## Fall 2002. 10.34. Numerical Methods Applied to Chemical Engineering

## Homework \# 3. Nonlinear algebraic equations and matrix eigenvalue problems

## Assigned Friday 9/20/02. Due Friday 9/27/02

## Problem 1. Modeling chemical reaction with diffusion in a catalyst pellet

In HW \# 1, we considered the use of the finite difference method to convert a boundary value problem into a set of linear algebraic equations. In HW \# 2, we considered the use of Newton's method to solve sets of nonlinear algebraic equations. In this problem, we combine these two approaches to solve a boundary value problem that contains a nonlinear term involving chemical reaction. This problem is inspired by the discussion of nonisothermal catalyst particles in section 3.9 of G. F. Froment and K. B. Bischoff, Chemical Reactor Analysis and Design, 2nd ed., Wiley, 1990.

We consider the case of a spherical catalyst pellet of radius $R$ (see figure below).


FIGURE 1. Nonisothermal reaction/diffusion within a catalyst pellet. (left) Geometry of problem with known surface concentration, temperature. (right) Spherical shell control volume used to derive governing equations.

Within the catalyst pellet, we have the chemical reaction

$$
\begin{equation*}
A \rightarrow B \tag{EQ1}
\end{equation*}
$$

that follows a first order rate law,

$$
\begin{equation*}
R_{r x n}=k(T) c_{A} \tag{EQ2}
\end{equation*}
$$

The heat of reaction, $\Delta H$, is assumed to be negative (exothermic reaction), and we model the temperature dependence of the rate constant as

$$
\begin{equation*}
k(T)=k_{r e f} \exp \left[\frac{-E_{a}}{R T_{r e f}}\left(\frac{T_{r e f}}{T}-1\right)\right] \tag{EQ3}
\end{equation*}
$$

$E_{a}$ is the activation energy, $R$ is the ideal gas constant, and $k_{r e f}$ is the value of the rate constant at a reference temperature $T_{\text {ref }}$.

We wish to calculate the profiles of the concentration of $\mathrm{A}, c_{A}(r)$, and the temperature $T(r)$ within the catalyst pellet. We assume that at the surface of the catalyst pellet, the concentration and temperature are known, yielding the Dirichlet boundary conditions

$$
\begin{equation*}
c_{A}(R)=c_{A, s} \quad T(R)=T_{s} \tag{EQ4}
\end{equation*}
$$

We obtain the governing equation for the concentration of A by applying a mass balance to the shell control volume between $r$ and $r+d r$ (see figure above),

$$
\begin{equation*}
0=4 \pi r^{2}\left(-\left.D_{A} \frac{d c_{A}}{d r}\right|_{r}\right)-4 \pi(r+d r)^{2}\left(-\left.D_{A} \frac{d c_{A}}{d r}\right|_{r+d r}\right)+\left(4 \pi r^{2} d r\right)\left(-k c_{A}\right) \tag{EQ5}
\end{equation*}
$$

The first term is the flux of A into the control volume by diffusion, the second term is the corresponding flux out, and the third is the rate of disappearance of A due to chemical reaction. $D_{A}$ is the effective diffusion constant for A within the catalyst pellet. Dividing by $4 \pi d r$ yields,

$$
\begin{equation*}
0=\frac{1}{d r}\left\{D_{A}\left[\left.(r+d r)^{2} \frac{d c_{A}}{d r}\right|_{r+d r}-\left.r^{2} \frac{d c_{A}}{d r}\right|_{r}\right]\right\}-r^{2}\left(k c_{A}\right) \tag{EQ6}
\end{equation*}
$$

This yields the differential equation

$$
\begin{equation*}
\frac{d}{d r}\left[r^{2} D_{A} \frac{d c_{A}}{d r}\right]-r^{2}\left(k c_{A}\right)=0 \tag{EQ7}
\end{equation*}
$$

Similarly, we derive a governing equation for the temperature field by writing an energy balance on the spherical shell control volume,

$$
\begin{equation*}
0=4 \pi r^{2}\left(-\left.\lambda \frac{d T}{d r}\right|_{r}\right)-4 \pi(r+d r)^{2}\left(-\left.\lambda \frac{d T}{d r}\right|_{r+d r}\right)+\left(4 \pi r^{2} d r\right)(-\Delta H)\left(k c_{A}\right) \tag{EQ8}
\end{equation*}
$$

The first and second terms are the fluxes in and out of the control volume due to heat conduction. $\lambda$ is the effective thermal conductivity of the catalyst pellet. The third term is the generation of heat due to chemical reaction. Division by $4 \pi d r$ yields

$$
\begin{equation*}
0=\frac{1}{d r}\left\{\lambda\left[\left.(r+d r)^{2} \frac{d T}{d r}\right|_{r+d r}-\left.r^{2} \frac{d T}{d r}\right|_{r}\right]\right\}+r^{2}(-\Delta H)\left(k c_{A}\right) \tag{EQ9}
\end{equation*}
$$

The governing equation for the temperature field is therefore

$$
\begin{equation*}
\frac{d}{d r}\left[r^{2} \lambda \frac{d T}{d r}\right]+r^{2}(-\Delta H)\left(k c_{A}\right)=0 \tag{EQ10}
\end{equation*}
$$

We now have a set of two coupled differential equations with the boundary conditions

$$
\begin{array}{lll}
\text { BC \# 1 } & c_{A}(R)=c_{A, s} & T(R)=T_{s} \\
\text { BC \# 2 } & \left.\frac{d c_{A}}{d r}\right|_{r=0}=0 & \left.\frac{d T}{d r}\right|_{r=0}=0 \tag{EQ12}
\end{array}
$$

The first boundary condition arises from the known concentration and temperature at the pellet surface. This boundary condition holds when we assume that there is no external resistance to heat and mass transfer in the surrounding fluid. The second boundary condition arises from the symmetry condition at the center of the catalyst pellet.

We now simplify the problem for the case where the heat of reaction, diffusivity, and thermal conductivity are assumed to be constant. We divide the energy balance by $-\Delta H$,

$$
\begin{equation*}
\frac{d}{d r}\left[r^{2} \frac{\lambda}{(-\Delta H)} \frac{d T}{d r}\right]+r^{2}\left(k c_{A}\right)=0 \tag{EQ13}
\end{equation*}
$$

When we add this equation to the mass balance on A , we obtain,

$$
\begin{equation*}
\frac{d}{d r}\left[r^{2} D_{A} \frac{d c_{A}}{d r}\right]+\frac{d}{d r}\left[r^{2} \frac{\lambda}{(-\Delta H)} \frac{d T}{d r}\right]=0 \tag{EQ14}
\end{equation*}
$$

Integrating this equation once yields,

$$
\begin{equation*}
r^{2}\left[D_{A} \frac{d c_{A}}{d r}+\frac{\lambda}{(-\Delta H)} \frac{d T}{d r}\right]=C_{1} \tag{EQ15}
\end{equation*}
$$

Dividing by $r^{2}$ yields,

$$
\begin{equation*}
\frac{d}{d r}\left[D_{A} c_{A}+\frac{\lambda}{(-\Delta H)} T\right]=\frac{C_{1}}{r^{2}} \tag{EQ16}
\end{equation*}
$$

From the symmetry boundary condition at the center of the spherical pellet, we know that $C_{1}$ must be zero, so that a second integration yields

$$
\begin{equation*}
D_{A} c_{A}+\frac{\lambda}{(-\Delta H)} T=C_{2}=D_{A} c_{A, s}+\frac{\lambda}{(-\Delta H)} T_{s} \tag{EQ17}
\end{equation*}
$$

We have employed the known concentration and temperature at the catalyst surface (from the first boundary condition) to obtain the value of $C_{2}$.

Upon rearrangement, this yields a linear relation between the temperature and concentration fields.

$$
\begin{equation*}
T-T_{s}=\frac{D_{A}(\Delta H)}{\lambda}\left[c_{A}-c_{A, s}\right] \tag{EQ18}
\end{equation*}
$$

Writing the temperature dependence of the rate constant explicitly, the boundary value problem that we must solve is the following,

Find the function $c_{A}(r)$ that satisfies on $r \in[0, R]$ the differential equation

$$
\begin{equation*}
D_{A} \frac{d}{d r}\left[r^{2} \frac{d c_{A}}{d r}\right]-r^{2} k_{r e f} \exp \left[\frac{-E_{a}}{R T_{r e f}}\left(\frac{T_{r e f}}{T}-1\right)\right] c_{A}=0 \tag{EQ19}
\end{equation*}
$$

subject to the boundary conditions

$$
\begin{equation*}
c_{A}(R)=\left.c_{A, s} \quad \frac{d c_{A}}{d r}\right|_{r=0}=0 \tag{EQ20}
\end{equation*}
$$

where the temperature field is calculated directly from the concentration field as

$$
\begin{equation*}
T(r)=T_{s}+\frac{D_{A}(\Delta H)}{\lambda}\left[c_{A}(r)-c_{A, s}\right] \tag{EQ21}
\end{equation*}
$$

To solve this problem, we again use the method finite differences to convert the boundary value problem into a system of algebraic equations. Now, however, the system of algebraic equations is nonlinear and must be solved iteratively.

To implement the finite difference method in spherical coordinates, we place a grid of points $\left\{r_{1}, r_{2}, \ldots, r_{N}\right\}$ within the interior of the domain, with $0<r_{1}<r_{2}<\ldots<r_{N}<R$, and require that at every grid point $j$, the differential equation be satisfied locally,

$$
\begin{equation*}
\left.D_{A} \frac{d}{d r}\left[r^{2} \frac{d c_{A}}{d r}\right]\right|_{r_{j}}-r_{j}^{2} k_{r e f} \exp \left[\frac{-E_{a}}{R T_{r e f}}\left(\frac{T_{r e f}}{T_{j}}-1\right)\right] c_{A, j}=0 \tag{EQ22}
\end{equation*}
$$

Here we have used the notation $T_{j} \equiv T\left(r_{j}\right), c_{A, j} \equiv c_{A}\left(r_{j}\right)$.
We define the values of $r$ midway between the $j^{\text {th }}$ grid point and its neighbors as

$$
\begin{equation*}
r_{j+1 / 2} \equiv \frac{1}{2}\left(r_{j}+r_{j+1}\right) \quad r_{j-1 / 2} \equiv \frac{1}{2}\left(r_{j}+r_{j-1}\right) \tag{EQ23}
\end{equation*}
$$

and form a central difference approximation for the second derivative,

$$
\begin{equation*}
\left.\frac{d}{d r}\left[r^{2} \frac{d c_{A}}{d r}\right]\right|_{r_{j}} \approx \frac{r_{j+1 / 2}^{2}\left(\left.\frac{d c_{A}}{d r}\right|_{r_{j+1 / 2}}\right)-r_{j-1 / 2}^{2}\left(\left.\frac{d c_{A}}{d r}\right|_{r_{j-1 / 2}}\right)}{\left(r_{j+1 / 2}-r_{j-1 / 2}\right)} \tag{EQ24}
\end{equation*}
$$

For each of the mid-point first derivatives, we use another finite difference approximation,

$$
\begin{align*}
& \left.\frac{d c_{A}}{d r}\right|_{r_{j+1 / 2}} \approx \frac{c_{A, j+1}-c_{A, j}}{r_{j+1}-r_{j}}  \tag{EQ25}\\
& \left.\frac{d c_{A}}{d r}\right|_{r_{j-1 / 2}} \approx \frac{c_{A, j}-c_{A, j-1}}{r_{j}-r_{j-1}} \tag{EQ26}
\end{align*}
$$

We can write the finite difference approximation for the second derivative as

$$
\begin{equation*}
\left.\frac{d}{d r}\left[r^{2} \frac{d c_{A}}{d r}\right]\right|_{r_{j}} \approx A_{j, j-1} c_{A, j-1}+A_{j j} c_{A, j}+A_{j, j+1} c_{A, j+1} \tag{EQ27}
\end{equation*}
$$

in which case the nonlinear algebraic equation for interior grid point $j$ takes the form

$$
\begin{align*}
& A_{j, j-1} c_{A, j-1}+A_{j j} c_{A, j}+A_{j, j+1} c_{A, j+1} \\
& \quad-D_{A}^{-1} r_{j}^{2} k_{r e f} \exp \left[\frac{-E_{a}}{R T_{r e f}}\left(\frac{T_{r e f}}{T_{j}}-1\right)\right] c_{A, j}=0 \tag{EQ28}
\end{align*}
$$

In our previous calculation using finite differences in one dimension, we saw that the resulting set of linear equations had non-zero matrix elements only on the principal diagonal, the diagonal immediately above, and the diagonal immediately below. This tridiagonal structure meant that the equations could be solved very quickly in $O(N)$ operations using Gaussian elimination. Here, we have a set of nonlinear equations; however, we see that once again, the equation for grid point $j$ depends only on the values of the concentration at grid points $j, j-1$, and $j+1$. This means that the Jacobian matrix will have a tridiagonal structure, and that we can solve very quickly the linear equation at each Newton's method iteration,

$$
\begin{equation*}
J^{[k]} \Delta x^{[k]}=-f\left(x^{[k]}\right) \quad x^{[k+1]}=x^{[k]}+\lambda \Delta x^{[k]} \quad \lambda \in(0,1] \tag{EQ29}
\end{equation*}
$$

We note that some modification of the above equation is required for the first and last grid points. At the last grid point, $j=N$, the discretized form of the differential equation is

$$
\begin{align*}
& A_{N, N-1} c_{A, N-1}+A_{N N} c_{A, N}+A_{N, N+1} c_{A, N+1} \\
& \quad-D_{A}^{-1} r_{N}^{2} k_{r e f} \exp \left[\frac{-E_{a}}{R T_{r e f}}\left(\frac{T_{r e f}}{T_{N}}-1\right)\right] c_{A, N}=0 \tag{EQ30}
\end{align*}
$$

We see that this equation refers to the value of the concentration at the non-existent grid point $N+1$. We correct this problem by placing the fictitious grid point at the boundary, i.e. $r_{N+1}=R$, and employ the boundary condition to write $c_{A, N+1}=c_{A, s}$. The algebraic equation for grid point $N$ then becomes

$$
\begin{align*}
& A_{N, N-1} c_{A, N-1}+A_{N N} c_{A, N}+A_{N, N+1} c_{A, s} \\
& \quad-D_{A}^{-1} r_{N}^{2} k_{r e f} \exp \left[\frac{-E_{a}}{R T_{r e f}}\left(\frac{T_{r e f}}{T_{N}}-1\right)\right] c_{A, N}=0 \tag{EQ31}
\end{align*}
$$

We have a similar problem at the first grid point $j=1$, where the discretized form of the differential equation is
$A_{10} c_{A, 0}+A_{11} c_{A, 1}+A_{12} c_{A, 2}-D_{A}^{-1} r_{1}^{2} k_{r e f} \exp \left[\frac{-E_{a}}{R T_{r e f}}\left(\frac{T_{r e f}}{T_{1}}-1\right)\right] c_{A, 1}=0$
Again, we need to employ a boundary condition to remove the dependence on the fictitious grid point concentration $c_{A, 0}$. We place the zeroth grid point at the origin, $r_{0}=0$, and use the symmetry boundary condition,

$$
\begin{equation*}
\left.\frac{d c_{A}}{d r}\right|_{r_{0}}=0 \tag{EQ32}
\end{equation*}
$$

If we were evaluating the derivative at an interior point, we would use the central difference approximation,

$$
\begin{equation*}
\left.\frac{d c_{A}}{d r}\right|_{r_{j}} \approx \frac{c_{A, j+1}-c_{A, j-1}}{r_{j+1}-r_{j-1}} \tag{EQ33}
\end{equation*}
$$

When we try to apply this formula at $r_{0}=0$, we obtain a formula

$$
\begin{equation*}
\left.\frac{d c_{A}}{d r}\right|_{r_{0}} \approx \frac{c_{A, 1}-c_{A,-1}}{r_{1}-r_{-1}} \tag{EQ34}
\end{equation*}
$$

that we cannot use because there is no grid point at $r_{-1}$. We could use the one-sided difference formula,

$$
\begin{equation*}
\left.\frac{d c_{A}}{d r}\right|_{r_{0}} \approx \frac{c_{A, 1}-c_{A, 0}}{r_{1}-r_{0}} \tag{EQ35}
\end{equation*}
$$

but this is not as accurate as a central difference approximation. To obtain a more-accurate one-sided finite difference approximation for the boundary derivative, we use the values at $r_{0}, r_{1}, r_{2}$ to fit locally a quadratic description of the concentration profile,

$$
\begin{equation*}
c_{A}(r) \approx a_{0}+a_{1} r+a_{2} r^{2} \tag{EQ36}
\end{equation*}
$$

We can immediately determine the value of $a_{0}$ by noticing that at $r_{0}=0$,

$$
\begin{equation*}
c_{A}(0)=a_{0}=c_{A, 0} \tag{EQ37}
\end{equation*}
$$

Similarly, evaluating the polynomial approximation at $r_{1}$ and $r_{2}$ yields the equations

$$
\begin{align*}
& c_{A, 1}-c_{A, 0}=a_{1} r_{1}+a_{2} r_{1}^{2}  \tag{EQ38}\\
& c_{A, 2}-c_{A, 0}=a_{1} r_{2}+a_{2} r_{2}^{2} \tag{EQ39}
\end{align*}
$$

When these equations are solved for $a_{1}$ and $a_{2}$, we can approximate the derivative at $r_{0}=0$ by

$$
\begin{equation*}
\left.\left.\frac{d c_{A}}{d r}\right|_{r_{0}} \approx \frac{d}{d r}\left[a_{0}+a_{1} r+a_{2} r^{2}\right]\right|_{r=0}=a_{1} \tag{EQ40}
\end{equation*}
$$

When the grid points are uniformly spaced, this yields the approximation formula,

$$
\begin{equation*}
\left.\frac{d c_{A}}{d r}\right|_{r_{0}} \approx \frac{-c_{A, 2}+4 c_{A, 1}-3 c_{A, 0}}{2(\Delta r)} \tag{EQ41}
\end{equation*}
$$

As the symmetry boundary condition states that this derivative is zero, we have the following expression to estimate $c_{A, 0}$ from $c_{A, 1}$ and $c_{A, 2}$,

$$
\begin{equation*}
c_{A, 0}=\frac{4}{3} c_{A, 1}-\frac{1}{3} c_{A, 2} \tag{EQ42}
\end{equation*}
$$

The modified algebraic equation for the first grid point is therefore

$$
\begin{align*}
& {\left[A_{11}+\frac{4}{3} A_{10}\right] c_{A, 1}+\left[A_{12}-\frac{1}{3} A_{10}\right] c_{A, 2}} \\
& \quad-D_{A}^{-1} r_{1}^{2} k_{r e f} \exp \left[\frac{-E_{a}}{R T_{r e f}}\left(\frac{T_{r e f}}{T_{1}}-1\right)\right] c_{A, 1}=0 \tag{EQ43}
\end{align*}
$$

We have introduced the problem in terms of the familiar real-life parameters such as diffusivity and activation energy; however, we can use dimensional analysis to convert the problem to a dimensionless form that provides clearer insight into the physical behavior.

First, we define a dimensionless distance $\xi$ from

$$
\begin{equation*}
r=\xi R \tag{EQ44}
\end{equation*}
$$

The governing equation for the concentration field, written in terms of this scaled distance, is

$$
\begin{equation*}
D_{A} \frac{d}{d \xi}\left[\xi^{2} \frac{d c_{A}}{d \xi}\right]-\xi^{2} R^{2} k_{r e f} \exp \left[\frac{-E_{a}}{R T_{r e f}}\left(\frac{T_{r e f}}{T}-1\right)\right] c_{A}=0 \tag{EQ45}
\end{equation*}
$$

Next, we define a scaled concentration variable $\Psi_{A}$,

$$
\begin{equation*}
\Psi_{A} \equiv c_{A} / c_{A, s} \tag{EQ46}
\end{equation*}
$$

The governing equation of this scaled concentration is

$$
\begin{equation*}
\frac{d}{d \xi}\left[\xi^{2} \frac{d \Psi_{A}}{d \xi}\right]-\xi^{2}\left(\frac{R^{2} k_{r e f}}{D_{A}}\right) \exp \left[\frac{-E_{a}}{R T_{r e f}}\left(\frac{T_{r e f}}{T}-1\right)\right] \Psi_{A}=0 \tag{EQ47}
\end{equation*}
$$

We now take as the reference condition for the rate constant the known surface temperature,

$$
\begin{equation*}
k_{r e f} \equiv k_{s}=k\left(T_{s}\right) \quad T_{r e f} \equiv T_{s} \tag{EQ48}
\end{equation*}
$$

The governing equation then becomes

$$
\begin{equation*}
\frac{d}{d \xi}\left[\xi^{2} \frac{d \Psi_{A}}{d \xi}\right]-\xi^{2}\left(\frac{R^{2} k_{s}}{D_{A}}\right) \exp \left[\frac{-E_{a}}{R T_{s}}\left(\frac{T_{s}}{T}-1\right)\right] \Psi_{A}=0 \tag{EQ49}
\end{equation*}
$$

We now define the Thiele modulus $\Phi$ as,

$$
\begin{equation*}
\Phi \equiv R \sqrt{k_{S} / D_{A}} \tag{EQ50}
\end{equation*}
$$

When $\Phi$ «1, the effect of diffusion limitation is minimal, but when $\Phi » 1$, we expect that the reaction rate will be affected by the slow diffusion of A into the catalyst pellet.

Similarly, we write the activation energy in dimensionless form as the parameter

$$
\begin{equation*}
\gamma \equiv \frac{E_{a}}{R T_{s}} \tag{EQ51}
\end{equation*}
$$

The governing equation in dimensionless form is now

$$
\begin{equation*}
\frac{d}{d \xi}\left[\xi^{2} \frac{d \Psi_{A}}{d \xi}\right]-\xi^{2} \Phi^{2} \exp \left[\gamma\left(1-\frac{T_{s}}{T}\right)\right] \Psi_{A}=0 \tag{EQ52}
\end{equation*}
$$

Finally, we use the linear relation between the temperature and concentration fields to write

$$
\begin{equation*}
\frac{T}{T_{s}}-1=\frac{D_{A}(-\Delta H) c_{A, s}}{\lambda T_{s}}\left(1-\Psi_{A}\right) \tag{EQ53}
\end{equation*}
$$

We now define the dimensionless number $\beta$ as the relative importance of the heat of reaction compared to thermal conduction,

$$
\begin{equation*}
\beta \equiv \frac{D_{A}(-\Delta H) c_{A, s}}{\lambda T_{s}} \tag{EQ54}
\end{equation*}
$$

We then write the exponential term in the governing equation as,

$$
\begin{equation*}
\exp \left[\gamma\left(1-\frac{T_{s}}{T}\right)\right]=\exp \left[\frac{\gamma \beta\left(1-\Psi_{A}\right)}{1+\beta\left(1-\Psi_{A}\right)}\right] \tag{EQ55}
\end{equation*}
$$

so that the differential equation becomes,

$$
\begin{equation*}
\frac{d}{d \xi}\left[\xi^{2} \frac{d \Psi_{A}}{d \xi}\right]-\xi^{2} \Phi^{2} \exp \left[\frac{\gamma \beta\left(1-\Psi_{A}\right)}{1+\beta\left(1-\Psi_{A}\right)}\right] \Psi_{A}=0 \tag{EQ56}
\end{equation*}
$$

The boundary conditions in dimensionless form are

$$
\begin{equation*}
\Psi_{A}(1)=\left.1 \quad \frac{d \Psi_{A}}{d \xi}\right|_{\xi=0}=0 \tag{EQ57}
\end{equation*}
$$

The number of independent system parameters has now been reduced to three, $\Phi, \gamma$, and $\beta$.

Question A.1. Write a MATLAB program that employs the finite difference method outlined above to solve the problem in dimensionless form. As input, take the values of the three dimensionless parameters, $\Phi, \gamma$, and $\beta$. The program should plot the dimensionless concentration profile and compute the value of the effectiveness factor (defined below).

To determine the effectiveness factor, we calculate the total rate of reaction within the catalyst pellet,

$$
\begin{equation*}
R_{t o t}=\int_{0}^{R} k(T) c_{A}(r)\left(4 \pi r^{2}\right) d r \tag{EQ58}
\end{equation*}
$$

Rewriting this integral in terms of the dimensionless quantities yields,

$$
\begin{equation*}
R_{\text {tot }}=\left(\frac{4}{3} \pi R^{3}\right)\left(k_{s} c_{A, s}\right)\left[3 \int_{0}^{1} \Psi_{A}(\xi) \exp \left[\frac{\gamma \beta\left(1-\Psi_{A}(\xi)\right)}{1+\beta\left(1-\Psi_{A}(\xi)\right)}\right] \xi^{2} d \xi\right] \tag{EQ59}
\end{equation*}
$$

The product of the first two factors is the total reaction rate that we would observe if there were no concentration (or temperature) gradients within the catalyst particle. We define the effectiveness factor from

$$
\begin{equation*}
R_{t o t}=\left(\frac{4}{3} \pi R^{3}\right)\left(k_{s} c_{A, s}\right) \eta \tag{EQ60}
\end{equation*}
$$

so that we can calculate the effectiveness factor from the dimensionless profile,

$$
\begin{equation*}
\eta=3 \int_{0}^{1} \Psi_{A}(\xi) \exp \left[\frac{\gamma \beta\left(1-\Psi_{A}(\xi)\right)}{1+\beta\left(1-\Psi_{A}(\xi)\right)}\right] \xi^{2} d \xi \tag{EQ61}
\end{equation*}
$$

To perform this integration, you can use the MATLAB integration function trapz(), using as input the vector of values of $\xi$ at each grid point (including $\xi_{0}=0$ and $\xi_{N+1}=1$ ) and the vector of integrand values at each grid point.

## Hints:

1. A reasonable initial guess is that $\Psi_{A}$ is uniformly equal to one when the values of all three coefficients are zero or very small.
2. If you call the MATLAB solver fsolve() without informing it that the Jacobian is sparse, the amount of CPU time required to solve the problem will be very large. You have one of two options. First, you know where the non-zero elements of the Jacobian will be, even if you don't calculate their exact values. You can set with optimset() the options flag 'JacobPattern' to tell MATLAB that you are providing a sparse matrix $S$ with the same pattern of non-zero elements as the Jacobian. With this information, fsolve() can perform the finite difference estimation of the Jacobian more effectively. For a tridiagonal system, the sparsity pattern matrix is generated by the following code:

$$
\begin{aligned}
& S=\text { spalloc }(\mathrm{N}, \mathrm{~N}, 3 * \mathrm{~N}) \\
& \mathrm{S}=\mathrm{S}+\operatorname{diag}(\text { ones }(\mathrm{N}, 1)) \\
& \mathrm{S}=\mathrm{S}+\operatorname{diag}(\operatorname{ones}(\mathrm{N}-1,1), 1) ; \\
& \mathrm{S}=\mathrm{S}+\operatorname{diag}(\text { ones }(\mathrm{N}-1,1),-1) ;
\end{aligned}
$$

Alternatively, for this problem, the Jacobian may be calculated analytically in the routine that you provide. This is even more computationally efficient than the method above, but requires a little more programming on your part. In this case, use the optimset() function to set the 'Jacobian' flag to 'on'. I have found for typical values of the grid point size a speed-up of a factor of $10 x$ when I compute the Jacobian analytically.
3. For better convergence of fsolve(), I would use optimset() to set the 'LargeScale' flag to 'off'.
4. You should increase the number of grid points until you can no longer see any significant change in the plot of the concentration profile of the value of the effectiveness factor. Physically, we expect the highest gradients to occur near the particle surface, so you may wish to generate a grid that has a tighter spacing of points in this region. This will yield more accurate results with the same overall number of grid points. Note that the finite difference equations derived above did not assume a uniform grid point spacing, except for the boundary derivative at $r=0$. Therefore, you want to make sure that you maintain

$$
\begin{equation*}
r_{2}-r_{1}=r_{1}-r_{0}=r_{1} \tag{EQ62}
\end{equation*}
$$

Question A.2. Using this program, makes plots of the effectiveness factor $\eta$ vs. the Thiele modulus $\Phi$ for the case $\gamma=20$ and the following values of $\beta$,

$$
\begin{equation*}
\beta=-0.2,-0.1,0,0.05 \tag{EQ64}
\end{equation*}
$$

Make a single master plot with all curves.

## Problem 2. Eigenvalues of $\mathbf{3 x} 3$ matrices

Consider the following three matrices,

$$
A=\left[\begin{array}{ccc}
2 & 1 & -1  \tag{EQ65}\\
1 & 3 & 0 \\
-1 & 0 & 4
\end{array}\right] \quad B=\left[\begin{array}{ccc}
1 & 2 & -3 \\
-2 & -3 & 4 \\
3 & -4 & 5
\end{array}\right] \quad C=\left[\begin{array}{lll}
1 & 0 & 0 \\
0 & 0 & 1 \\
0 & 1 & 0
\end{array}\right]
$$

Question 2.A. Which of these matrices can you tell by inspection, without computation, must have all eigenvalues be real numbers?

Question 2.B. Using Gershorgin's theorem, what are the bounds on the possible values of the eigenvalues of $A$ ? Is is possible that any of the eigenvalues of $A$ are negative?

Question 2.C. Which of these matrices are normal?
Question 2.D.For every matrix that you know has all real eigenvalues, compute the eigenvalues and the normalized (unit-length) eigenvectors by hand. Show your calculations.

