Solution of a System of Nonlinear Algebraic Equations (NLE) with POLYMATH and MATLAB, Parametric Studies with MATLAB

A system of nonlinear algebraic equations is defined by:

$$\mathbf{f}(\mathbf{x}) = \mathbf{0}$$

where **f** is an *n* vector of functions, **x** is an *n* vector of unknowns. Note that the number of equations is equal to the number of the unknowns.

Typical examples belonging to this category include:

❖Bubble Point, dew point and isothermal flash calculations for non-ideal multi-component mixtures

❖Adiabatic flash calculations for multi-component mixtures

❖Flow distribution in pipeline networks.

❖ Complex chemical equilibrium calculations.

❖Material and energy balance for multi-stage, multi-component systems

Complex Chemical Equilibrium – Problem Statement

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

$$A + B \leftrightarrow C + D$$
$$B + C \leftrightarrow X + Y$$
$$A + X \leftrightarrow Z$$

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.

$$K_{C1} = \frac{C_C C_D}{C_A C_B} \qquad K_{C2} = \frac{C_X C_Y}{C_B C_C} \qquad K_{C3} = \frac{C_Z}{C_A C_X}$$

$$C_A = C_{A0} - C_D - C_Z \qquad C_B = C_{B0} - C_D - C_Y$$

$$C_C = C_D - C_Y \qquad C_Y = C_X + C_Z$$

Complex Chemical Equilibrium – Problem Statement

The equilibrium coefficients K_{C1}, K_{C2} and K_{C3} can be expressed as function of the temperature (T) as

$$\ln\frac{0.7}{K_{C1}} = -2396.301\left(\frac{1}{330} - \frac{1}{T}\right)$$

$$\ln\frac{4.0}{K_{C2}} = 2421.518\left(\frac{1}{330} - \frac{1}{T}\right)$$

$$\ln\frac{(T/330)}{K_{C3}} = -8954.7\left(\frac{1}{330} - \frac{1}{T}\right)$$

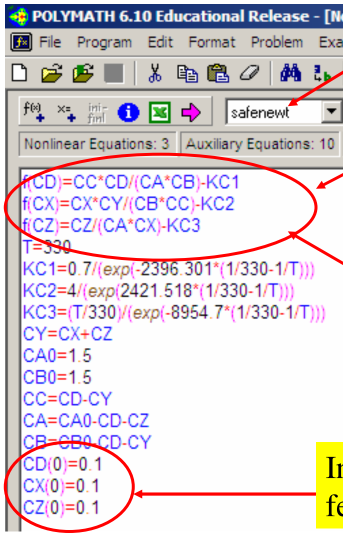
where T is the temperature (K)

Complex Chemical Equilibrium – Assignments

a. Calculate the equilibrium concentrations of all reaction components at T = 330 K. The initial concentrations of the reactants are $C_{A0} = C_{B0}$ = 1.5 g-mol/L.

b. Calculate and plot the equilibrium concentrations of all reaction components at 41 temperature values, starting from T = 330 K up to T = 370 K. The initial concentrations of the reactants are $C_{A0} = C_{B0}$ = 1.5 g-mol/L.

Complex Chemical Equilibrium – POLYMATH Code



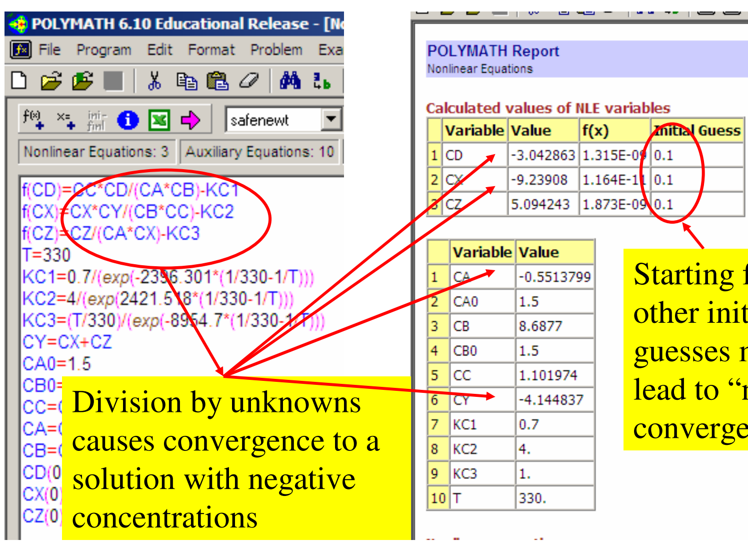
Solution algorithm

Note the particular form of the implicit equations

Divisions by the unknowns are likely to cause difficulties in the solution process

Initial guesses must be physically feasible (no negative or zero values)

Complex Chemical Equilibrium – POLYMATH Solution



	Variable	Value	f(x)	Initial Guess
1	CD	-3.042863	1.315E-09	0.1
2	CX	-9.23908	1.164E-11	0.1
3	CZ	5.094243	1.873E-09	0.1

	Variable	Value
1	CA	-0.5513799
2	CA0	1.5
3	CB	8.6877
4	CB0	1.5
5	CC	1.101974
6	CY	-4.144837
7	KC1	0.7
8	KC2	4.
9	KC3	1.
10	T	330.

Division by unknowns causes convergence to a solution with negative concentrations

Starting from other initial guesses may lead to "no convergence"

Complex Chemical Equilibrium – POLYMATH Solution

POLYMATH 6.10 Educational Release

Nonlinear Equations: 3 | Auxiliary Equations: 10

```
f(CD)=CC*CD-KC1*CA*CB
f(CX)=CX*CY-KC2*CB*CC
f(CZ)=CZ-KC3*CA*CX
T=330
KC1=0.7/(exp(-2396.301*(1/330-1/T)))
KC2=4/(exp(2421.518*(1/330-1/T)))
KC3=(T/330)/(exp(-8954.7*(1/330-1/T)))
CY=CX+CZ
CA0=1.5
CB0=1.5
CC=CD-CY
CA=CA0-CD-CZ
CB=CB0-CD-CY
CD(0)=0.1
CX(0)=0.1
CZ(0)=0.1
```

An alternative formulation (without division by the unknowns) enables convergence to the correct solution

POLYMATH Report
Nonlinear Equations

Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	CD	0.6966934	-2.117E-08	0.1
2	CX	0.3324635	-1.859E-08	0.1
3	CZ	0.2004334	1.481E-08	0.1

	Variable	Value
1	CA	0.6028733
2	CA0	1.5
3	CB	0.2704098
4	CB0	1.5
5	CC	0.1637965
6	CY	0.5328968
7	KC1	0.7
8	KC2	4.
9	KC3	1.
10	T	330.

Complex Chemical Equilibrium – A MATLAB function Generated by POLYMATH

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```
xguess = [0.1 0.1 0.1]; % initial guess vec
function fx = MNLEfun(x);
CD = x(1);
CX = x(2);
CZ = x(3);
T = 330;
KC1 = .7 / exp(-2396.301 * (1 / 330 - (1 / T)));
KC2 = 4 / exp(2421.518 * (1 / 330 - (1 / T)));
KC3 = T / 330 / exp(-8954.7 * (1 / 330 - (1 / T)));
CY = CX + CZ;
CA0 = 1.5;
CB0 = 1.5;
CC = CD - CY;
CA = CA0 - CD - CZ;
CB = CB0 - CD - CY;
fx(1,1) = CC * CD - (KC1 * CA * CB);
fx(2,1) = CX * CY - (KC2 * CB * CC);
fx(3,1) = CZ - (KC3 * CA * CX);
```

Initial guess is put into a row vector

Input parameters are transferred to the function in an array

Output parameters are should be placed into a column vector

Template for solving an NLE System*

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```
function % Insert here your file name after function (Use Alphanumberic names only)
clear, clc, format short g, format compact
xguess=   % Replace this line with the xguess line(s) from Polymath report.
disp('Variable values at the initial estimate');
fguess=MNLEfun(xguess);
disp(' Variable    Value   Function Value')
for i=1:size(xguess,2);
disp([' x' int2str(i) '        ' num2str(xguess(i)) '       ' num2str(fguess(i))]);
end
options = optimset('Diagnostics',['off'],'TolFun',[1e-9],'TolX',[1e-9]);
xsolv=fsolve(@MNLEfun,xguess,options);
disp('Variable values at the solution');
fsolv=MNLEfun(xsolv);
disp(' Variable    Value   Function Value')
for i=1:size(xguess,2);
disp([' x' int2str(i) '         ' num2str(xsolv(i
end
%---------------------
% Replace this and the following line with the function copied from the Polymath report
% Do not include the xguess line(s)
```

The MATLAB library function *fsolve* is used to solve the NLE system (in optimization toolbox)

*Available in the HELP section of POLYMATH

Complex Chemical Equilibrium – Modifying the Template for Parametric Runs

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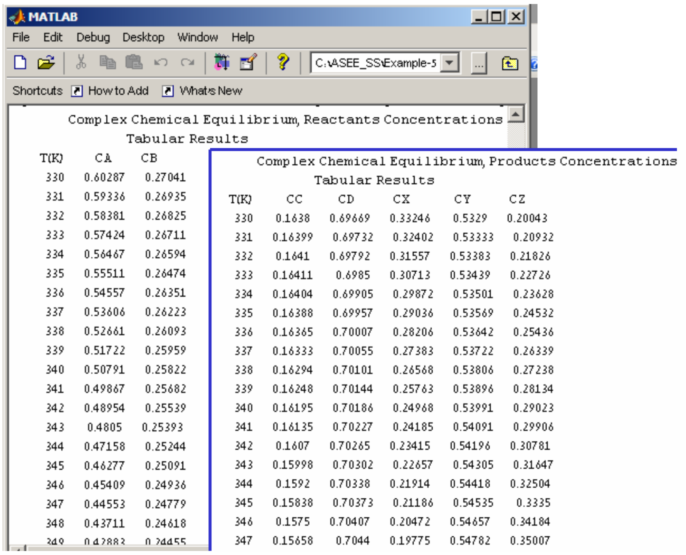
```
function Example5B
clear, clc, format short g, format compact
xguess = [0.1 0.1 0.1]; % initial guess vector
options = optimset('Diagnostics',['off'],'TolFun',[1e-9],'TolX',[1e-9]);
CA0 = 1.5;
CB0 = 1.5;
for i=1:41
  T(i,1)=330+(i-1);
  xsolv=fsolve(@MNLEfun,xguess,options,T(i));
  xguess=xsolv;
  CD(i,1)=xsolv(1);
  CX(i,1)=xsolv(2);
  CZ(i,1)=xsolv(3);
  CY (i,1)= CX (i)+ CZ(i);
  CC(i,1) = CD(i) - CY(i);
  CA(i,1) = CA0 - CD(i) - CZ(i);
  CB(i,1) = CB0 - CD(i) - CY(i);
end
disp('         Complex Chemical Equilibrium, Reactants Concentrations');
disp('                  Tabular Results');
```

Input *T* as a parameter into the function

Use the current solution as initial guess for the next *T* value

Complex Chemical Equilibrium – Results of Parametric Runs



File Edit Debug Desktop Window Help

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Shortcuts How to Add What's New

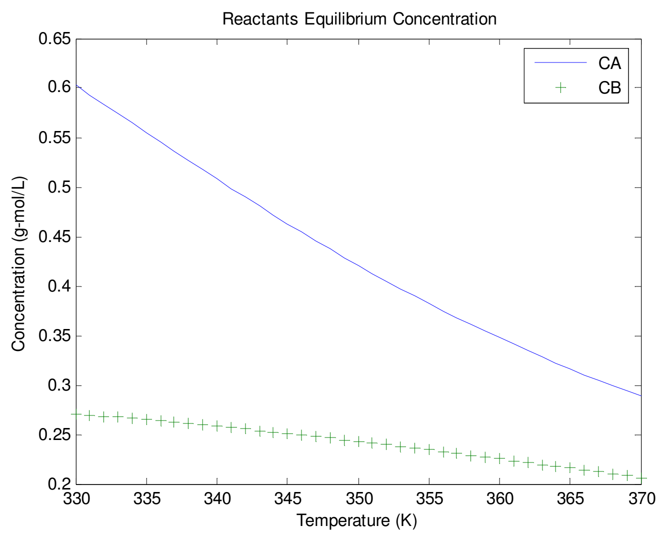
Complex Chemical Equilibrium, Reactants Concentrations
Tabular Results

T(K)	CA	CB
330	0.60287	0.27041
331	0.59336	0.26935
332	0.58381	0.26825
333	0.57424	0.26711
334	0.56467	0.26594
335	0.55511	0.26474
336	0.54557	0.26351
337	0.53606	0.26223
338	0.52661	0.26093
339	0.51722	0.25959
340	0.50791	0.25822
341	0.49867	0.25682
342	0.48954	0.25539
343	0.4805	0.25393
344	0.47158	0.25244
345	0.46277	0.25091
346	0.45409	0.24936
347	0.44553	0.24779
348	0.43711	0.24618
349	0.42883	0.24455

Complex Chemical Equilibrium, Products Concentrations
Tabular Results

T(K)	CC	CD	CX	CY	CZ
330	0.1638	0.69669	0.33246	0.5329	0.20043
331	0.16399	0.69732	0.32402	0.53333	0.20932
332	0.1641	0.69792	0.31557	0.53383	0.21826
333	0.16411	0.6985	0.30713	0.53439	0.22726
334	0.16404	0.69905	0.29872	0.53501	0.23628
335	0.16388	0.69957	0.29036	0.53569	0.24532
336	0.16365	0.70007	0.28206	0.53642	0.25436
337	0.16333	0.70055	0.27383	0.53722	0.26339
338	0.16294	0.70101	0.26568	0.53806	0.27238
339	0.16248	0.70144	0.25763	0.53896	0.28134
340	0.16195	0.70186	0.24968	0.53991	0.29023
341	0.16135	0.70227	0.24185	0.54091	0.29906
342	0.1607	0.70265	0.23415	0.54196	0.30781
343	0.15998	0.70302	0.22657	0.54305	0.31647
344	0.1592	0.70338	0.21914	0.54418	0.32504
345	0.15838	0.70373	0.21186	0.54535	0.3335
346	0.1575	0.70407	0.20472	0.54657	0.34184
347	0.15658	0.7044	0.19775	0.54782	0.35007

Complex Chemical Equilibrium – Results of Parametric Runs



Complex Chemical Equilibrium – Results of Parametric Runs