Solution of a System of ODEs with POLYMATH and MATLAB, Boundary Value Iterations with MATLAB

For a system of *n* simultaneous first-order ODEs:

$$\frac{dy_1}{dx} = f_1(y_1, y_2, \dots y_n, x)$$
$$\frac{dy_2}{dx} = f_2(y_1, y_2, \dots y_n, x)$$
$$\vdots$$
$$\frac{dy_n}{dx} = f_n(y_1, y_2, \dots y_n, x)$$

where x is the independent variable and $y_1, y_2, \dots y_n$ are dependent variables

Some initial and some final values of the dependent variables are specified and some of the problem parameters may not be known. Such a problem is a ***boundary value problem*** and iterative methods should be used to identify the unknown initial values and/or problem parameters

Simultaneous Multicomponent Diffusion of Gases

Gases A and B are diffusing through stagnant gas C between two points 1 and 2 where the compositions and distance apart are known. Calculate and plot the concentration profiles and determine the molar fluxes.

Component	Point 1 Concentration kg-mol/m^3	Point 2 Concentration kg-mol/m^3	Diffusivities at 0.2 atm m^2/s
A	2.229×10^{-4}	0	$D_{AC} = 1.075 \times 10^{-4}$
B	0	2.701×10^{-3}	$D_{BC} = 1.245 \times 10^{-4}$
C	7.208×10^{-3}	4.730×10^{-3}	$D_{AB} = 1.47 \times 10^{-4}$

Simultaneous Multicomponent Diffusion of Gases

The Stefan-Maxwell equations describe this multi-component diffusion process

$$\frac{dC_A}{dz} = \frac{(x_A N_B - x_B N_A)}{D_{AB}} + \frac{(x_A N_C - x_C N_A)}{D_{AC}}$$

$$\frac{dC_B}{dz} = \frac{(x_B N_A - x_A N_B)}{D_{AB}} + \frac{(x_B N_C - x_C N_B)}{D_{BC}}$$

$$\frac{dC_C}{dz} = \frac{(x_C N_A - x_A N_C)}{D_{AC}} + \frac{(x_C N_B - x_B N_C)}{D_{BC}}$$

where

$$D_{BA} = D_{AB},\ D_{CA} = D_{AC},\ \text{and}\ D_{CB} = D_{BC}$$

Simultaneous Multicomponent Diffusion of Gases

$$\frac{dC_A}{dz} = \frac{(x_A N_B - x_B N_A)}{D_{AB}} + \frac{(x_A N_C - x_C N_A)}{D_{AC}}$$

The parameters N_A and N_B (the molar fluxes of components A and B respectively) are unknown. They can be calculated using the **boundary conditions: at point 2 (z = 0.001m) CA = 0 and CB = 2.701.**

Estimates of NA and NB can be obtained from application of the Fick's law assuming simple binary diffusion. Estimates for N_A and N_B can be obtained from:

$$N_A = -D_{AC}\frac{(C_A|_2 - C_A|_1)}{(z|_2 - z|_1)} = -1.075 \times 10^{-4}\frac{(0 - 2.229 \times 10^{-4})}{(0.001 - 0)} = 2.396 \times 10^{-5}$$

$$N_B = -D_{BC}\frac{(C_B|_2 - C_B|_1)}{(z|_2 - z|_1)} = -1.245 \times 10^{-4}\frac{(2.701 \times 10^{-3} - 0)}{(0.001 - 0)} = -3.363 \times 10^{-4}$$

Simultaneous Multi-Component Diffusion of Gases – POLYMATH Code

No.	Equation # Comment
1	d(CA)/d(z) = (xA * NB - xB * NA) / DAB + (xA * NC - xC * NA) / DAC # Concentration of A (g-mol/L)
2	d(CB)/d(z) = (xB * NA - xA * NB) / DAB + (xB * NC - xC * NB) / DBC # Concentration of B (g-mol/L)
3	d(CC)/d(z) = (xC * NA - xA * NC) / DAC + (xC * NB - xB * NC) / DBC # Concentration of C (g-mol/L)
4	NB = -0.0003363 # Molal flux of component B (kg-mol/m^2*s)
5	NA = 2.396e-5 # Molal flux of component A (kg-mol/m^2*s)
6	DAB = 1.47e-4 # Diffusivity of A through B (m^2/s)
7	NC = 0 # Molal flux of stagnant component C (kg-mol/m^2*s)
8	DAC = 1.075e-4# Diffusivity of A through C (m^2/s)
9	DBC = 1.245e-4 # Diffusivity of B through C (m^2/s)
10	CT = 0.2 / (82.057e-3 * 328) # Gas concentration g-mol/L
11	xA = CA / CT # Mole fraction of A
12	xB = CB / CT # Mole fraction of B
13	xC = CC / CT # Mole fraction of C
14	z(0) = 0 # Length coordinate at point 1
15	CB(0) = 0 # Concentration of B at point 1
16	CA(0) = 0.0002229 # Concentration of A at point 1
17	CC(0) = 0.007208 # Concentration of C at point 1
18	z(f) = 0.001 # Length coordinate at point 2

Estimated Values

Simultaneous Multi-Component Diffusion of Gases – POLYMATH Solution for Estimated N_A and N_B values

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	CA	0.0002229	-1.692E-05	0.0002229	-1.692E-05
2	CB	0	0	0.002284	0.002284
3	CC	0.007208	0.0051638	0.007208	0.0051638
15	xC	0.9700056	0.6949123	0.9700056	0.6949123
16	z	0	0	0.001	0.001

No match between the specified and calculated final values

Component	Point 1 Concentration kg-mol/m^3	Point 2 Concentration kg-mol/m^3
A	2.229×10^{-4}	0
B	0	2.701×10^{-3}
C	7.208×10^{-3}	4.730×10^{-3}

Application of the Newton-Raphson Method for the Solution of Two Point Boundary Value Problems

Let us define **x** as the vector of unknown parameters (in this particular case $\mathbf{x} = (N_A\ N_B)^T$) and **f** as a vector of functions representing the difference between the desired and calculated concentration values as point 2 , thus

$$\mathbf{f} = \begin{bmatrix} C_A|_2 - 0 \\ C_B|_2 - 2.701\times 10^{-3} \end{bmatrix}$$

The Newton-Raphson Method using Forward Difference to Calculate the Derivatives

The Newton-Raphson (NR) method can be written

$$\mathbf{x}_{k+1} = \mathbf{x}_k - \frac{\partial \mathbf{f}}{\partial \mathbf{x}}^{-1} \mathbf{f}(\mathbf{x}_k) \quad k = 0, 1, 2\ldots$$

where k is the iteration number, $\mathbf{x}_0$ is the initial estimate and $\partial\mathbf{f}/\partial\mathbf{x}$ is the matrix of partial derivatives at $\mathbf{x} = \mathbf{x}_k$. The matrix of partial derivatives can be calculated using forward differences, thus

$$\frac{\partial f_i}{\partial x_j} = \frac{f_i(\mathbf{x}_k + \boldsymbol{\delta}_j) - f_i(\mathbf{x}_k)}{\delta_j} \quad i = 1, 2; \quad j = 1, 2$$

where $\boldsymbol{\delta}_j$ is a vector containing the value of δ_j at the j^{th} position and zeroes elsewhere..

Simultaneous Multi-Component Diffusion of Gases – A MATLAB function Generated by POLYMATH

Editor - C:\ASEE_SS\Example-6\MultDiffusA.m

```
function dYfuncvecdz = ODEfun(z,Yfuncvec);
CA = Yfuncvec(1);
CB = Yfuncvec(2);
CC = Yfuncvec(3);
NB = -.0003363; % Molal flux of component B (kg-mol/m^2*s)
NA = .00002396; % Molal flux of component A (kg-mol/m^2*s)
DAB = .000147; % Diffusivity of A through B (m^2/s)
NC = 0; % Molal flux of stagnant component A (kg-mol/m^2*s)
DAC = .0001075; % Diffusivity of A through C (m^2/s)
DBC = .0001245; % Diffusivity of B through C (m^2/s)
CT = .2 / (.082057 * 328); % Gas concentration g-m
xA = CA / CT; % Mole fraction of A
xB = CB / CT; % Mole fraction of B
xC = CC / CT; % Mole fraction of C
dCAdz = (xA * NB - (xB * NA)) / DAB + (xA * NC - (xC * NA)) / DAC; % Concentration of A (g-mol/L)
dCBdz = (xB * NA - (xA * NB)) / DAB + (xB * NC - (xC * NB)) / DBC; % Concentration of B (g-mol/L)
dCCdz = (xC * NA - (xA * NC)) / DAC + (xC * NB - (xB * NC)) / DBC; % Concentration of C (g-mol/L)
dYfuncvecdz = [dCAdz; dCBdz; dCCdz];
```

Input parameters are transferred to the function in an array

Output parameters should be placed into a column vector

Template for solving an ODE System*

Editor - C:\ASEE_SS\Example-6\MultDiffusA.m*

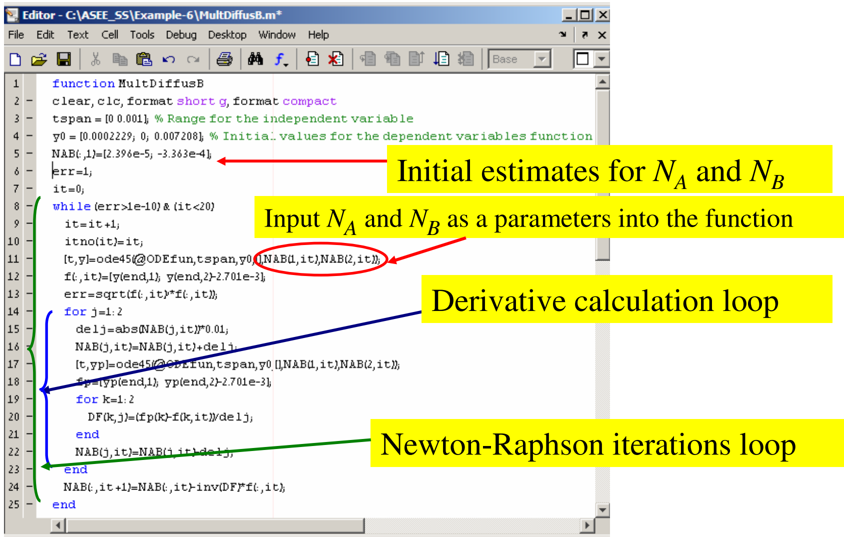
```
function MultDiffusA
clear, clc, format short g, format compact
tspan = [0 0.001]; % Range for the independent
y0 = [0.0002229; 0; 0.007208]; % Initial values for the dependent variables function
disp(' Variable values at the initial point ');
disp([' t  = ' num2str(tspan(1))]);
disp('      y          dy/dt      ');
disp([y0 ODEfun(tspan(1),y0)]);
[t,y]=ode45(@ODEfun,tspan,y0);
for i=1:size(y,2)
  disp([' Solution for dependent variable y' int2str(i)]);
  disp(['        t            y' int2str(i)]);
  disp([t y(:,i)]);
  plot(t,y(:,i));
  title([' Plot of dependent variable y' int2str(i)]);
  xlabel(' Independent variable (t)');
  ylabel([' Dependent variable y' int2str(i)]);
  pause
end
```

Data Generated by POLYMATH

The MATLAB library function *ode45* is used to solve the ODE system

*Available in the HELP section of POLYMATH

Simultaneous Multi-Component Diffusion of Gases – Newton-Rapson Iterations for Identifying the Parameters



Multi-Component Diffusion – Results of Parameter Values

Note that five NR iterations, as shown below, are required for convergence with error tolerance of $\varepsilon_d = 10^{-10}$. The iterations of the NR method are stopped when

$$\left\|\mathbf{f}(\mathbf{x}_k)\right\| \le \varepsilon_d$$

and where ε_d is the desired error tolerance set at $1\text{x}10^{-10}$.

The converged solution values are N_A = 2.1149e-5 and N_B = -4.1425e-4. Using these solution values, the difference between the calculated and desired values of C_A and C_B at point 2 are $<10^{-10}$.

Iteration No.	N_A	N_B	f_1	f_2
0	2.3960E-05	3.3630E-04	3.35E-05	-5.99E-03
1	2.2076E-05	-1.7614E-04	7.53E-06	-1.40E-03
2	2.1252E-05	-3.8575E-04	8.52E-07	-1.49E-04
3	2.1150E-05	-4.1375E-04	1.77E-08	-2.56E-06
4	2.1149E-05	-4.1424E-04	7.05E-11	-6.41E-09
5	2.1149E-05	-4.1425E-04	1.67E-13	-1.43E-11