

6.6 EXPEDITING THE SOLUTION OF SYSTEMS OF NONLINEAR ALGEBRAIC EQUATIONS

6.6.1 Concepts Demonstrated

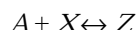
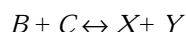
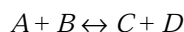
Complex chemical equilibrium calculations.

6.6.2 Numerical Methods Utilized

Solution of systems of nonlinear algebraic equations, and techniques useful for effective solutions and for examining possible multiple solutions of such systems.

6.6.3 Problem Statement

The following reactions are taking place in a constant volume, gas-phase batch reactor:



A system of algebraic equations describes the equilibrium of the preceding reactions. The nonlinear equilibrium relationships utilize the thermodynamic equilibrium expressions, and the linear relationships have been obtained from the stoichiometry of the reactions.

$$\begin{aligned} K_{C1} &= \frac{C_C C_D}{C_A C_B} & K_{C2} &= \frac{C_X C_Y}{C_B C_C} & K_{C3} &= \frac{C_Z}{C_A C_X} \\ C_A &= C_{A0} - C_D - C_Z & C_B &= C_{B0} - C_D - C_Y \\ C_C &= C_D - C_Y & C_Y &= C_X + C_Z \end{aligned} \quad (6-28)$$

In this equation set C_A , C_B , C_C , C_D , C_X , C_Y and C_Z are concentrations of the various species at equilibrium resulting from initial concentrations of only C_{A0} and C_{B0} . The equilibrium constants K_{C1} , K_{C2} and K_{C3} have known values.

Solve this system of equations when $C_{A0} = C_{B0} = 1.5$, $K_{C1} = 1.06$, $K_{C2} = 2.63$, and $K_{C3} = 5$ starting from three sets of initial estimates.

- (a) $C_D = C_X = C_Z = 0$
- (b) $C_D = C_X = C_Z = 1$
- (c) $C_D = C_X = C_Z = 10$

6.6.4 Solution and Partial Solution

The equation set (6-28) can be entered into the POLYMATH *Simultaneous Algebraic Equation Solver*; but the nonlinear equilibrium expressions must be writ-

ten as functions that are equal to zero at the solution. A simple transformation of the equilibrium expressions to the required functional form yields

$$\begin{aligned} f(C_D) &= \frac{C_C C_D}{C_A C_B} - K_{C1} \\ f(C_X) &= \frac{C_X C_Y}{C_B C_C} - K_{C2} \\ f(C_Z) &= \frac{C_Z}{C_A C_X} - K_{C3} \end{aligned} \quad (6-29)$$

The POLYMATH equation set utilizing the transformed nonlinear equations is given in Table 6-15.

Table 6-15 Polymath Program - File P6-06A.POL

Line	Equation
1	f(CD)=CC*CD/(CA*CB)-KC1
2	f(CX)=CX*CY/(CB*CC)-KC2
3	f(CZ)=CZ/(CA*CX)-KC3
4	KC1=1.06
5	CY=CX+CZ
6	KC2=2.63
7	KC3=5
8	CA0=1.5
9	CB0=1.5
10	CC=CD-CY
11	CA=CA0-CD-CZ
12	CB=CB0-CD-CY
13	CD(0)=0
14	CX(0)=0
15	CZ(0)=0

When the preceding equations are used in POLYMATH, the available algorithms will fail to solve the problem for all sets of initial estimates specified in (a), (b), and (c). An error message such as “*Error: Zero denominator not allowed*” [for part (a)] or an error message such as “*Solution did not converge*” [parts (b) and (c)] will be displayed. The failure of POLYMATH and most other programs for solving nonlinear equations is that division by unknowns makes the equations very nonlinear or sometimes undefined. The solution methods that are based on linearization (such as the Newton-Raphson method) may diverge for highly nonlinear systems or cannot continue for undefined functions.

Expediting the Solution of Nonlinear Equations

A 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 (6-29) can be modified to

$$\begin{aligned}
 f(C_D) &= C_C C_D - K_{C1} C_A C_B \\
 f(C_X) &= C_X C_Y - K_{C2} C_B C_C \\
 f(C_Z) &= C_Z - K_{C3} C_A C_X
 \end{aligned}
 \tag{6-30}$$

Using the modified nonlinear equations in POLYMATH produces the solutions summarized in Table 6-16 for the three sets of initial conditions in parts

Table 6-16 Multiple Solutions of the Chemical Equilibrium Problem

Variable	Part (a)	Part (b)	Part (c)
CD	0.705334	0.0555561	1.0701
CX	0.177792	0.59722	-0.322716
CZ	0.373977	1.08207	1.13053
CA	0.420689	0.36237	-0.700638
CB	0.242897	-0.234849	-0.377922
CC	0.153565	-1.62374	0.262286
CY	0.551769	1.67929	0.807818

(a), (b), and (c). 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 6-16 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.

This problem illustrates the desirability of entering nonlinear functions in a way in which the unknown variable will not lead to highly nonlinear behavior or division by zero. Another option to alleviate the solution of systems of algebraic equations is to convert them to a system where there is only one implicit equation, and the rest of the variables can be calculated from explicit expressions. This approach is demonstrated in Problem 6.3 although it cannot be applied to this chemical equilibrium problem.

Additionally, this problem shows that a correct numerical solution to a properly posed problem may be an infeasible solution, and thus it should be rejected as an unrealistic solution (for example negative concentrations). *In all cases where the solutions of simultaneous nonlinear equations are required, it is very important to specify initial estimates inside the feasible region and as close to the ultimate solution as possible*



The POLYMATH problem solution file for part (a) is found in the *Simultaneous Algebraic Equation Solver Library* located in directory CHAPTER 6 with file named **P6-06A1.POL**. This problem is also solved with Excel, Maple, MathCAD, MATLAB, Mathematica, and POLYMATH as problem 4 in the Set of Ten Problems discussed in Appendix F.