_r - x_2 \end{bmatrix}$$

Initial conditions:

$$x := \begin{bmatrix} T_r \\ T_r \\ T_r \\ 0 \end{bmatrix}$$

Initial time: $t_0 := 0$

Final time: $t_f := 200$

Time step: $\Delta t := 0.1$

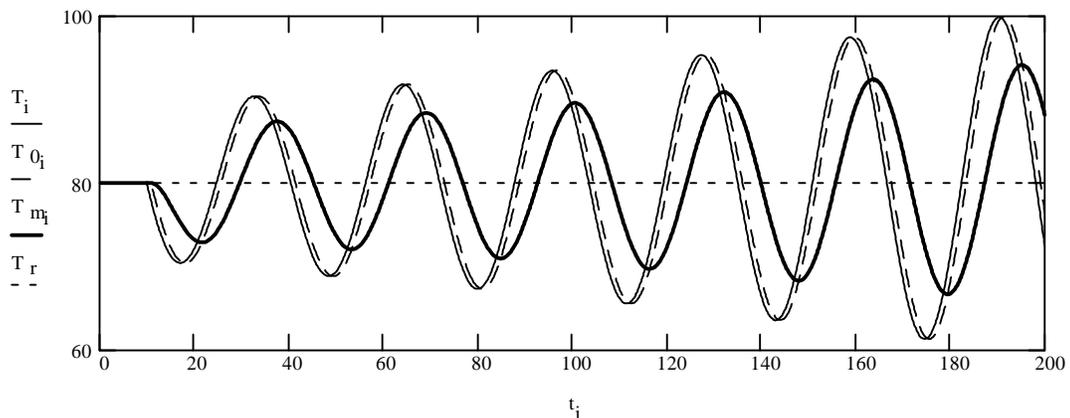
$npoints := \frac{t_f - t_0}{\Delta t} + 1$ $i := 1 \dots npoints$

Solve the system of ODEs using the adaptive Runge-Kutta method

$$Z := Rkadapt(x, t_0, t_f, npoints, D)$$

Assign columns of the solution array to vectors for clarity

$$t_i := Z_{i,0} \quad T_i := Z_{i,1} \quad T_{0_i} := Z_{i,2} \quad T_{m_i} := Z_{i,3} \quad errsum_i := Z_{i,4}$$



d) Closed loop performance - Proportional only controller

Controller gain: Controller integral time:

$$K_C := 500$$

$$\tau_I := 0$$

$$q(T_m, e) := q_s + K_C \cdot (T_r - T_m)$$

Define the vector of functions representing the right hand side of the ODEs

$$D(t, x) := \begin{bmatrix} \frac{WC_p \cdot (T_i(t) - x_0) + q(x_2, x_3)}{\rho VC_p} \\ x_0 - x_1 - \frac{\tau_d}{2} \cdot \left[\frac{WC_p \cdot (T_i(t) - x_0) + q(x_2, x_3)}{\rho VC_p} \right] \cdot \frac{2}{\tau_d} \\ \frac{x_1 - x_2}{\tau_m} \\ T_r - x_2 \end{bmatrix}$$

Initial conditions:

$$x := \begin{bmatrix} T_r \\ T_r \\ T_r \\ 0 \end{bmatrix}$$

Initial time: $t_0 := 0$

Final time: $t_f := 60$

Time step: $\Delta t := 0.1$

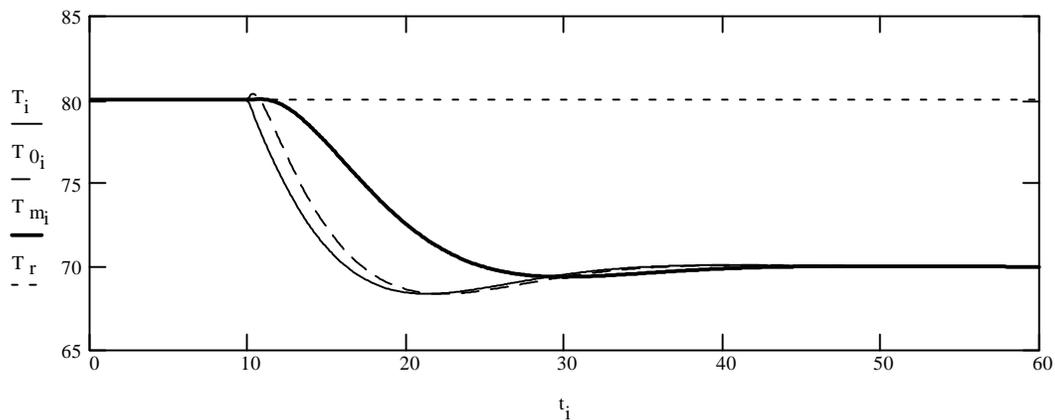
$npoints := \frac{t_f - t_0}{\Delta t} + 1$ $i := 1 \dots npoints$

Solve the system of ODEs using the adaptive Runge-Kutta method

$$Z := Rkadapt(x, t_0, t_f, npoints, D)$$

Assign columns of the solution array to vectors for clarity

$$t_i := Z_{i,0} \quad T_i := Z_{i,1} \quad T_{0_i} := Z_{i,2} \quad T_{m_i} := Z_{i,3} \quad errsum_i := Z_{i,4}$$



e) Closed loop performance - Heater output limited

Inlet temperature: $T_{is} := 60$ Initial set point temperature: $T_{r0} := 80$

Tank dead time $\tau_d := 1$ Thermocouple time constant: $\tau_m := 5$

Calculate steady state heat input: $q_s := WC_p \cdot (T_{r0} - T_{is})$

$K_C := 5000$ $\tau_I := 2000000$

Define the step increase in set point at time 10 using Mathcad // function.

$T_i(t) := T_{is}$ $T_r(t) := \text{if}(t < 10, T_{r0}, T_{r0} + 10)$

Define the limiting behavior of the heater using nested Mathcad // functions.

$q_0(T_m, e, t) := q_s + K_C \cdot (T_r(t) - T_m) + \frac{K_C}{\tau_I} \cdot e$
 $q(T_m, e, t) := \text{if}(q_0(T_m, e, t) < 0, 0, \text{if}(q_0(T_m, e, t) > 2.6 \cdot q_s, 2.6 \cdot q_s, q_0(T_m, e, t)))$

Define the vector of functions representing the right hand side of the ODEs

$$D(t, x) := \begin{bmatrix} \frac{WC_p \cdot (T_{is} - x_0) + q(x_2, x_3, t)}{\rho VC_p} \\ x_0 - x_1 - \frac{\tau_d}{2} \cdot \left[\frac{WC_p \cdot (T_{is} - x_0) + q(x_2, x_3, t)}{\rho VC_p} \right] \cdot \frac{2}{\tau_d} \\ \frac{x_1 - x_2}{\tau_m} \\ T_r(t) - x_2 \end{bmatrix}$$

Initial conditions:

$$x := \begin{bmatrix} T_{r0} \\ T_{r0} \\ T_{r0} \\ 0 \end{bmatrix}$$

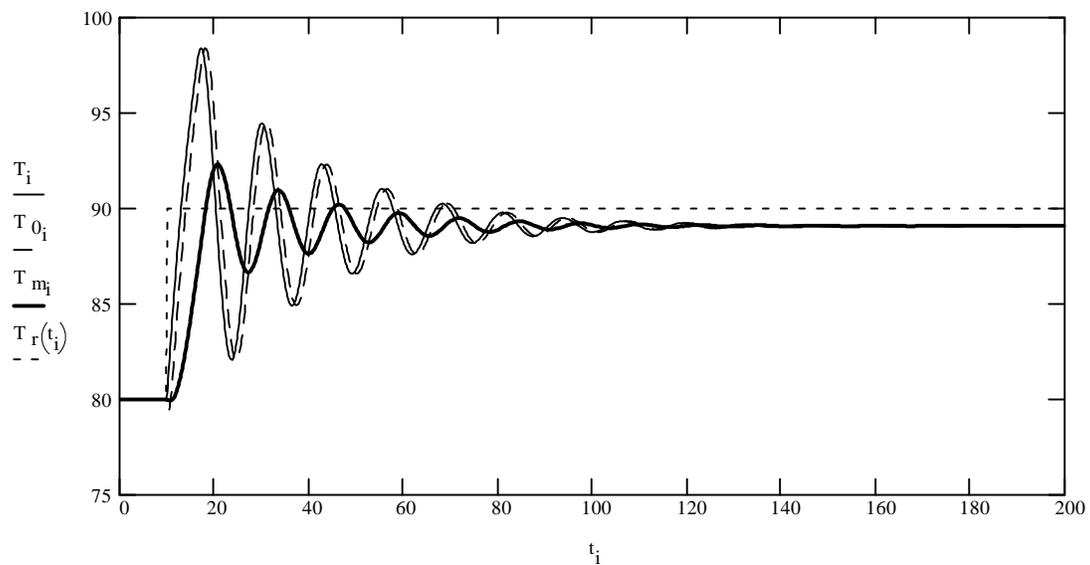
Initial time: $t_0 := 0$
 Final time: $t_f := 200$
 Time step: $\Delta t := 0.1$
 $npoints := \frac{t_f - t_0}{\Delta t} + 1$ $i := 1 \dots npoints$

Solve the system of ODEs using the fixed interval Runge-Kutta method. The adaptive method was too slow!

$$Z := \text{rkfixed}(x, t_0, t_f, \text{npoints}, D)$$

Assign columns of the solution array to vectors for clarity

$$t_i := Z_{i,0} \quad T_i := Z_{i,1} \quad T_{0_i} := Z_{i,2} \quad T_{m_i} := Z_{i,3} \quad \text{errsum}_i := Z_{i,4}$$



Heater behavior with and without limits

