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:

\[ \frac{d^2c}{dx^2} = f(c) \]  

(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 \( \phi \) 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 concentration, \( dc/dx = 0 \).

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:

\[ y_1 = c \text{ and } y_2 = dc/dx \]  

(2)

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

\[ \frac{dy_1}{dx} = y_2(= dc/dx) \]  

(3)

and

\[ \frac{dy_2}{dx} = f(y_1) = (d^2c/dx^2) \]  

(4)

The boundary conditions are as follows:

at \( x = 0 \); \( y_1 = 1 \) Pore mouth

(5)

and

at \( x = 1 \); \( y_2 = 0 \) Pore end

(6)

The solution for the concentration profile and also for the local values of the gradient can then be obtained using the function bvp4c in matlab. The effectiveness factor is related to the gradient at the pore mouth and is calculated as:

\[ \eta = -y_2(0)/\phi^2 \]  

(7)

(verify)

The sample code for solving this problem is as follows:

```matlab
% 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
```
% a function odes to define the set of first order differential equations
% and a function bcs to specify the boundary conditions.
% Also define a function to provide initial starting solutions.
phi = 2.0 ; % thiele modulus for first reaction
m = 2.0 ; % order of reaction
n mesh = 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
       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.
\[
\frac{d^2c_A}{dx^2} = \phi_1^2 c_A \quad (8)
\]
\[
\frac{d^2c_B}{dx^2} = -\phi_1^2 c_A + \phi_2^2 c_B \quad (9)
\]
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:

\[
\vec{y} = \begin{pmatrix}
y_1 = c_A \\
y_2 = dc_A/dx \\
y_3 = c_B \\
y_4 = dc_B/dx
\end{pmatrix}
\] (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:

\[
\text{Yield} = \frac{\text{flux of B out of the pore mouth}}{\text{flux of A into the pore}}
\]

which can be stated as:

\[
\text{Yield} = -\frac{(dc_b/dx)_{x=0}}{(dc_a/dx)_{x=0}}
\] (11)

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

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

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

with \( C_{A0} \) and \( C_{B0} \) representing the pore mouth concentrations.

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.

Example simulated with matlab for a particular case illustrates this point. ).

Consider \( \phi_1 = 2 \) and \( \phi_2 = 1 \). Also \( c_{a0} = 1 \) and \( c_{b0} = 0 \) which may correspond to the inlet of the reactor (with no recycle). Yield is found as 0.8067.

Now let the catalyst size be reduced to one half the original size. Then both \( \phi_1 \) and \( \phi_2 \) decrease. The new value of yield is found to be 0.8764. Maximum yield is 1 for both of these cases. The pore diffusion resistance has decreased the yield but the reduction is even more for the larger particles.

Students should verify these using matlab.

2 Asymptotic Solution to diffusion-reaction problems

For a single non-linear reaction problem, a solution can be obtained analytically for large values of Thiele modulus. This asymptotic solution can then be used to define a generalized Thiele modulus and can be extended to obtain approximate analytical solutions even for low Thiele modulus. This avoids solution by numerical methods and is useful in reactor design where repeated calculation of the effectiveness factor at different points in the reactor is often needed. The procedure is illustrated below.

Consider a model problem represented as:

\[
D_e \frac{d^2c}{dx^2} = f(C)
\] (12)
where \( f(C) \) is the rate (dimensional) of consumption of species. The order of the differential equation can be reduced by one by using the transformation \( p = \frac{dC}{dx} \). Noting that

\[
\frac{d^2C}{dx^2} = p \frac{dp}{dC}
\]  

we find that Eq. (12) can be written as

\[
D_e p \frac{dp}{dC} = f(C)
\]  

The above equation can be solved by separation of variables. Two limits are needed to obtain the value of the concentration gradient at the surface, \( p_s \). At the pore end, the value of the gradient \( p \) is zero. Also for large values of Thiele modulus the concentration drops to nearly zero at some interior point in the catalyst. Hence the concentration can be set as zero at the pore end. Thus we can set \( C = 0 \) at \( p = 0 \) as one of the limits for integration of Eqn. (14). Let the surface gradient be designated as \( p_s \) and the concentration at the surface as \( c_s \). This sets another limit for integration of Eqn 13 which can be now be written as:

\[
D_e \int_0^{p_s} pdp = \int_0^{c_s} f(C)dC
\]  

Integrating and rearranging

\[
p_s = - \left[ \frac{2}{D_e} \left( \int_0^{c_s} f(C)dC \right) \right]^{1/2}
\]  

The minus sign is used for the square root since the concentration is decreasing with increase in \( x \). The effectiveness factor is given by the ratio of the actual rate to that based on surface concentration.

\[
\text{Actual rate} = - D_e p_s S_p
\]  

by Ficks law applied at the surface. Hence the effectiveness factor is given by:

\[
\eta = - \frac{D_e p_s S_p}{V_p} f(C_s)
\]  

Using the Eq. 16 for \( p_s \) we find

\[
\eta = \left( \frac{S_p}{V_p} \right) f(C_s) \left[ 2D_e \int_0^{C_s} f(C)dC \right]^{1/2}
\]  

The above result is applicable for any kinetics provided we are in the asymptotic region. For a first order reaction \( \eta = 1/\Lambda \) for large Thiele modulus. In order to make the results in the same format it is convenient to define a Thiele modulus for any kinetics as:

\[
\Lambda = \left( \frac{V_p}{S_p} \right) f(C_s) \left[ 2D_e \int_0^{C_s} f(C)dC \right]^{-1/2}
\]  

which is known as the generalized Thiele modulus. Now we have \( \eta = 1/\Lambda \) for any kinetics but only in the asymptotic case. The expression for \( \eta \) is now generalized as:

\[
\eta = \frac{\tanh(\Lambda)}{\Lambda}
\]  

The above expression is strictly valid only in the asymptotic region where \( \tanh(\Lambda) \) tend one but is used for the entire range of \( \Lambda \) values as an approximate solution.
Problems on asymptotic solution

1. What form does the Thiele modulus take for an m-th reaction? What is the effect of surface concentration of the Thiele modulus? What is the effect of surface concentration on the effectiveness factor in the asymptotic region for (a) second order reaction, (b) half order reaction?

2. What form does the expression for the generalized Thiele modulus take for a L-H kinetics of the form

\[ f(C) = \frac{kC}{1 + KC} \]

Write an analytical expression for the effectiveness factor for such reactions. Express the result in terms of the two dimensionless groups: (i) \( kL^2/D_e \) and (ii) \( KC_s \). Find the values of \( \eta \) for some chosen values of these parameters and compare it with the numerical solution generated using matlab. Find the region where the errors are maximum. What is the order of maximum error in the approximate analytical solution?

3. Zero order kinetics have special features. The effectiveness factor is equal to 1 up to a value of Thiele modulus at which the concentration at the center of catalyst becomes zero. Find this critical Thiele modulus. What are the operational implications of this result?

3 Effective Diffusion Coefficient

The pore diffusion rate plays an important role in affecting the rate of gas-solid reactions as shown in the earlier sections. The effective diffusivity in the pore \( D_e \) is however a medium properly and some models are useful to estimate these in the absence of actual data. The diffusion within the catalyst proceed by two mechanisms: (1) Bulk diffusion within the pores. (2) Bombardment with the walls of the pore if the pore radius is small. The second mechanism is known as Knudsen diffusion.

The bulk diffusion within the pores is a result of gas-gas collision and for a single pore the diffusivity is the same as the gas phase binary diffusivity (for ab binary pair). This value of diffusivity is corrected for the pore structure by incorporating two factors (1) porosity, \( \varepsilon \) which accounts for the reduced area accessible for diffusion and (2) tortuosity, \( \tau \) which accounts for the non-straight path for diffusion.

\[ D_{b, \text{eff}} = D_{12} \frac{\varepsilon}{\tau} \]

Knudsen diffusion occurs when the size is the pores of the order of mean free path of the diffusivity molecule. The molecules now collide more frequently with the pore walls rather than with other molecules. the Knudsen diffusion coefficient in a cylindrical pore is given as:

\[ D_K = \frac{2}{3} r_e V_1 \]

where \( r_e \) = is the effective pore radius and \( V_1 \) is the average molecular speed of species 1. This is given from the kinetic theory of gases as:

\[ V_1 = \left( \frac{8 RT}{\pi M_1} \right)^{1/2} \]

Substituting the values of gas constants, we find the following dimensional equation for the Knudsen diffusion coefficient for species 1:

\[ D_{K,1} = 97 r_e \left( \frac{T}{M_1} \right)^{1/2} \]  \( (22) \)
in \( m^2/s \) with \( r_e \) in \( m \) and \( T \) in Kelvins.

The Knudsen diffusion coefficient in the actual pore is then corrected for the porosity and tortuosity and is given by:

\[
D_{K, \text{eff}} = \frac{\varepsilon}{\tau} D_K
\]

The phenomena of ordinary diffusion and Knudsen diffusion, may be occurring simultaneously. The two can be combined by the following formula:

\[
\frac{1}{D_{b, \text{eff}}} = \frac{1}{D_{b, \text{eff}}} + \frac{1}{D_{K, \text{eff}}}
\]

Additional mechanism is the surface diffusion where the adsorbed species migrates along the surface. The effects are often ignored if the pores are relatively large. This phenomena may be of importance in monolith type of catalysts.

### 4 Diffusion in bidisperse media

Catalysts often have a bimodal pore size distribution with micropores and macropores. The model of Wakao-Smith is useful for predicting the effective diffusion coefficients in such systems. According to their model, the effective diffusivity is given as:

\[
D_e = \varepsilon_M^2 D_M \varepsilon_M^2 \left(1 + 3\varepsilon_M \right) D_\mu
\]  \hspace{1cm} (23)

where \( \varepsilon_M \) is the void fraction associated with the macropores and \( D_M \) is the diffusivity associated with it. Similarly, the term \( \varepsilon_\mu \) is the void fraction associated with the micropores and \( D_\mu \) is the diffusion coefficient associated with the micropores. The diffusivities are calculated by combining the molecular and Knudsen contributions in parallel as:

\[
D_M = D_m D_K/(D_m + D_K)
\]  \hspace{1cm} (24)

where \( D_m \) is the molecular diffusivity and \( D_K \) is the Knudsen diffusivity calculated according to Eqn. (22). The macropore radius, \( r_M \) and micropore radius, \( r_\mu \) are needed for the Knudsen calculations.

Surface area of catalyst associated with pores depend on the pore radius and can be represented as:

\[
S_{in} = 2\varepsilon_M/r_M + 2\varepsilon_\mu/r_\mu
\]  \hspace{1cm} (25)

where \( S_{in} \) is the internal surface area per unit catalyst volume. The above expression assumes that the pores are cylindrical. The rate is generally proportional to the surface area. Thus if \( k_s \) is the rate constant per unit surface area, then the rate constant \( k_v \) based on the catalyst volume is:

\[
k_v = k_s S_{in}
\]  \hspace{1cm} (26)

The Thiele modulus for a first order reaction defined earlier as:

\[
\Lambda = (V_p/S_p)(k_v S_{in}/D_e)^{1/2}
\]  \hspace{1cm} (27)

is thus a complex function of the pore structure. Qualitatively speaking, the micropores increase the area but have lower diffusivity. The macropores have the opposite effect. They are easily accessible (larger diffusivity) but contribute less to the rate constant since they have lower surface area per volume. Hence there is an optimum catalyst structure for a given reaction that gives the best effectiveness factor. The above considerations provide a simple basis to optimize the pore structures of the catalysts.
5 Stefan-Maxwell model for multicomponent diffusion

Mass transport in isothermal multicomponent systems in the gas phase is described by the following constitutive equation.

\[-\frac{dC_i}{dx} = \sum_{j=1}^{n} \frac{y_j N_i - y_i N_j}{D_{ij}}\]  

(28)

where \(n\) is the number of components and \(D_{ij}\) is the binary pair diffusivity in the gas phase.

For porous catalysts the equation is modified by including both Knudsen and bulk diffusion.

\[-\frac{dC_i}{dx} = \frac{N_i}{D_{Ke,i}} + \sum_{j=1}^{n} \frac{y_j N_i - y_i N_j}{D_{ij,e}}\]  

(29)

The mass balance for a differential control volume (for a 1-D slab geometry) gives

\[\frac{dN_i}{dx} = \sum_{i}^{nr} \nu_{ji} r_j\]  

(30)

where the RHS is the total rate of production of species \(i\) from the various reactions. The term \(r_j\) is the rate function for the \(j\)-th reaction which is the function of the local concentrations of the various species. Eqn. (29 and 30) have to be integrated together now.

Note that Eqn. 29 can be written in terms of the component partial pressures as:

\[-\frac{1}{R_G T} \frac{dP_i}{dx} = \frac{N_i}{D_{Ke,i}} + \sum_{j=1}^{n} \frac{p_j N_i - p_i N_j}{P_i D_{ij,e}}\]  

(31)

where \(P_t\) is the total pressure and \(R_G\) is the gas constant. Since the rates of reactions are usually correlated as a function of partial pressures, the above form is often more convenient. The viscous contribution to flow is neglected in these equations. It does not mean that the catalyst pellets are isobaric; pressure gradients can exist in the pellets and they are implicitly accounted for by the use of the constitutive equations in terms of the partial pressures rather than in terms of component mole fractions.

A structure of a matlab program for solving these equations is presented here.

function StefanMaxwell ()

% program calculates the concentration profiles and the effectiveness
% factor based on Stefan-Maxwell model.
% 3-07-05 written by P. A. Ramachandran
% test problem 1 in the paper by Haynes
% 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.
% also define rate in the function ratemodel.

global ns neq
ns = 4 % four species
neq = 8 % 4*2 equations
% Eight variables Y(1) to y(4) are the concentrations of CO, H2O, CO2 and
% H2, y(5) to y(8) are the flux values.
% parameters used are as follows:

global temp pressure
global ctot
temp = 400+273.;
pressure = 25.0; % atm
Rgas = 82.06 % gas contant in cm^3 atm /g-mole K
ctot = pressure/Rgas/temp; % total concentration mole/c.c

% surface (pore mouth) mole fraction
global ys
ys(1) = 0.1; ys(2) = 0.6; ys(3) = 0.08; ys(4) = 0.22;
ys = ys * ctot % surface molar concentrations.

% rate and other parameters
global k rhop Keq
k = 2.05e-04;
rhop = 1.84;
Keq = 12.0

% diffusion parameters; dk = knudsen ; db = binary pair (a matrix)
global dk db
dk(1) = 0.00649;
dk(2) = 0.00494;
dk(3) = 0.0098;
dk(4) = 0.0231;
% ***** add db values for binary pairs
% catalyst properties
length = 0.1588;
rate_s = reactionrate(ys); % rate based on surface values
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, length, nplot );
y = deval(sol, x);
% concentration profiles of various components.
y(1,:) y(3,:)
y(2,:)
y(4,:);
plot ( x, y(1,:), '->' ); % hold on ; plot (x, y(2,:), '->') % these are plotted.
% flux values for the four species.
y(5,1)
y(6,1)
y(7,1)
y(8,1)
rate_s
\eta = y(5,1)/rate_s /0.1588

function yinit = guess (x)
global phi m phi2 n
global ys
global k rhop Keq
% find rate based on surface values and use it as trial value for flux
%rate = rhop* k * ys(1)^0.9 * ys(2)^0.3 * ys(3)^(-0.6) * (1.- ys(3) * ys(4)/Keq/ys(1) /ys(2) )
rate= reactionrate(ys) ;
yinit = [ys(1)
    ys(2)
    ys(3)
    ys(4)
    -rate
    -rate
    rate
    rate ] ; % guess values here

function dydx = odes ( x, y )

global ns neq
global ctot
global k rhop Keq
global dk db
rate = reactionrate(y);
% bulk diffusion terms to be added. Currently set as zero
bulkterm = zeros (ns,1);
dydx = [- y(5) /dk(1) + bulkterm(1)
    - y(6)/dk(2)
    -y(7)/dk(3)
    -y(8)/dk(4)
    -rate
    -rate
    rate
    rate ] ;

function res = bcs ( ya , yb)
global a0 b0
global ys
res = [ ya(1) - ys(1)
    ya(2) - ys(2)
    ya(3) - ys(3)
    ya(4) - ys(4)
    yb(5)
yb(6)
yb(7)
yb(8) ] ;

function ratemodel = reactionrate(y)
global k rhop Keq
global temp pressure
global ctot
p = y*82.06*temp  % species partial pressures
ratemodel =rhop* k * p(1)^0.9 * p(2)^0.3 * p(3)^(-0.6) * (1.- p(3) * p(4)/Keq/p(1) /p(2) ) ;
6 Temperature Effects

The simultaneous transport of heat and mass in a porous catalyst can be represented by the following set of equations.

\[ D_e \frac{d^2 C}{dx^2} = f(C, T) \]  

(32)  

\[ k_e \frac{d^2 T}{dx^2} = (\Delta H) f(C, T) \]  

(33)  

where \( k_e \) is the effective conductivity of the catalyst and \( \Delta H \) is the heat of reaction. The local rate (of disappearance) \( f(C, T) \) is now a function of both the pore concentration and the temperature at any point in the pellet.

The boundary conditions are specified as follows: No flux condition is imposed at the pore end \((x = 0)\) for both heat and mass.

\[ \text{at } x=0 \quad dC/dx = 0; \quad dT/dx = 0 \]

At the pore mouth \((x = L)\) the flux into the pellet must match the transport through the gas film. This leads to the following boundary conditions.

For mass transport

\[ D_e \left( \frac{dT}{dx} \right)_{x=L} = k_m (C_g - C_{x=L}) \]

For heat transport

\[ k_e \left( \frac{dT}{dx} \right)_{x=L} = h (T_g - T_{x=L}) \]

The equations can be put in terms of dimensionless variables by scaling the concentration and temperature by reference values. The bulk concentration and temperature can be used as the reference values if the particle scale model is being analyzed. For reactor scale models, the inlet feed conditions can be used as reference.

The dimensionless mass and heat transport equations are then as follows:

\[ \frac{d^2 c}{d\xi^2} = \frac{f(C_{ref}, T_{ref})L^2}{D_e C_{ref}} [f^*(c, \theta)] \]  

(34)  

where \( \xi \) is dimensionless distance \( x/L \) and \( f^* \) is a dimensionless rate defined as:

\[ f^* = \frac{f(C, T)}{[f(C_{ref}, T_{ref})]} \]

The first term on the RHS of 34 can be identified as a Thiele parameter

\[ \text{Let } \phi^2 = \frac{f(C_{ref}, T_{ref})L^2}{D_e C_{ref}} \]

Then the mass balance equation is:

\[ \frac{d^2 c}{d\xi^2} = \phi^2 f^*(c, \theta) \]  

(35)  

The heat balance equation can be represented as:

\[ \frac{d^2 \theta}{d\xi^2} = -\beta \phi^2 f^*(c, \theta) \]  

(36)
where $\beta$ is the dimensionless parameter (thermicity group) defined as:

$$
\beta = \frac{(-\Delta H)D_cC_{ref}}{k_eT_{ref}} \quad (37)
$$

Note the $\beta$ takes a positive value for exothermic reactions and a negative value for endothermic reactions.

The boundary conditions can be normalized as:

at $\xi = 0$ \quad $dc/d\xi = 0$; \quad $d\theta/d\xi = 0$

and the conditions at $\xi = 1$ can be related to the Biot numbers for heat and mass

$$
\left(\frac{dc}{d\xi}\right)_s = Bi_m(c_g - c_s) \quad (35)
$$

$$
\left(\frac{d\theta}{d\xi}\right)_s = Bi_h(\theta_g - \theta_s) \quad (36)
$$

where the subscript $s$ is used for the $\xi = 1$ i.e., the surface values. Here we define

$$
Bi_m = k_mL/D_e \quad (35)
$$

and

$$
Bi_h = hL/k_e \quad (36)
$$

The magnitude of the internal temperature gradient can be assessed by combining the above two equations without even actually solving the equations. The mass and heat transport equations 35 and 36 can be combined as:

$$
\frac{d^2\theta}{d\xi^2} + \beta \frac{d^2c}{d\xi^2} \quad (38)
$$

Hence the integration of the above equation twice leads to

$$
\theta - \theta_s = \beta(c_s - c) \quad (39)
$$

The maximum value of the temperature occurs for an exothermic reaction when the center concentration drops to zero. This occurs in the strong pore diffusion resistance for mass transfer. Hence an estimate of the internal gradients is:

$$
\text{Max } \theta_c - \theta_s = \beta c_s = O(\beta) \quad (40)
$$

where $\theta_c$ is the center temperature and the symbol $O$ means ‘of the order of’.

Also the magnitudes of the external gradients can be estimated by the following procedure: Here we introduce the overall effectiveness factor $\eta_0$ defined as: $\eta_0$= actual rate / rate based on reference conditions

Rate of transport to the surface is equal to $S_p k_m (C_g - C_s)$

Rate of reaction is $V_p f(C_{ref}, T_{ref}) \eta_0$.

Equating the two and using the dimensionless groups we find as estimate of the external concentration gradients.

$$
C_g - c_s = \frac{\phi^2 \eta_0}{Bi_m} \quad (41)
$$
Note that $\phi^2\eta_0$ is the same as the Weisz modulus and can be directly calculated if the measured data is available. The value of $\eta_0$ need not be explicitly evaluated in order to use the above equation for diagnostic purposes.

$$\phi^2\eta_0 = \frac{-R_{\text{measured}}L^2}{(D_eC_{\text{ref}})}$$  \hspace{1cm} (42)

Similar analysis equating the heat transport in the film to the total heat released from the reaction leads to an estimate the film temperature difference.

$$\theta_s - \theta_g = \frac{\beta\phi^2\eta_0}{Bi_h}$$ \hspace{1cm} (43)

The above relations enables a rapid determination or the relative importance of external and internal temperature gradients. It can be, for instance, used to determine if the pellet is operating under near isothermal conditions or whether a temperature correction to the data is necessary.

The temperature rise in the pellet can be assessed as follows: Combining 41 and 43 we find:

$$\theta_c - \theta_s = c_g\beta\left(1 - \frac{\phi^2\eta_0}{Bi_m}\right)$$ \hspace{1cm} (44)

which is a closer estimate of the pellet temperature rise than the earlier equation based on the surface concentration.

7 Numerical Solutions

Numerical solution for a first order reaction is indicated in this section. The dimensionless rate for a first order reaction can be expressed as:

$$f^* = c \exp[\gamma(1 - 1/\theta)]$$ \hspace{1cm} (45)

where $\gamma = E/R_gT_{\text{ref}}$. The governing equations and the boundary conditions shown in the earlier section are summarized for convenience here: The mass balance:

$$\frac{d^2c}{d\xi^2} = \phi^2c \exp[\gamma(1 - 1/\theta)]$$ \hspace{1cm} (46)

The heat balance:

$$\frac{d^2\theta}{d\xi^2} = -\beta \phi^2c \exp[\gamma(1 - 1/\theta)]$$ \hspace{1cm} (47)

The boundary conditions are:

at $\xi = 0$ \hspace{0.5cm} $dc/d\xi = 0; \hspace{0.5cm} d\theta/d\xi = 0$

and $\xi = 1$

$$\left(\frac{dc}{d\xi}\right)_s = Bi_mC(c_g - c_s)$$

$$\left(\frac{d\theta}{d\xi}\right)_s = Bi_h(\theta_g - \theta_s)$$

For the particle problem (local particle scale model) we set $c_g$ and $\theta_g$ as one.

We find that even for this simple first order reaction, the overall effectiveness factor is a function of five parameters: $\phi$, $\beta$, $\gamma$, $Bi_m$ and $Bi_h$. 

13
An illustrative plot of the effectiveness factor vs Thiele modulus is shown in Fig 1 based on the work of Aris and Hatfield. It is clear that the behavior is complex and multiple steady states are observed. For one case in the fig we see two distinct regions of multiple solutions. The region at low Thiele modulus is caused by intraparticle gradients while the second one is due to interparticle gradients. The two regions may overlap producing five steady states as seen in the second case shown in Fig 1.

Sample result was simulated using the matlab program for the following value of the parameters. $\phi = 0.5$, $\beta = 1/3$, $\gamma = 27$, $Bi_m = 300$ and $Bi_h = 100$.

**Model for Isothermal Pellet**

An useful simplification is to assume that there are no internal gradients for temperature. The temperature changes are confined only to the gas film. This simplifies the calculations since the only the intraparticle concentration profiles need to be solved. Approximate analytical solutions shown earlier can be used for the internal effectiveness factor. The particle temperature is not known and has to be solved iteratively. The calculation procedure is indicated below for a first order reaction.

The Thiele modulus is defined on the basis of the surface temperature

$$\psi = \phi \exp[\gamma/2.(1 - 1/\theta_s)]$$

where $\phi$ is the Thiele modulus based on reference conditions. The catalytic effectiveness factor is then equal to:

$$\eta_c = \frac{\tanh \psi}{\psi}$$

and overall effectiveness factor for a first order reaction was shown earlier as:

$$\eta_0 = \frac{\eta_c B_i_m}{\eta_c \psi^2 + B_i_m} \exp[\gamma (1 - 1/\theta_s)]$$

The surface temperature is related to the gas phase temperature by the equation shown earlier which is reproduced below for completeness.

$$\theta_s = \theta_0 + \frac{\beta \phi^2 \eta_0}{B_i_h}$$

The above equations are solved simultaneously or by trial and error to obtain the overall effectiveness factor and the surface temperature.

**Example**: Calculate the effectiveness factor for the following conditions:

$\phi = 2$, $\beta = 0.05$, $\gamma = 20$, $Bi_m = 200$ and $Bi_h = 20$.

Solution: Since $\beta$ is small let us assume that all the temperature drop in confined to the gas film. To start off the calculations assume a particle temperature of 1.05. Then the following set of results can be obtained.

$\psi = 3.2119$; $\eta_c = 0.32$; $\eta_0 = 0.7899$ and $\theta_s = 1.007$. This is not close to the trial value of 1.05 and the calculations are repeated.

The final value of the surface temperature is calculated using 51 as:

$\theta_s = 1.005$; and $\eta_c = 0.4617$ and $\eta_0 = 0.5049$. The overall effectiveness factor is greater than the catalytic value since it based on the bulk temperature and not the surface temperature.