1 Matlab solution to diffusion-reaction problems

Diffusion-Reaction problems are very common in chemical reaction engineering and often numerical solutions are needed. Here we look at using matlab to obtain such solutions and get results of design interest. Consider a model problem represented as:

$$\frac{d^2c}{dx^2} = f(c) \tag{1}$$

which is a dimensionless form of the diffusion with reaction problem. Here $f(c)$ is a measure of the reaction rate; For example, $f(c) = \phi^2 c$ for a first order reaction where ϕ is the Thiele modulus. The variable x is a dimensionless distance along the pore. The point $x = 0$ is taken as the pore mouth and $x = 1$ pore end. The boundary conditions are taken as follows:

At $x = 0$, the dimensionless concentration, $c = 1$.

At $x = 1$, the gradient of the conncentration, $dc/dx = 0$.

We use the matlab program bvp4c to solve this problem. This requires that the Eqn. (1) be written as two first order equations rather than as a single second order differential equation. This can be done as follows: Consider a solution vector $\vec{y}$ with components y_1 and y_2 defined as follows:

$$y_1 = c \text{ and } y_2 = dc/dx \tag{2}$$

Eqn. (1) is then equivalent to the following two first order equations.

$$\frac{dy_1}{dx} = y_2 (= dc/dx) \tag{3}$$

and

$$\frac{dy_2}{dx} = f(y_1) = (d^2c/dx^2) \tag{4}$$

The boundary conditions are as follows:

$$\text{at x= 0; } y_1 = 1 \text{ Pore mouth} \tag{5}$$

and

$$\text{at x = 1 } y_2 = 0 \text{ Pore end} \tag{6}$$

The solution for the concentration profile and also for the local values of the gradient can then be obtained using the function bvp4d in matlab. The

effectiveness factor is related to the gradient at the pore mouth and is calculated as:

$$\eta = -y_2(0)/\phi^2 \qquad (7)$$

The sample code for solving this problem is as follows:

```
-----------------------------------------------------------------------------------
% program calculates the concentration profiles and the effectiveness
% factor for m-th order reaction in  a slab geometry.
global phi m phi2 n
global eta

% user actions, Specify parameters, a guess function for trial solution, a
% function odes to define the set of first order differential equations
% and a function bcs to specify the boundary conditions.
phi = 2.0 ;   % thiele modulus for first reaction
m =2.0 ;       % order of reaction
nmesh = 21  % intial mesh
nplot = nmesh ;  % meshes for plotting the result.
% solution block.
x = linspace ( 0, 1, nmesh ) ;
solinit =bvpinit ( x , @guess ) % trial solution given by guess function
sol = bvp4c (@odes, @bcs, solinit) % bvp solved,
% post processing. plot concentration profiles, find eta
 x = linspace ( 0, 1, nplot) ;
 y = deval(sol, x) ;
 y(1,:) % concentration profiles displayed
 plot ( x, y(1,:) ) ; % these are plotted.
 eta = -y(2,1) / phi^2
%_____
function yinit = guess (x)
% provides a trial solution to start off
global phi m phi2 n
y1= exp(-phi*x)
y2= 0. * y1
yinit = [y1
          y2 ] ;
%-------------------------------------------------------
function dydx = odes ( x, y )
% defines the rhs of set of first order differential equations
global phi m phi2 n

dydx = [  y(2)
          phi^2 * y(1)^m
      ] ;
%-------------------------------------------------------
function res = bcs ( ya , yb)
```
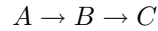
```
% provides the boundary conditions at the end points a and b
res = [ ya(1) - 1
        yb(2) ] ;
```

It is fairly easy to extend the code to multiple reactions. As an example consider a series reaction represented as:

$$A \rightarrow B \rightarrow C$$

The governing equations are as follows assuming both reactions to be first order.

$$\frac{d^2 c_A}{dx^2} = \phi_1^2 c_A \tag{8}$$

$$\frac{d^2 c_B}{dx^2} = -\phi_1^2 c_A + \phi_2^2 c_B \tag{9}$$

The boundary condition at $x = 0$ (pore mouth) depend on the bulk concentrations of A and B. The boundary condition at $x = 1$ (pore end) is the no flux condition for both A and B.

The solution vector y has size of four and consists of:

$$\vec{y} = \begin{pmatrix} y_1 = c_A \\ y_2 = dc_A/dx \\ y_3 = c_B \\ y_4 = dc_B/dx \end{pmatrix} \tag{10}$$

The system is now formulated as four first order ODEs for the four components of the solution vector and solved by bvp4c in exactly the same way. Details are left out as homework problem.

An important consideration in this type of problem is how the selectivity is affected by pore diffusion. The yield of B is defined as:

Yield = flux of B out of the pore mouth / flux of A into the pore

which can be stated as:

$$\text{Yield} = -(dc_b/dx)_{x=0}/(dc_a/dx)_{x=0} \tag{11}$$

The relative concentration gradients of A and B at the pore mouth deterimines the local yield of B. A smaller catalyst size is favrobale to B production. A larger paricle traps B in the interior of the pores allowing it to react further and form C. This reduces the yield.

Maximum yield $= (k_1 C_{A0} - k_2 C_{B0})/k_1 C_{A0}$ which is also equal to

$$\text{maximum yield} = 1 - \frac{k_2 C_{B0}}{k_1 C_{A0}}$$

Pore diffusion resistance causes the yield to decrease from the above maximum value. Maximum yield is realized only at low values of the Thiele parameters.

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Example simulated with matlab for a particular case illustartes this point. Also $c_{a0} = 1$ and $c_{b0} = 0$ which may correspong to the inlet of the reactor (with no recycle).

Consider $\phi_1 = 2$ and $\phi_2 = 1$. Yield is found as 0.8067.

Now let the catalyst size be reduced to one half the original size. Then both ϕ_1 and ϕ_2 decrease. The new value of yield is found to be 0.8764. Maximum yield is 1 for this case. The pore diffusion resistance has decreased the yield. Students should verify these using matlab.

2 Solution For gas-liquid reactions

$$A(g->l) + \nu B(l) \rightarrow \text{ Products}$$
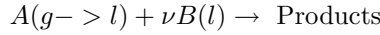
Governing equations are as follows:

$$D_A \frac{d^2 C_A}{dx^2} = k_2 C_A C_B \tag{12}$$

$$D_B \frac{d^2 C_B}{dx^2} = \nu k_2 C_A C_B \tag{13}$$

Here x is the acutal distance into the flim with $x = 0$ representing the gas-liquid interface.

We now introduce the following dimensionless parameters.

$$a = C_A / C_A^*$$

where C_A^* is the equilibrium solubility of gas A in the liquid corresponding to the partial pressure of A in th bulk gas.

$C_A^* = p_{gA}/H_A$ where H_A is the Henry's law constant for the species A.

$$b = C_B / C_{Bl}$$

where c_{Bl} is bulk liquid concentration of B.

Finally let ζ be the dimensional distance in the film $(= x/\delta)$. With these variables. the governing equations are the following:

$$\frac{d^2 a}{d\zeta^2} = Ha^2 ab \tag{14}$$

$$\frac{d^2 a}{d\zeta^2} = Ha^2 ab/q \tag{15}$$

where HA and q are two dimensionless quantities.

$$Ha^2 = \delta^2 \frac{k_2 C_{Bl}}{D_A}$$

and

$$q = \frac{D_B C_{BL}}{\nu D_A C_A^*}$$

Noting that $k_L = D_A/\delta$, the Hatta number can also be expressed as:

$$Ha^2 = \frac{D_A k_2 C_{Bl}}{k_L^2} \tag{16}$$

The boundary conditions for species A are as follows:

Case 1: No gas flim resistance:

At $\zeta = 0$, $C_A = C_A^*$ and Hence $a = 1$.

At $\zeta = 1$, $C_A = C_{AL}$ is some specified value depending on the bulk processes. In other words, C_{AL} will depend on the extent of bulk reactions, convective and dispersive flow into the bulk etc. But even for moderately fast reactions, the bulk concentration of dissolved gas turns out be zero and we take this value to be zero. Hence $a = 0$ at $\zeta = 1$ will be used as the second boudnary condition. The validity of this assumption can be checked after a solution is obtained and modified if needed.

Case 2: Gas film resistance included. A balance over the gas film provides the boundary condition:

$$k_g(p_{gA} - p_{iA}) = -D_A \frac{dC_A}{dx} \tag{17}$$

Also note that p_{iA} the interfacial partial pressure of A is related to the interfacial concentration of A in the liquid by Henry's law. Thus $C_A(x = 0) = P_{ia}/H$. Using these the boundary condition can be expressed in dimensionless form as

$$Bi_g(1 - a_{\zeta=0}) = -\left(\frac{da}{d\zeta}\right)_{\zeta=0} \tag{18}$$

where $Bi_G = k_g H/k_L$, A biot number for gas side mass transfer. The boundary condition is now of the Robin type. The boundary conditon at $\zeta = 1$ is the same as before. (take as $a = 0$ if the reactions are reasonably fast. Otherwise a need a mass balance for A in the bulk liquid as well.)

The boundary condition for species B are specified as follows:

At $\zeta = 0$ we use $db/d\zeta = 0$ since B is non-volatile and the flux is therefore zero.

At $\zeta = 1$, we have $b = 1$. This completes the problem definition. In order to solve this using matlab, the governing (two) equations are cast as four first order differential equation. The solution vector $\vec{y}$ is now given by:

$$\vec{y} = \begin{pmatrix} y_1 = a \\ y_2 = da/d\zeta \\ y_3 = b \\ y_4 = db/d\zeta \end{pmatrix} \tag{19}$$

The matlab program to do these calculations is shown below. The program structure is similar to Thiele. Note that A and B are counterdiffusing in this

case and the boundary condition section reflects these changes. The program can be used to calculate the rate of absorption or to learn how the regime of absorption changes with dimensionless parameters. Thus the program is an effective learning tool. In the following sections, these features are illustrated.

```
function hatta
% program calculates the concentration profiles  for gas A
% and liquid reactant B in the film.
%  11-1-03 P. A. Ramachandran
global  m q  bi_gas
% The dimensionless parameters are calculated in a separate function.
% m  = Hatta number, q = q parameter, bi_Gas = Biot number for gas.
t = 1.0 ;  % a dummy parameter
 [ m , q , bi_gas ] = calculate_these ( t ) ;
%  numerical solution.
nmesh = 21  % intial mesh
nplot = nmesh ;  % meshes for plotting the result.
% solution block.
x = linspace ( 0, 1, nmesh ) ;
solinit =bvpinit ( x , @guess ) % trial solution generated by guess function
sol = bvp4c (@odes, @bcs, solinit) % bvp solved,
% post processing. plot concentration profiles, find eta
 x = linspace ( 0, 1, nplot) ;
 y = deval(sol, x) ;
 y(1,:) % concentration profiles displayed
 y(3,:) % concentration profile of B
 plot ( x, y(1,:) ) ; hold on ; plot (x, y(3,:) ) % these are plotted.
 EnhanceFactor = -y(2,1)
 b_interface = y(3,1)
 bi = 1. + 1/q - EnhanceFactor /q
%_____
function yinit = guess (x)

global  m q bi_gas


y1= exp(-m*x)

y2= 0. * y1
yinit = [y1
         y2
         y2
          y2] ; % some arbitrary guess values here
%-------------------------------------------------------
function dydx = odes ( x, y )
```

```
global  m q bi_gas

dydx = [ y(2)
          (m^2 * y(1)* y(3)  )
          y(4)
      (m^2 * y(1)* y(3) )/q ] ;
%-------------------------------------------------------------
function res = bcs ( ya , yb)
% This is set up for na gas film resistance.
res = [ (ya(1) - 1)
         (ya(4))
         (yb(1)  )
         (yb(3) -1) ] ;
%_____
function [ m , q , bi_gas ] = calculate_these ( t )

da = 1.40e-09 ;
k2= 10.02;
db = 0.77e-09 ;
kl = 2.2e-04;
b0 = 1000. ;
astar = 6.25 ;
msq = da* k2 * b0 / kl^2
m = msq^(0.5)
db = 0.77e-09;
z = 2. ;
q = db * b0 / ( z * da* astar  )
bi_gas = 1000.0;  % assigned here.
--------------------------------------------------------------------
```

A result of sample simulation fixing q and varying Hatta is shown in Figure 1.

The effect of large Hatta is shown in figure 2 where the reaction approaches an instantaneous asymptote.

$$E_\infty = 1 + 1$$

Example; H_2S Removal

Lo-Cat is a process for removing H_2S from refinery flue gases and uses a chelated $Fe(3+) - EDTA$ solution. A simple representation of the reaction is:

$$H_2S + 2Fe^{+3} \rightarrow 2H^+ + S^0 + Fe^{+2}$$
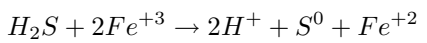
Find the rate of absorption of H2S if the partial pressure in the gas phase is 0.05 atm and the concentration of Fe^{+++} in the liquid is 60 mol/m^3.

The kinetic rate constant is 9m^3 /mol. s (A second order reaction).
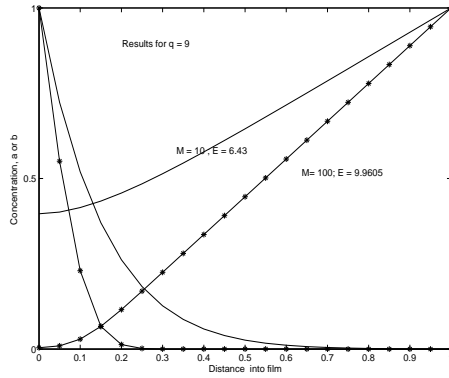
The diffusion coefficients in the liquid are:

Figure 1: Concentration profiles for dissolved gas A and liquid phase reactant B for two values of Hatta number for a fixed value of q. Note that the species B depletes more in the flim for larger value of $M = Ha$,

$D_A = 1.44 \times 10^{-9} m^2/s$

$D_B = 0.54 \times 10^{-9} m^2/s.$

Henry' law coefficient is 1950 Pa/mol m^3

Liquid side mass transfer coefficient, $k_L = 2 \times 10^{-4} m/s$,.

Solution:

The equilibrium concentration of H2S at the interface $= C_A^* = p_{gA}/H = 2.56$ mol/m^3. The q parameter is calculated as:

$$q = \frac{D_B C_{BL}}{\nu D_A C_A^*} = 4.4$$

The Hatta number is calculated as:

$$Ha = \frac{\sqrt{D_A k_2 C_B l}}{k_L} = 4.4$$

Running the Matlab program Hatta.m for these parameters gives the enhancement factor as 3.12. The program also gives the complete concentration profiles for H_2S abnd $Fe - EDTA$ complex in the film.

Using the calculated enhancement factor, thh rate of absorption is calculated as;

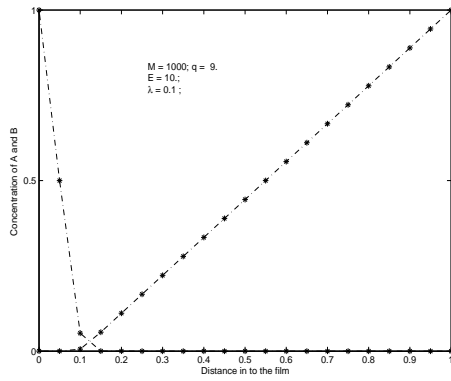Rate of absorption per unit interfacial area $= k_L C_A^* E = 0.0016 mol/m^2 s.$

Figure 2: Concentration profiles for dissolved gas A and liquid phase reactant B for a large values of Hatta number for a fixed value of q. The reaction is now instantaneous; Note that the reaction is now confined to a narrow zone.