Smart Computing In Undergraduate Courses - Improved Understanding of Fundamentals

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Introduction

Availability of fast, efficient computers

→ increased role of computing in analysis and solution of engineering problems and graphical communication of results

→ greater need for computer application skills in the curricula and practice of chemical engineering

Commercial computational packages

- **reduction in the time and effort required for engineering calculations**
- **efficient solution of problems**
- **essential for better understanding of fundamentals**
- **solve relatively complex problems with limited or no formal training in programming**

Introduction (contd.)

Why use Mathcad?

- ease of use
- need to know very little of the Mathcad syntax and about numerical analysis → focus on problem solution
- combines some of the best features of spreadsheets and symbolic math programs
- efficient manipulation of large data arrays, symbolic calculations, and easy construction of graphs
- ability to perform calculations with units

Advanced and special capabilities of Mathcad

- solution of stiff differential equations
- statistical methods for nonlinear parameter estimation
- programming
- courses in process control, reaction engineering, separations, and thermodynamics

This Presentation

- **Experience in using Mathcad in three undergraduate courses**
- **Pertinent illustrations – in the order of increasing complexity of problems**

  - benefits of using Mathcad in accelerating the learning and strengthening the fundamental knowledge base

Examples In This Presentation

(1) Linear algebraic equations (LAEs)

(2) Nonlinear algebraic equations (NLAEs)

(3) Ordinary differential equations (ODEs)

(4) Integral equations (IEs)

(5) Integral algebraic equations (IAEs)

Sources of Examples Considered

Felder, R.M., R.W. Rousseau, R.W., and L.G. Bullard, L.G., *Elementary Principles of Chemical Processes*, Fourth Edition, John Wiley and Sons, Inc., New York (2016).

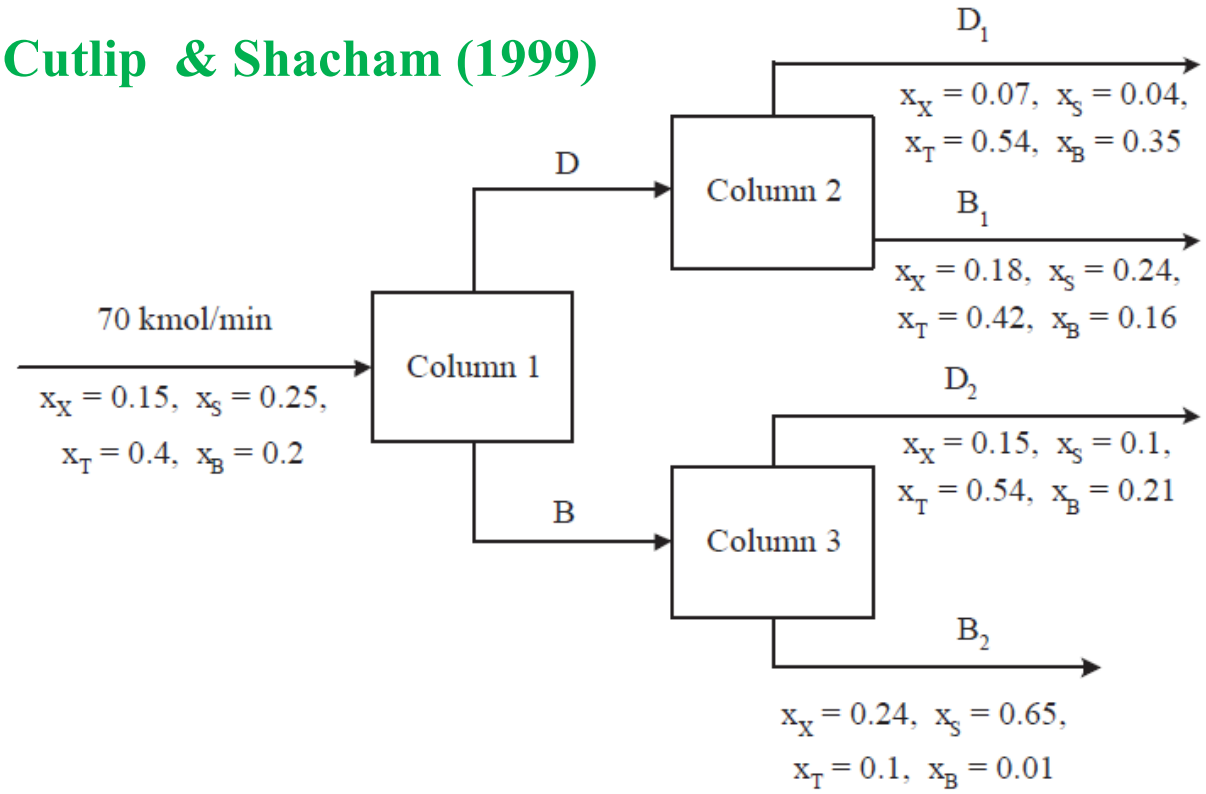
Fogler, H.S., *Elements of Chemical Reaction Engineering*, Fifth Edition, Prentice Hall, Upper Saddle River, New Jersey (2016).

Froment, G.F., Bischoff, K.B., De Wilde, J., *Chemical Reactor Analysis and Design*, Third Edition, Wiley, New York (2011).

Cutlip, M.B., Shacham, M., Prentice Hall PTR (1999).

Example 1 – Separation of Mixture (LAEs)

Cutlip & Shacham (1999)



Benzene (B)
Styrene (S)
Toluene (T)
Xylene (X)

$$A := \begin{pmatrix} 0.07 & 0.18 & 0.15 & 0.24 \\ 0.04 & 0.24 & 0.1 & 0.65 \\ 0.54 & 0.42 & 0.54 & 0.1 \\ 0.35 & 0.16 & 0.21 & 0.01 \end{pmatrix} \qquad b := 70 \cdot \begin{pmatrix} 0.15 \\ 0.25 \\ 0.4 \\ 0.2 \end{pmatrix} \qquad \begin{pmatrix} D_1 \\ B_1 \\ D_2 \\ B_2 \end{pmatrix} := A^{-1} \cdot b$$

$D_1 = 26.25 \qquad B_1 = 17.5 \qquad D_2 = 8.75 \qquad B_2 = 17.5$

Example 2 - Parameter Estimation (LAEs)

$$y = y_p + e, \quad y_p = x_1\theta_1 + x_2\theta_2 + \ldots + x_m\theta_m$$

$\theta_1, \theta_2, \ldots, \theta_m$ – **unknown parameters**

Fogler (2016)

data available – $y,\ x_1, x_2, \ldots, x_m$

$$\mathbf{A\Theta = b}, \quad \mathbf{A = X^T X}, \quad \mathbf{b = X^T Y} \quad \Rightarrow \quad \mathbf{\Theta = (X^T X)^{-1} X^T Y}$$

$$\mathbf{X} = \begin{bmatrix} x_{11} & x_{12} & \ldots & x_{1m} \\ x_{21} & x_{22} & \ldots & x_{2m} \\ \ldots & \ldots & \ldots & \ldots \\ x_{n1} & x_{n2} & \ldots & x_{nm} \end{bmatrix}, \quad \mathbf{Y} = \begin{bmatrix} y_1 \\ y_2 \\ \ldots \\ y_n \end{bmatrix}, \quad \mathbf{\Theta} = \begin{bmatrix} \theta_1 \\ \theta_2 \\ \ldots \\ \theta_m \end{bmatrix}$$

$$r = k p_A^{\alpha} p_B^{\beta}$$

$$\ln(r) = \ln(k) + \alpha \ln(p_A) + \beta \ln(p_B)$$

Example 2 – Linear Regression (contd.)

$$r := \begin{pmatrix} 0.42 \\ 0.96 \\ 0.18 \\ 0.78 \\ 1.2 \\ 0.28 \\ 2.88 \end{pmatrix} \quad p_A := \begin{pmatrix} 0.1 \\ 0.2 \\ 0.05 \\ 0.3 \\ 0.4 \\ 0.05 \\ 0.5 \end{pmatrix} \quad p_B := \begin{pmatrix} 0.1 \\ 0.2 \\ 0.05 \\ 0.01 \\ 0.02 \\ 0.4 \\ 0.5 \end{pmatrix} \quad X_1 := \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}$$

$$X_2 := \ln(p_A) \qquad X_3 := \ln(p_B) \qquad Y := \ln(r)$$

X := augment(X_1, X_2, X_3)

$$Q := \text{stack}\left(X_1^T, X_2^T, X_3^T\right) \qquad X := Q^T$$

Fogler (2016)

$$\theta := \left(X^T \cdot X\right)^{-1} \cdot X^T \cdot Y$$

$$r_p := \exp\left(\theta_1 \cdot X_1 + \theta_2 \cdot X_2 + \theta_3 \cdot X_3\right)$$

$$k := \exp(\theta_1) \qquad \alpha := \theta_2$$

$$\beta := \theta_3$$

$$k = 6.652 \qquad \alpha = 0.997$$

$$\beta = 0.205$$

$$\frac{\overrightarrow{(r - r_p)}}{r} = \begin{pmatrix} 4.871 \times 10^{-3} \\ -1.481 \times 10^{-3} \\ -9.417 \times 10^{-3} \\ 1.073 \times 10^{-3} \\ 2.959 \times 10^{-3} \\ 6.006 \times 10^{-3} \\ -4.098 \times 10^{-3} \end{pmatrix}$$

Example 3 - Rate Expressions for Catalytic Reactions

Association Reaction: (A + B) to (C + D), B and D Only Involved in Surface Reaction

$r_1 := k_1 \cdot C_A \cdot C_S - k_2 \cdot C_{AS}$ $\quad r_2 := k_3 \cdot C_{AS} \cdot C_B - k_4 \cdot C_{CS} \cdot C_D$ $\quad r_3 := k_5 \cdot C_{CS} - k_6 \cdot C_C \cdot C_S$

$(r_1 - r_2) \rightarrow C_A \cdot C_S \cdot k_1 - C_{AS} \cdot k_2 - C_B \cdot C_{AS} \cdot k_3 + C_D \cdot C_{CS} \cdot k_4$

$(r_2 - r_3) \rightarrow C_C \cdot C_S \cdot k_6 - C_{CS} \cdot k_5 + C_B \cdot C_{AS} \cdot k_3 - C_D \cdot C_{CS} \cdot k_4$

C_S – vacant active sites

Symbolic Algebra

$r_1 \text{ solve }, C_{AS} \rightarrow \frac{C_A \cdot C_S \cdot k_1}{k_2}$ $\quad r_2 \text{ solve }, C_{CS} \rightarrow \frac{C_B \cdot C_{AS} \cdot k_3}{C_D \cdot k_4}$

$r_3 \text{ solve }, C_{CS} \rightarrow \frac{C_C \cdot C_S \cdot k_6}{k_5}$

PSSH approach – single rate expression for a given reaction mechanism. Rate determining step (RDS) approach – n steps in mechanism – up to n rate expressions.

PSSH for Active Site Forms

$$A := \begin{bmatrix} k_1 \cdot C_A & -(k_2 + k_3 \cdot C_B) & k_4 \cdot C_D \\ k_6 \cdot C_C & k_3 \cdot C_B & -(k_4 \cdot C_D + k_5) \\ 1 & 1 & 1 \end{bmatrix} \quad b := \begin{pmatrix} 0 \\ 0 \\ C_t \end{pmatrix} \quad \begin{pmatrix} C_S \\ C_{AS} \\ C_{CS} \end{pmatrix} := A^{-1} \cdot b$$

Third relation - active sites balance

Catalytic Reactions - Symbolic Algebra

$$\begin{pmatrix} C_S \\ C_{AS} \\ C_{CS} \end{pmatrix} \text{simplify} \rightarrow \begin{bmatrix} \frac{C_t\cdot(k_2\cdot k_5 + C_B\cdot k_3\cdot k_5 + C_D\cdot k_2\cdot k_4)}{k_2\cdot k_5 + C_A\cdot k_1\cdot k_5 + C_B\cdot k_3\cdot k_5 + C_D\cdot k_2\cdot k_4 + C_C\cdot k_2\cdot k_6 + C_A\cdot C_B\cdot k_1\cdot k_3 + C_A\cdot C_D\cdot k_1\cdot k_4 + C_B\cdot C_C\cdot k_3\cdot k_6 + C_C\cdot C} \\ \frac{C_t\cdot(C_A\cdot k_1\cdot k_5 + C_A\cdot C_D\cdot k_1\cdot k_4 + C_C\cdot C_D\cdot k_4\cdot k_6)}{k_2\cdot k_5 + C_A\cdot k_1\cdot k_5 + C_B\cdot k_3\cdot k_5 + C_D\cdot k_2\cdot k_4 + C_C\cdot k_2\cdot k_6 + C_A\cdot C_B\cdot k_1\cdot k_3 + C_A\cdot C_D\cdot k_1\cdot k_4 + C_B\cdot C_C\cdot k_3\cdot k_6 + C_C\cdot C} \\ \frac{C_t\cdot(C_C\cdot k_2\cdot k_6 + C_A\cdot C_B\cdot k_1\cdot k_3 + C_B\cdot C_C\cdot k_3\cdot k_6)}{k_2\cdot k_5 + C_A\cdot k_1\cdot k_5 + C_B\cdot k_3\cdot k_5 + C_D\cdot k_2\cdot k_4 + C_C\cdot k_2\cdot k_6 + C_A\cdot C_B\cdot k_1\cdot k_3 + C_A\cdot C_D\cdot k_1\cdot k_4 + C_B\cdot C_C\cdot k_3\cdot k_6 + C_C\cdot C} \end{bmatrix}$$

$$r := (k_1\cdot C_A\cdot C_S - k_2\cdot C_{AS})$$

$$r \text{ simplify} \rightarrow \frac{C_t\cdot(C_A\cdot C_B\cdot k_1\cdot k_3\cdot k_5 - C_C\cdot C_D\cdot k_2\cdot k_4\cdot k_6)}{k_2\cdot k_5 + C_A\cdot k_1\cdot k_5 + C_B\cdot k_3\cdot k_5 + C_D\cdot k_2\cdot k_4 + C_C\cdot k_2\cdot k_6 + C_A\cdot C_B\cdot k_1\cdot k_3 + C_A\cdot C_D\cdot k_1\cdot k_4 + C_B\cdot C_C\cdot k_3\cdot k_6 + C_C\cdot C_D\cdot k_4\cdot k_6}$$

Special Cases:

(1)

$$r \left|\begin{array}{l}\text{substitute}, k_2 = 0 \\ \text{simplify}\end{array}\right. \rightarrow \frac{C_A\cdot C_B\cdot C_t\cdot k_1\cdot k_3\cdot k_5}{C_A\cdot k_1\cdot k_5 + C_B\cdot k_3\cdot k_5 + C_A\cdot C_B\cdot k_1\cdot k_3 + C_A\cdot C_D\cdot k_1\cdot k_4 + C_B\cdot C_C\cdot k_3\cdot k_6 + C_C\cdot C_D\cdot k_4\cdot k_6}$$

(2)

$$r \left|\begin{array}{l}\text{substitute}, k_4 = 0 \\ \text{simplify}\end{array}\right. \rightarrow \frac{C_A\cdot C_B\cdot C_t\cdot k_1\cdot k_3\cdot k_5}{k_2\cdot k_5 + C_A\cdot k_1\cdot k_5 + C_B\cdot k_3\cdot k_5 + C_C\cdot k_2\cdot k_6 + C_A\cdot C_B\cdot k_1\cdot k_3 + C_B\cdot C_C\cdot k_3\cdot k_6}$$

Catalytic Reactions - Symbolic Algebra

(3)

$$r \left| \begin{array}{l} \text{substitute}\ ,k_6 = 0 \\ \text{simplify} \end{array} \right. \rightarrow \frac{C_A \cdot C_B \cdot C_t \cdot k_1 \cdot k_3 \cdot k_5}{k_2 \cdot k_5 + C_A \cdot k_1 \cdot k_5 + C_B \cdot k_3 \cdot k_5 + C_D \cdot k_2 \cdot k_4 + C_A \cdot C_B \cdot k_1 \cdot k_3 + C_A \cdot C_D \cdot k_1 \cdot k_4}$$

(4)

$$r \left| \begin{array}{l} \text{substitute}\ ,k_2 = 0 \\ \text{substitute}\ ,k_4 = 0 \\ \text{simplify} \end{array} \right. \rightarrow \frac{C_A \cdot C_B \cdot C_t \cdot k_1 \cdot k_3 \cdot k_5}{C_A \cdot k_1 \cdot k_5 + C_B \cdot k_3 \cdot k_5 + C_A \cdot C_B \cdot k_1 \cdot k_3 + C_B \cdot C_C \cdot k_3 \cdot k_6}$$

(5)

$$r \left| \begin{array}{l} \text{substitute}\ ,k_2 = 0 \\ \text{substitute}\ ,k_6 = 0 \\ \text{simplify} \end{array} \right. \rightarrow \frac{C_A \cdot C_B \cdot C_t \cdot k_1 \cdot k_3 \cdot k_5}{C_A \cdot k_1 \cdot k_5 + C_B \cdot k_3 \cdot k_5 + C_A \cdot C_B \cdot k_1 \cdot k_3 + C_A \cdot C_D \cdot k_1 \cdot k_4}$$

(6)

$$r \left| \begin{array}{l} \text{substitute}\ ,k_4 = 0 \\ \text{substitute}\ ,k_6 = 0 \\ \text{simplify} \end{array} \right. \rightarrow \frac{C_A \cdot C_B \cdot C_t \cdot k_1 \cdot k_3 \cdot k_5}{k_2 \cdot k_5 + C_A \cdot k_1 \cdot k_5 + C_B \cdot k_3 \cdot k_5 + C_A \cdot C_B \cdot k_1 \cdot k_3}$$

(7)

$$r \left| \begin{array}{l} \text{substitute}\ ,k_2 = 0 \\ \text{substitute}\ ,k_4 = 0 \\ \text{substitute}\ ,k_6 = 0 \\ \text{simplify} \end{array} \right. \rightarrow \frac{C_A \cdot C_B \cdot C_t \cdot k_1 \cdot k_3 \cdot k_5}{C_A \cdot k_1 \cdot k_5 + C_B \cdot k_3 \cdot k_5 + C_A \cdot C_B \cdot k_1 \cdot k_3}$$

Example 4 – Redlich-Kwong Equation of State (NLAE)

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+b)\sqrt{T}}, \quad a = 0.42747\frac{R^2T_c^{2.5}}{P_c}, \quad b = 0.08664\frac{RT_c}{P_c}$$

$R := 0.08206$ $T_c := 405.5$ $P_c := 111.3$ $V := 0.57$

$$a := 0.42747\frac{R^2 \cdot T_c^{2.5}}{P_c} \qquad b := \frac{0.08664 R \cdot T_c}{P_c}$$

Ammonia
- given P, T – what is V?

Iterative solution

Given

$$P - \frac{R \cdot T}{(V-b)} + \frac{a}{V \cdot (V+b) \cdot T^{0.5}} = 0 \qquad V(P,T) := \text{Find}(V)$$

$$re(P,T) := 1.0 - \frac{R \cdot T}{P \cdot (V(P,T) - b)} + \frac{a}{P \cdot V(P,T) \cdot (V(P,T) + b) \cdot T^{0.5}}$$

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

$$W1(P,T) := \begin{pmatrix} P \\ T \\ V(P,T) \\ Z(P,T) \\ re(P,T) \end{pmatrix}^T$$

U =

	1	2	3	4	5
1	56	450	0.57	0.864	0
2	111.3	450	0.233	0.703	0
3	222.6	450	0.074	0.444	0
4	445.2	450	0.051	0.613	0
5	$1.113 \cdot 10^3$	450	0.04	1.2	0
6	$2.226 \cdot 10^3$	450	0.035	2.1	0
7	56	350	0.324	0.631	0
8	56	400	0.465	0.793	0
9	56	550	0.751	0.932	0
10	56	650	0.917	0.962	0
11	56	750	1.075	0.979	0
12	56	850	1.231	0.988	0

Felder et al. (2016)

$U1 := \text{stack}(W1(56,450), W1(111.3,450), W1(222.6,450), W1(445.2,450))$

$U2 := \text{stack}(W1(1113,450), W1(2226,450), W1(56,350), W1(56,400), W1(56,550))$

$U3 := \text{stack}(W1(56,650), W1(56,750), W1(56,850))$

$U := \text{stack}(U1, U2, U3)$

Alternate - symbolic algebra – no guess work

Example 5 – Multi-Reaction Equilibrium (NLAEs)

(1) $2CO_2\ (A) \rightleftharpoons 2CO\ (B) + O_2\ (C)$,

$$y_B^2 y_C / y_A^2 = 0.1071$$

(2) $O_2\ (C) + N_2\ (D) \rightleftharpoons 2NO\ (E)$

$$y_E^2 / y_C y_D = 0.01493$$

$n_{A0} := \frac{1}{5}$ $n_{B0} := \frac{1}{5}$ $n_{C0} := \frac{1}{5}$ $n_{D0} := \frac{1}{5}$ $n_{E0} := \frac{1}{5}$

Equilibrium relations

$\xi_1 := -0.022$ $\xi_2 := -0.083$ $n_{t0} := n_{A0} + n_{B0} + n_{C0} + n_{D0} + n_{E0}$

Iterative solution

Given

$$\frac{(n_{B0} + 2\cdot\xi_1)^2 \cdot (n_{C0} + \xi_1 - \xi_2)}{(n_{t0} + \xi_1)\cdot(n_{A0} - 2\cdot\xi_1)^2} - 0.1071 = 0 \qquad \frac{(n_{E0} + 2\cdot\xi_2)^2}{(n_{C0} + \xi_1 - \xi_2)\cdot(n_{D0} - \xi_2)} - 0.01493 = 0$$

$\begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix} := \text{Find}(\xi_1, \xi_2)$ $\xi_1 = -0.022$ $\xi_2 = -0.083$

Felder et al. (2016)

Equilibrium composition

$n_A := n_{A0} - 2\cdot\xi_1$ $n_B := n_{B0} + 2\cdot\xi_1$ $n_C := n_{C0} + \xi_1 - \xi_2$ $n_D := n_{D0} - \xi_2$

$n_E := n_{E0} + 2\cdot\xi_2$ $n_t := n_{t0} + \xi_1$ $y_A := \frac{n_A}{n_t}$ $y_B := \frac{n_B}{n_t}$ $y_C := \frac{n_C}{n_t}$

$y_D := \frac{n_D}{n_t}$ $y_E := \frac{n_E}{n_t}$

$n_A = 0.245$ $n_B = 0.155$ $n_C = 0.261$ $n_D = 0.283$ $n_E = 0.033$ $n_t = 0.978$

$y_A = 0.251$ $y_B = 0.159$ $y_C = 0.267$ $y_D = 0.29$ $y_E = 0.034$

Verification of solution

$$\frac{(n_{B0} + 2\cdot\xi_1)^2 \cdot (n_{C0} + \xi_1 - \xi_2)}{(n_{t0} + \xi_1)\cdot(n_{A0} - 2\cdot\xi_1)^2} - 0.1071 = 0$$

$$\frac{(n_{E0} + 2\cdot\xi_2)^2}{(n_{C0} + \xi_1 - \xi_2)\cdot(n_{D0} - \xi_2)} - 0.01493 = 0$$

Example 5 – Multi-Reaction Equilibrium (NLAEs)

Equilibrium composition of a reaction mixture.

$2CO_2$ (A) = 2CO (B) + O_2 (C), O_2 (C) + N_2 (D) = 2NO (E), P = 1 atm.

Relations: $N_{t0} := 1$ **(Continuous flow reactor - Replace N_J's by F_J's.)**

$N_A := N_{t0}\cdot(y_{A0} - 2\cdot\Lambda_1)$ $N_B := N_{t0}\cdot(y_{B0} + 2\cdot\Lambda_1)$ $N_C := N_{t0}\cdot(y_{C0} + \Lambda_1 - \Lambda_2)$

$N_D := N_{t0}\cdot(y_{D0} - \Lambda_2)$ $N_E := N_{t0}\cdot(y_{E0} + 2\cdot\Lambda_2)$ $N_t := N_{t0}\cdot(1 + \Lambda_1)$

$K_{P1} := 0.1071$ $K_{P2} := 0.0149$ $P := 1$

$$f_1(\Lambda_1,\Lambda_2,y_{A0},y_{B0},y_{C0}) := \frac{(y_{B0} + 2\cdot\Lambda_1)^2\cdot(y_{C0} + \Lambda_1 - \Lambda_2)}{(1 + \Lambda_1)\cdot(y_{A0} - 2\cdot\Lambda_1)^2}\cdot P - K_{P1}$$

Felder et al. (2016)

$$f_2(\Lambda_1,\Lambda_2,y_{C0},y_{D0},y_{E0}) := \frac{(y_{E0} + 2\cdot\Lambda_2)^2}{(y_{C0} + \Lambda_1 - \Lambda_2)\cdot(y_{D0} - \Lambda_2)} - K_{P2}$$

Symbolic Algebra

$y_{A0} := \frac{1}{3}$ $y_{B0} := 0$ $y_{C0} := \frac{1}{3}$ $y_{D0} := \frac{1}{3}$ $y_{E0} := 0$

$$f(x1) := f_1(x1,x2,y_{A0},y_{B0},y_{C0}) \text{ solve },x2 \rightarrow \frac{0.0000083333333333333333333(107148.0x1^3 + 31432.0x1^2 + 3927.0x1 - 357.0)}{x1^2}$$

Example 5 – Multi-Reaction Equilibrium (NLAEs)

$g(x1) := f_2(x1, x2, y_{C0}, y_{D0}, y_{E0})$ substitute , $x2 = f(x1)$ $\rightarrow$ $-\dfrac{1.0\cdot\left(2.87145845080083e56\cdot x1^{6} + 1.68469186593444e56\cdot x1^{5} + 4.5696371\right.}{8.60666310000000000003e54\cdot x1^{6} + 5.0495508e54\cdot x1^{5} - 2}$

Master equation

$\Lambda_1 := g(x1)$ solve , $x1 \rightarrow$

$$\begin{pmatrix} 0.059305078169702959332 \\ 0.057229522364275026425 \\ -0.18122064960135852005 - 0.15104588520604354084\,i \\ -0.17039790313884509186 + 0.17171979247546263374\,i \\ -0.17039790313884509186 - 0.17171979247546263374\,i \\ -0.18122064960135852005 + 0.15104588520604354084\,i \end{pmatrix}$$

6^{th} order polynomial in x1

Symbolic Algebra

$$\Lambda_1 := \begin{pmatrix} \Lambda_{1_1} \\ \Lambda_{1_2} \end{pmatrix} \qquad \Lambda_2 := \overrightarrow{f(\Lambda_1)} \qquad \Lambda_1 = \begin{pmatrix} 0.059 \\ 0.057 \end{pmatrix} \qquad \Lambda_2 = \begin{pmatrix} 0.021 \\ -0.023 \end{pmatrix}$$

Verify

$$\overrightarrow{f_1(\Lambda_1, \Lambda_2, y_{A0}, y_{B0}, y_{C0})} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \qquad \overrightarrow{f_2(\Lambda_1, \Lambda_2, y_{C0}, y_{D0}, y_{E0})} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$N_A := N_{t0}\cdot(y_{A0} - 2\cdot\Lambda_1) \qquad N_B := N_{t0}\cdot(y_{B0} + 2\cdot\Lambda_1) \qquad N_C := N_{t0}\cdot(y_{C0} + \Lambda_1 - \Lambda_2)$$

$$N_D := N_{t0}\cdot(y_{D0} - \Lambda_2) \qquad N_E := N_{t0}\cdot(y_{E0} + 2\cdot\Lambda_2) \qquad N_t := N_{t0}\cdot(1 + \Lambda_1)$$

Example 5 – Multi-Reaction Equilibrium (NLAEs)

$$N_A = \begin{pmatrix} 0.215 \\ 0.219 \end{pmatrix} \qquad N_B = \begin{pmatrix} 0.119 \\ 0.114 \end{pmatrix} \qquad N_C = \begin{pmatrix} 0.372 \\ 0.414 \end{pmatrix} \qquad N_D = \begin{pmatrix} 0.313 \\ 0.357 \end{pmatrix}$$

$$N_E = \begin{pmatrix} 0.042 \\ -0.047 \end{pmatrix} \qquad N_t = \begin{pmatrix} 1.059 \\ 1.057 \end{pmatrix} \qquad P_0 := \frac{\overrightarrow{P}}{1 + \Lambda_1} \qquad P_0 = \begin{pmatrix} 0.944 \\ 0.946 \end{pmatrix}$$

$$y_A := \frac{\overrightarrow{N_A}}{N_t} \qquad y_B := \frac{\overrightarrow{N_B}}{N_t} \qquad y_C := \frac{\overrightarrow{N_C}}{N_t} \qquad y_D := \frac{\overrightarrow{N_D}}{N_t} \qquad y_E := \frac{\overrightarrow{N_E}}{N_t}$$

$$y_A = \begin{pmatrix} 0.203 \\ 0.207 \end{pmatrix} \qquad y_B = \begin{pmatrix} 0.112 \\ 0.108 \end{pmatrix} \qquad y_C = \begin{pmatrix} 0.351 \\ 0.392 \end{pmatrix} \qquad y_D = \begin{pmatrix} 0.295 \\ 0.338 \end{pmatrix} \qquad y_E = \begin{pmatrix} 0.039 \\ -0.044 \end{pmatrix}$$

No iterations required. y_J's and N_J's cannot be negative.

Example 6 – Vapor-Liquid Equilibrium (Benzene – Toluene Mixtures, NLAE)

$$y_J P = x_J p_J^*(T), \quad \log_{10} p_J^* = A_J - \frac{B_J}{T + C_J}$$

$$P = \sum_J x_J p_J^*(T) \quad \text{at} \quad T = T_{bp}$$

p_J^* in mm Hg, T in °C

$A_B := 6.89272$ $B_B := 1203.531$ $C_B := 219.888$

$A_T := 6.95805$ $B_T := 1346.773$ $C_T := 219.693$

Bubble point (bp) calculations $P := 760$ $T := 95$

Given

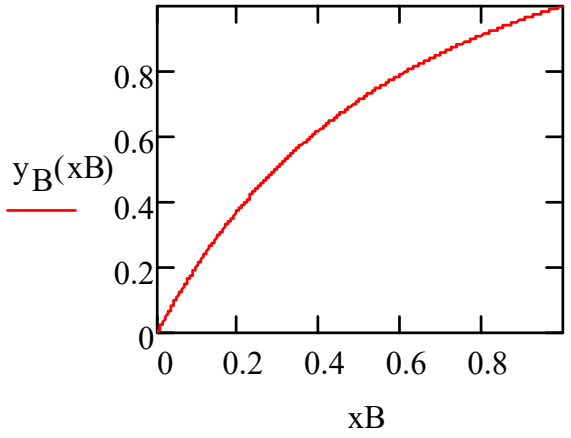
Iterative solution

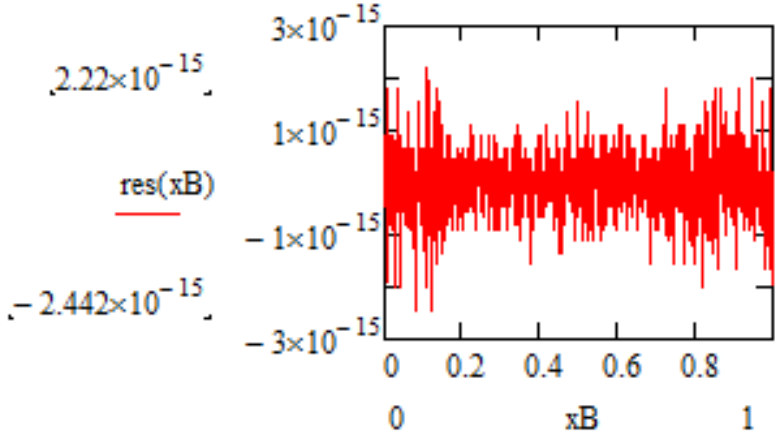
$$x_B \cdot 10^{A_B - \frac{B_B}{(T + C_B)}} + (1 - x_B) \cdot 10^{A_T - \frac{B_T}{(T + C_T)}} - P = 0$$

$T_{bp}(x_B) := \text{Find}(T)$

$$\text{res}(x_B) := \left[\frac{x_B}{P} \cdot 10^{A_B - \frac{B_B}{(T_{bp}(x_B) + C_B)}} + \frac{(1 - x_B)}{P} \cdot 10^{A_T - \frac{B_T}{(T_{bp}(x_B) + C_T)}} - 1 \right]$$

$$P_{Bv}(x_B) := 10^{A_B - \frac{B_B}{(T_{bp}(x_B) + C_B)}} \qquad y_B(x_B) := \frac{x_B \cdot P_{Bv}(x_B)}{P}$$





Felder et al. (2016)

Example 6 – Vapor-Liquid Equilibrium (NLAE, Contd.)

$$\sum_J \frac{y_J P}{p_J^*(T)} = 1 \quad \text{at} \quad T = T_{dp}$$

Dew-point (dp) calculations

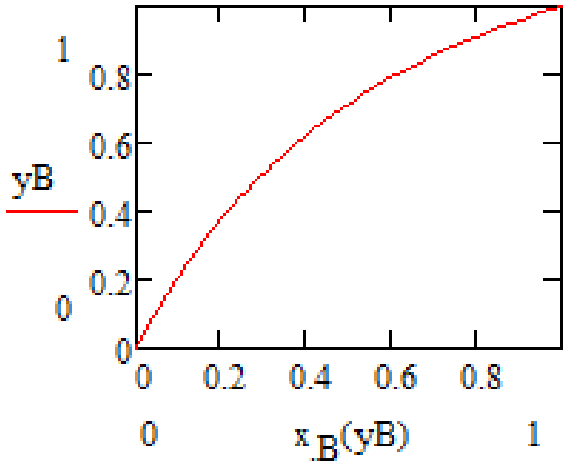
$T := 100$

Iterative solution

Given

$$y_B \cdot P \cdot 10^{-A_B + \frac{B_B}{(T + C_B)}} + (1 - y_B) \cdot P \cdot 10^{-A_T + \frac{B_T}{(T + C_T)}} - 1 = 0$$

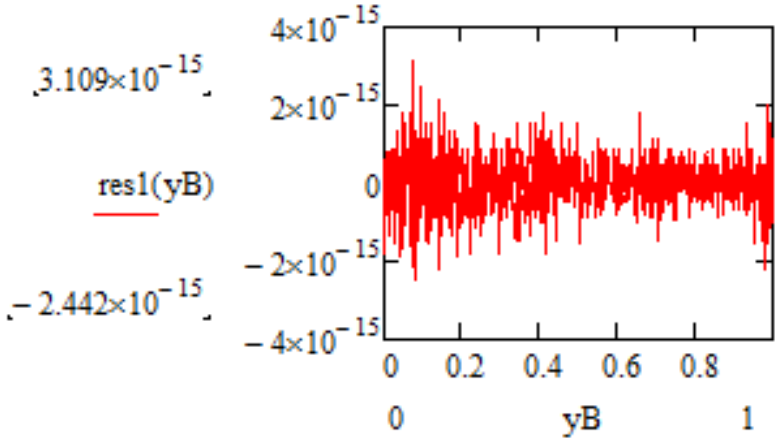
$T_{dp}(y_B) := \text{Find}(T)$

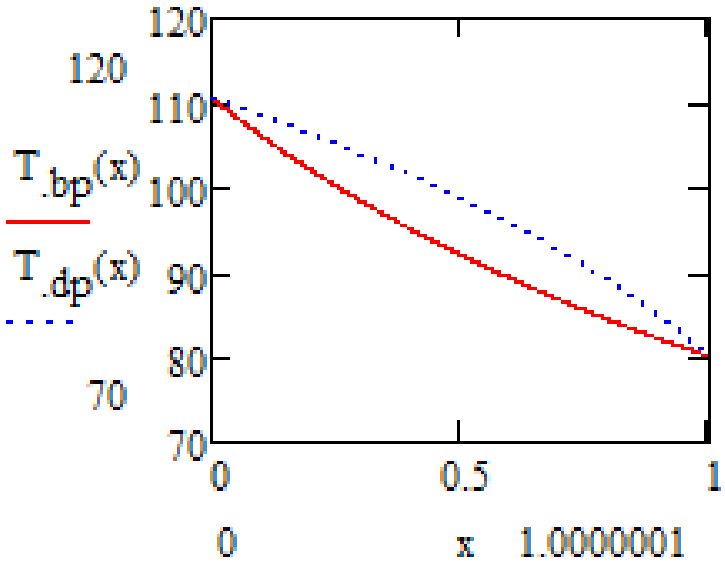


$$\text{res1}(y_B) := y_B \cdot P \cdot 10^{-A_B + \frac{B_B}{(T_{dp}(y_B) + C_B)}} + (1 - y_B) \cdot P \cdot 10^{-A_T + \frac{B_T}{(T_{dp}(y_B) + C_T)}} - 1$$

$$P_{Bv}(y_B) := 10^{A_B - \frac{B_B}{(T_{dp}(y_B) + C_B)}}$$

$$x_B(y_B) := \frac{y_B \cdot P}{P_{Bv}(y_B)}$$





Example 7 – Isothermal Series Parallel Reactions (NLAEs)

M = mesitylene, H = hydrogen, X = xylene,

Fogler (2016) Me = methane, T = toluene

$$M + H \rightarrow X + Me, \quad r_1 = k_1 C_M \sqrt{C_H}$$

$$X + H \rightarrow T + Me, \quad r_2 = k_2 C_X \sqrt{C_H}$$

Stoichiometric Relation

$$C_M = \frac{1}{2}(a + C_H - C_X), \quad a = 2C_{M0} + C_{X0} - C_{H0}.$$

$$k_1 = 55.2 \ (ft^3/lb\ mol)^{0.5}/h, \quad k_2 = 30.2 \ (ft^3/lb\ mol)^{0.5}/h,$$

$$C_{H0} = 0.021 \ lb\ mol/ft^3, \quad C_{M0} = 0.0105 \ lb\ mol/ft^3.$$

Fogler (2016)

Example 7 - NLAEs (contd.)

$k_1 := 55.2$ $k_2 := 30.2$ $C_{Ho} := 0.021$ $C_{Mo} := 0.0105$

$C_{Xo} := 0.0$ $a := 2 \cdot C_{Mo} + C_{Xo} - C_{Ho}$

Iterative solution

$C_H := 0.0089$ $C_X := 0.00312$ $a = 0$

Single set of guesses

Given

$$\frac{(C_H - C_{Ho})}{\tau_c} = -k_1 \cdot (C_H)^{0.5} \cdot (a + C_H - C_X) \cdot 0.5 - k_2 \cdot (C_H)^{0.5} \cdot C_X$$

$$\frac{C_X}{\tau_c} = k_1 \cdot (C_H)^{0.5} \cdot (a + C_H - C_X) \cdot 0.5 - k_2 \cdot (C_H)^{0.5} \cdot C_X$$

Family of solutions

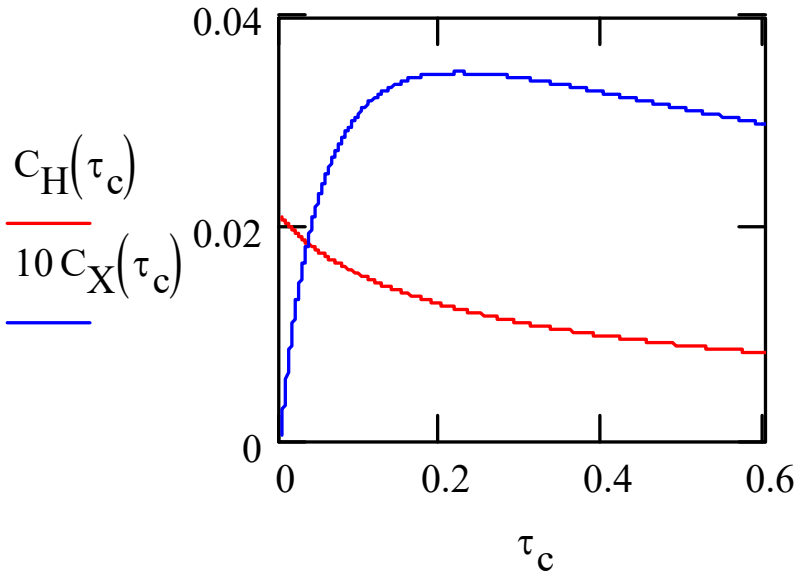
$Sol1(\tau_c) := Find(C_H, C_X)$ $C_H(\tau_c) := Sol1(\tau_c)_1$ $C_X(\tau_c) := Sol1(\tau_c)_2$

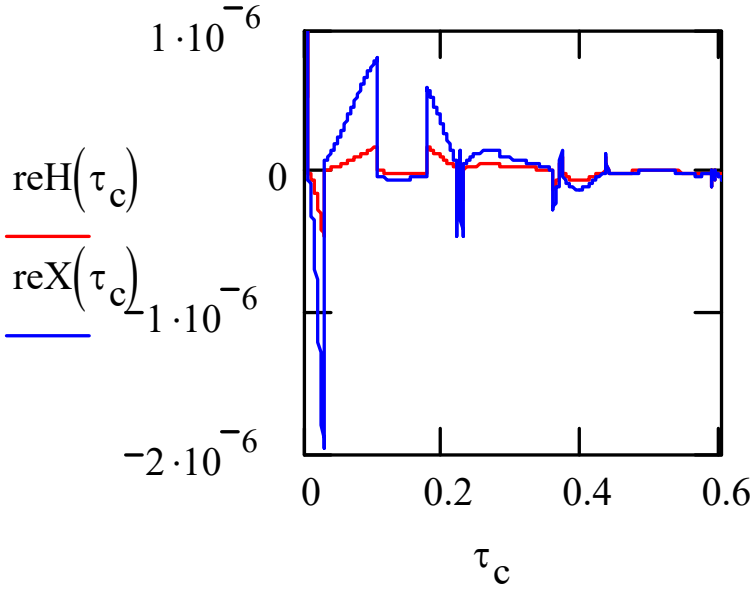
Example 7 - NLAEs (contd.)

Relative errors

$$reH(\tau) := \frac{\tau\cdot\left[-k_1\cdot\left(C_H(\tau)\right)^{0.5}\cdot\left(a + C_H(\tau) - C_X(\tau)\right)\cdot 0.5 - k_2\cdot\left(C_H(\tau)\right)^{0.5}\cdot C_X(\tau)\right]}{C_H(\tau) - C_{Ho}} - 1$$

$$reX(\tau) := \frac{\tau\cdot\left[k_1\cdot\left(C_H(\tau)\right)^{0.5}\cdot\left(a + C_H(\tau) - C_X(\tau)\right)\cdot 0.5 - k_2\cdot\left(C_H(\tau)\right)^{0.5}\cdot C_X(\tau)\right]}{C_X(\tau)} - 1$$





Example 8 – Three CSTRs In Series (NLAEs)

$2SO_2\,(A) + O_2\,(B) \rightarrow 2SO_3\,(C)$ $\qquad r = kC_A C_B$

$$r = kC_{A0}{}^2 f(X), \quad f(X) = \frac{(1-X)(0.54-0.5X)}{(1-0.14X)^2}$$

Fogler (2016)

Design Equation $\rightarrow$

$$X_i - X_{i-1} - \frac{Da}{3} f(X_i) = 0, \quad i = 1,\ 2,\ 3,$$

$$Da = kC_{A0}\tau$$

$V_1 = V_2 = V_3 = V/3$

Given $\rightarrow$ $X_3 := 0.9$ $\qquad Da := 2$ $\leftarrow$ **Guess**

Guesses $\rightarrow$ $X_1 := 0.3$ $\qquad X_2 := 0.6$.

Example 8 - NLAEs (contd.)

Given

$$\left[X_1 - \frac{Da}{3} \cdot \frac{(1 - X_1)\cdot(0.54 - 0.5X_1)}{(1 - 0.14\,X_1)^2} \right] = 0 \qquad \left[X_2 - X_1 - \frac{Da}{3} \cdot \frac{(1 - X_2)\cdot(0.54 - 0.5X_2)}{(1 - 0.14\,X_2)^2} \right] = 0$$

$$\left[X_3 - X_2 - \frac{Da}{3} \cdot \frac{(1 - X_3)\cdot(0.54 - 0.5X_3)}{(1 - 0.14\,X_3)^2} \right] = 0 \qquad \begin{pmatrix} Da \\ X_1 \\ X_2 \end{pmatrix} := \text{Find}(Da, X_1, X_2)$$

$Da = 19.502$ $X_1 = 0.635$ $X_2 = 0.823$

Iterative Solution

Verify

$$\left[X_1 - \frac{Da}{3} \cdot \frac{(1 - X_1)\cdot(0.54 - 0.5X_1)}{(1 - 0.14\,X_1)^2} \right] = -9.212 \times 10^{-9} \qquad \left[X_3 - X_2 - \frac{Da}{3} \cdot \frac{(1 - X_3)\cdot(0.54 - 0.5X_3)}{(1 - 0.14\,X_3)^2} \right] = 0$$

$$\left[X_2 - X_1 - \frac{Da}{3} \cdot \frac{(1 - X_2)\cdot(0.54 - 0.5X_2)}{(1 - 0.14\,X_2)^2} \right] = -3.984 \times 10^{-9}$$

Converged.

Equal Volume - V1 = V2 = V3 = V/3.

$X_3 := 0.9$

$$X_2 := X_3 - X_2 - \frac{Da}{3}\cdot\frac{(1 - X_3)\cdot(0.54 - 0.5\cdot X_3)}{(1 - 0.14\cdot X_3)^2} \text{ solve }, X_2 \rightarrow$$

$$X_1 := X_2 - X_1 - \frac{Da}{3}\cdot\frac{(1 - X_2)\cdot(0.54 - 0.5\cdot X_2)}{(1 - 0.14\cdot X_2)^2} \text{ solve }, X_1 \rightarrow$$

Three CSTRs In Series (NLAEs) – Non-Iterative Solution of Master Equation

Symbolic Algebra

$$g(Da) := X_1 - \frac{Da}{3}\cdot\frac{(1 - X_1)\cdot(0.54 - 0.5\cdot X_1)}{(1 - 0.14\cdot X_1)^2}$$

Master equation

$$g(Da) \text{ simplify } \rightarrow \frac{2.6084386407604857638e14}{Da + 137.54774986975299379} - 17.010730060080627824Da - \frac{2.6084386414308208663e14}{Da + 137.54774987579168295} - \frac{6.254160072816}{Da^2 + 3179.17916}$$

$$v := g(Da) \left|\begin{array}{l}\text{simplify}\\ \text{solve }, Da\end{array}\right. \rightarrow \begin{pmatrix} 19.502080484499384069 \\ -58.617254980492962358 - 20.007163854372121196i \\ -812.46606675159360577 - 777.25546597933857966i \\ -58.617254980492962358 - 20.007163854372121196i \\ -30.515240696864327306 - 45.890268386848379296i \\ -30.515240696864327306 - 45.890268386848379296i \\ 5.9709854455344495096 - 39.552587161657867641i \\ 5.9709854455344495096 - 39.552587161657867641i \\ -812.46606675159360577 - 777.25546597933857966i \end{pmatrix}$$

9th order polynomial in Da

Example 8 - Three CSTRs In Series (NLAEs) – Non-Iterative Solution of Master Equation

$$Da := 19.5020804724880536 \qquad X_2 := X_3 - \frac{Da}{3}\cdot\frac{(1 - X_3)\cdot(0.54 - 0.5\cdot X_3)}{(1 - 0.14 X_3)^2}$$

$$X_1 := X_2 - \frac{Da}{3}\cdot\frac{(1 - X_2)\cdot(0.54 - 0.5\cdot X_2)}{(1 - 0.14 X_2)^2} \qquad X_1 = 0.635 \qquad X_2 = 0.823$$

Verify

$$\left[X_1 - \frac{Da}{3}\cdot\frac{(1 - X_1)\cdot(0.54 - 0.5X_1)}{(1 - 0.14 X_1)^2}\right] = 0$$

Example 9 – Catalytic Reaction In A CSTR (NLAE)

$A \rightarrow$ Products (olefins hydrogenation) **Froment et al. (2011)**

$C_{A0} = 13$ mol/L, $V = 10$ L, $v_0 = 0.2$ L/s

Steady State CSTR

$v_0 := 0.2$ $C_{A0} := 13$ $V := 10$ $\tau := \frac{V}{v_0}$

$$r(C_A) := \frac{C_A}{(1 + C_A)^2} \qquad f(C_A) := \frac{(C_{A0} - C_A)}{\tau} - r(C_A)$$

$$C_{As} := f(C_A) \text{ solve}, C_A \rightarrow \begin{pmatrix} .7515357677521880442 \\ 2.130932562958723480 \\ 8.117531669289088474 \end{pmatrix} \qquad \overrightarrow{f(C_{As})} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

No iterations.

Example 9 – Which Steady State Is Reached? (ODE)

$t_i := 0.0$ $\quad t_f := 10000.0$ $\quad Npts := 200$

$C_1 = C_A$

$$D(t, C) := \left[\frac{C_{A0} - C_1}{\tau} - \frac{C_1}{(1 + C_1)^2} \right]$$

$C_{Ai1} := 2.1305$

Nearby steady state unstable.

$Sol := Rkadapt(C_{Ai1}, t_i, t_f, Npts, D)$ **Stable**

$C_{Af1} := Sol_{Npts, 2}$ $\quad C_{Af1} = 0.752$ $\quad C_{Ai2} := 2.1315$

$Sol := Rkadapt(C_{Ai2}, t_i, t_f, Npts, D)$ $\quad C_{Af2} := Sol_{Npts, 2}$

Stable $\quad C_{Af2} = 8.118$

Example 10 – Tubular Membrane Reactor (ODEs)

Fogler (2016)

A ↔ B + C

$$r = k(C_A - \frac{C_B C_C}{K_C}) = k_1[\frac{F_A}{F_T} - C\frac{(F_{A0} - F_A)F_B}{F_T{}^2}]$$

$$r_B = k_B C_B = k_{B1}\frac{F_B}{F_T}, \quad F_T = (F_{A0} + F_B)$$

$$k_1 = kC_{T0}, \quad k_{B1} = k_B C_{T0}, \quad C_{T0} = \frac{P}{RT}, \quad C = \frac{C_{T0}}{K_C}$$

$k = 0.7\ \text{min}^{-1}$, $K_C = 0.05\ \text{mol/L}$, $k_B = 1\ \text{min}^{-1}$,

$V = 300\ \text{L}$, $P = 8.2\ \text{atm}$, $T = 500\ \text{K}$.

Example 10 - Membrane Reactor - ODEs (contd.)

$P := 8.2$ $R := 0.082$ $T := 500$ $C_{To} := \frac{P}{R \cdot T}$ $C_{To} = 0.2$

$k := 0.7$ $K_C := 0.05$ $k_B := 1.0$ $F_{A0} := 10$ $F_{B0} := 0$

$k_1 := k \cdot C_{To}$ $k_{B1} := k_B \cdot C_{To}$ $C_1 := \frac{C_{To}}{K_C}$ $IC := \begin{pmatrix} F_{A0} \\ F_{B0} \end{pmatrix}$

$Npts := 100$ $V_i := 0.0$ $V_f := 300.0$ $F_1 = F_A$ & $F_2 = F_B$

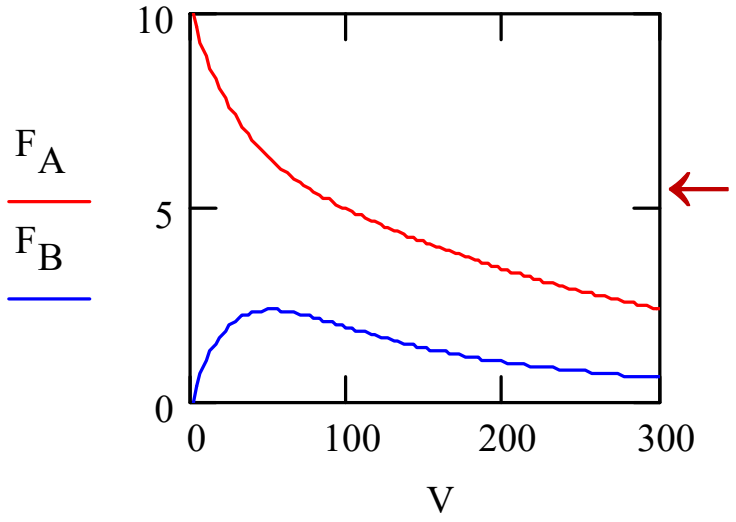
$$D(V,F) := \begin{bmatrix} -k_1 \cdot \left[\frac{F_1}{F_{A0} + F_2} - C_1 \cdot F_2 \cdot \frac{(F_{A0} - F_1)}{(F_{A0} + F_2)^2} \right] \\ k_1 \cdot \left[\frac{F_1}{F_{A0} + F_2} - C_1 \cdot F_2 \cdot \frac{(F_{A0} - F_1)}{(F_{A0} + F_2)^2} \right] - k_{B1} \cdot \frac{F_2}{(F_{A0} + F_2)} \end{bmatrix}$$

$Sol := Rkadapt(IC, V_i, V_f, Npts, D)$

Fogler (2016)

$V := Sol^{\langle 1 \rangle}$ $F_A := Sol^{\langle 2 \rangle}$ $F_B := Sol^{\langle 3 \rangle}$

Example 10 - Membrane Reactor (contd.)



Equilibrium for reaction only operation

$$G(F_1) := \left[\frac{F_1}{F_{A0} + F_2} - C_1 \cdot F_2 \cdot \frac{(F_{A0} - F_1)}{(F_{A0} + F_2)^2} \right]$$

$$G(F_1) \text{ substitute }, F_2 = F_{A0} - F_1 \rightarrow \frac{F_1}{(20 - F_1)} - 4.000000000000000000 \frac{(10 - F_1)^2}{(20 - F_1)^2}$$

$$\left[\frac{F_1}{(20 - F_1)} - 4 \cdot \frac{(10 - F_1)^2}{(20 - F_1)^2} \right] \text{solve}, F_1 \rightarrow \begin{pmatrix} 10 + 2 \cdot \sqrt{5} \\ 10 - 2 \cdot \sqrt{5} \end{pmatrix}$$

Symbolic algebra

$F_{Ae} := 10 - 2 \cdot \sqrt{5}$ $\quad F_{Ae} = 5.528$

Example 11 – CSTR vs. PFR (IE, AE, IAE)

Autocatalytic Reaction

$$A + B \rightarrow 2B \qquad r = kC_A C_B$$

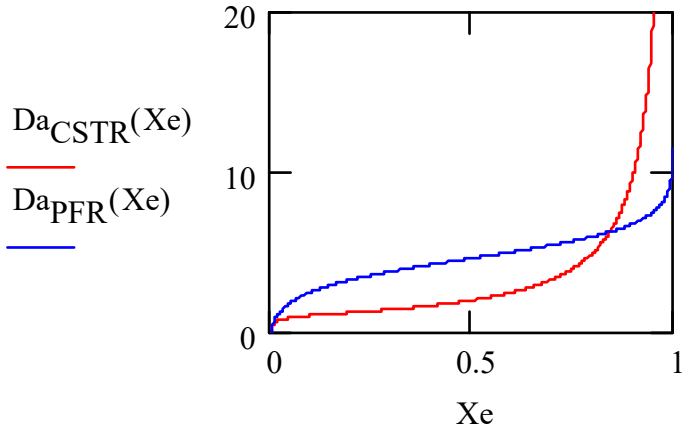
$$r = kC_{A0}{}^2 f(X),$$

$$f(X) = (1-X)(0.01+X),$$

$$Da = kC_{A0}\tau, \quad \tau = \frac{V}{v_0}.$$

$$Da_{PFR}(X_e) := \int_0^{X_e} \frac{1}{(1-X)\cdot(0.01+X)}\,dX$$

$$Da_{CSTR}(X_e) := \frac{X_e}{(1-X_e)\cdot(0.01+X_e)}$$



When is $Da_{CSTR} = Da_{PFR}$?

Iterative solution

$X_e := 0.7$

Given

$$\int_0^{X_e} \frac{1}{(1-X)\cdot(0.01+X)}\,dX - \frac{X_e}{(1-X_e)\cdot(0.01+X_e)} = 0$$

$X_c := \text{Find}(X_e)$ $\qquad X_c = 0.841$ $\qquad Da_{CSTR}(X_c) = 6.222$

Verify

$$\int_0^{X_c} \frac{1}{(1-X)\cdot(0.01+X)}\,dX - \frac{X_c}{(1-X_c)\cdot(0.01+X_c)} = -4.187\times 10^{-8}$$

Example 12 – Series-Parallel Reactions - Adiabatic (NLAEs)

$$A \xrightarrow{k_1} B, \quad C_A = \frac{C_{A0}}{(1+\tau k_1)}$$

Fogler (2016)

Energy Balance
($C_{PA} = C_{PB} = C_{PC} = C_P$)

$$B \xrightarrow{k_2} C, \quad C_B = \frac{\tau\ k_1 C_A}{(1+\tau k_2)}$$

$$C_{A0} C_P (T - T_0) + (k_1 C_A \Delta H_1 + k_2 C_B \Delta H_2)\tau = 0,$$

$$k_i = k_{i0} \exp(-\frac{E_i}{RT}), \quad i = 1,\ 2.$$

Master Equation

$$G(T) = R_m(T), \quad R_m(T) = C_P(T - T_0),$$

$$G(T) = \frac{\tau\ k_1(T)}{[1+\tau k_1(T)]}[\Delta H_1 + \Delta H_2 \frac{\tau\ k_2(T)}{\{1+\tau k_2(T)\}}].$$

Fogler (2016)

Example 12 C_P = J/{mol.K}; ΔH_1, ΔH_2 = J/mol; C_{A0} = mol/L; T_0 = K; τ = min; E_1, E_2 = cal/mol; k_1, k_2 = min^{-1}.

$C_P := 300$ $\Delta H_1 := -55000$ $\Delta H_2 := -71500$ $\tau := 0.01$

$E_1 := 9900$ $E_2 := 27000$ $C_{A0} := 0.3$ $T_0 := 300$

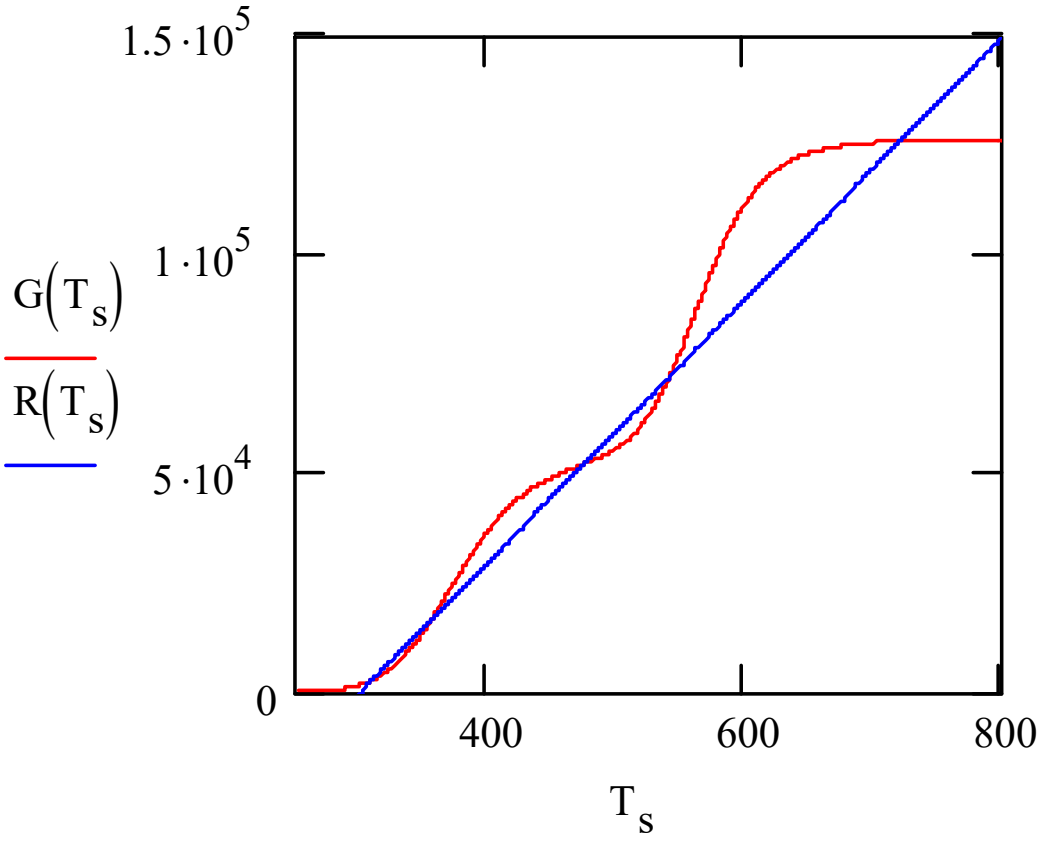
$$k_{10} := 3.3 \cdot \exp\left(\frac{E_1}{1.987} \cdot \frac{1}{300}\right) \qquad k_{20} := 4.58 \cdot \exp\left(\frac{E_2}{1.987} \cdot \frac{1}{500}\right)$$

$$k_1(T) := k_{10} \cdot \exp\left(\frac{-E_1}{1.987 \cdot T}\right) \qquad k_2(T) := k_{20} \cdot \exp\left(\frac{-E_2}{1.987 \cdot T}\right)$$

$$G(T) := \frac{-\tau \cdot k_1(T)}{\left(1 + \tau \cdot k_1(T)\right)} \cdot \left[\Delta H_1 + \Delta H_2 \cdot \frac{\tau \cdot k_2(T)}{\left(1 + \tau \cdot k_2(T)\right)}\right]$$

Example 12 - NLAEs (contd.) - Five Steady States

$$R(T) := C_P \cdot (T - T_0) \qquad dif(T) := \frac{G(T)}{R(T)} - 1.0$$



$$dif(309.59) = 6.249 \times 10^{-5}$$

$$dif(354.33) = 2.788 \times 10^{-5}$$

$$dif(473.85) = -4.697 \times 10^{-6}$$

$$dif(540.29) = -5.812 \times 10^{-6}$$

$$dif(719.58) = -1.027 \times 10^{-6}$$

Discussion

Use Matlab & Polymath in parallel to Mathcad

- **Expose students to different packages**
  - **to provide a broad spectrum of skills needed for problem solving**
  - **to observe differences in the packages' capabilities**

Use of computational software

  - **should enhance students' understanding**
  - **should enrich the logic and problem-solving skills**

- **Appropriate background on different numerical methods via instructor's handouts**
- **Some class sessions in computer laboratory**
  - **to supplement the lectures**
  - **to demonstrate applications of computing packages**
  - **to develop and enhance the skills of students in using these**
- **Integration of computational software - throughout the courses**

Closure

Computational Packages

- important tools for the future chemical and biological engineers
- enhance teaching and learning
- students appreciate the courses even more
- allow the teacher to cover more material
- develop the skills and flexibility necessary for ready adoption of different software packages for professional activities
- **Experience with Mathcad**

  - capabilities in symbolic manipulations useful in developing skills in solving complex problems

  - graphics capabilities help in visualization of results and reinforcing expected results and understanding not so expected results

- **Additional benefits**

  - time spent outside the courses on gaining further familiarity with different computational software and their applications

Thank you for your attention.

Questions & comments?