

Reaction and Diffusion (Symmetric)

Consider now a more general problem of diffusion with reaction, where the solution is symmetric about $x = 0$. The governing equation for planar, cylindrical and spherical geometry ($\gamma = 0, 1, 2$ respectively) is:

$$\frac{1}{x^\gamma} \frac{d}{dx} \left(D(y) x^\gamma \frac{dy}{dx} \right) + r(y) = 0 \quad (33)$$

with

$$D \frac{dy}{dx} + Bi y = 0 \text{ at } x = 1 \quad \text{and} \quad \frac{dy}{dx} = 0 \text{ at } x = 0$$

In addition to the third kind boundary condition at $x = 1$, we consider a nonlinear reaction rate and diffusion coefficient.

Since the solution will be symmetric, we use trial functions which are Lagrange interpolating polynomials in x^2 , Eq. (7):

$$y \cong \tilde{y} = \sum_{i=0}^{n+1} \tilde{y}_i \ell_i(x^2) \quad (34)$$

Although the application of a Method of Weighted Residuals is fundamentally the same, the symmetric trial functions, the boundary condition and the nonlinear diffusion cause some subtle differences to occur. Substituting the trial functions, the residual for the problem is:

$$R(x, \tilde{y}) = \sum_{i=1}^{n+1} \tilde{y}_i \frac{1}{x^\gamma} \frac{d}{dx} \left[D(\tilde{y}(x)) x^\gamma \frac{d\ell_i}{dx} \right] + r(\tilde{y}(x)) = 0 \quad (35)$$

Since orthogonal collocation is known to produce good results when it closely approximates the moments or Galerkin methods, we first consider these methods. To solve the problem by one of these methods Eq. (35) is substituted into Eq. (4) and then the integrals must be approximated. We next consider the accuracy needed in the approximate calculation of these integrals.

This problem is complicated by the nonlinear parameters, D and r . It can be simplified by interpolating these parameters into the trial space, like Eq. (19). Since the trial functions are n^{th} degree polynomials (in x^2) the interpolated reaction rate and diffusion coefficient will be of the same degree. If the diffusion were constant, the diffusion term in Eq. (35) would be of degree $n-1$. If D is interpolated, the diffusion term is of degree $2n-1$.

The weight functions, \mathbf{w} , in Eq. (4) are of degree $n-1$ (in x^2) for the moments method and n for the Galerkin method. After substituting Eq. (35) into Eq. (4) we get rate terms that are degree $2n-1$ for the moments method and $2n$ for the Galerkin method. These integrals can be calculated exactly with n point Gaussian quadrature for the moments method and n point Lobatto quadrature for the Galerkin method. The use of Gaussian quadrature with the Galerkin method will miss exact integration by one degree.

For constant D , the diffusion terms in the weighted residual are one degree less than the reaction terms. For nonlinear D , the integrals need not be calculated more accurately than for a constant diffusion coefficient, so either n point Gaussian or Lobatto quadrature is

sufficiently accurate. Using one of these quadrature methods, the problem for the interior points is:

$$\sum_{k=1}^{n+1} W_k w_j(x_k) \left[\sum_{i=1}^{n+1} \tilde{y}_i \frac{1}{x_k^\gamma} \frac{d}{dx} \left[D(\tilde{y}) x^\gamma \frac{d\ell_i}{dx} \right]_{x_k} + r(\tilde{y}_k) \right] = 0 \quad (36)$$

We have n equations of this type corresponding to the n weight functions, \mathbf{w} . The final equation needed for a solution comes from the boundary condition.

For the moments method, the approximate solution should satisfy the boundary condition exactly:

$$D(\tilde{y}_{n+1}) \sum_{i=0}^{n+1} A_{n+1,i} \tilde{y}_i + B_i \tilde{y}_{n+1} = 0 \quad (37)$$

where, as before:

$$A_{ki} = \left. \frac{d\ell_i}{dx} \right|_{x_k}$$

To solve the complete problem, Eqs. (36) and (37), the residual must be zero at the n interior points. Thus, the moments method with n point Gaussian quadrature reduces to a collocation method, for both the interior and boundary.

For the Galerkin method, Eq. (37) should not be used for the boundary condition. Following variational methods, it should be treated as a weak boundary condition. The weak treatment follows by first integrating the diffusion term by parts:

$$D \ell_j \left. \frac{d\tilde{y}}{dx} \right|_{x=1} - \int_0^1 \left(\sum_{i=1}^{n+1} \left(D \frac{d\ell_j}{dx} \frac{d\ell_i}{dx} \right) \tilde{y}_i - \ell_j(x) r(\tilde{y}) \right) x^\gamma dx = 0 \quad (38)$$

for $j = 1, \dots, n+1$. The boundary condition of Eq. (33) is substituted for the boundary flux term in Eq. (38). With n point quadrature the Galerkin method Eq. (38) reduces to:

$$\delta_{j,n+1} B_i \tilde{y}_{n+1} + \sum_{i=1}^{n+1} \sum_{k=1}^{n+1} D(\tilde{y}_k) W_k A_{kj} A_{ki} \tilde{y}_i - W_j r(\tilde{y}_j) = 0 \quad (39)$$

As before, we define the following matrices:

$$B_{ki} = \frac{1}{x_k^\gamma} \frac{d}{dx} \left[x^\gamma \frac{d\ell_i}{dx} \right]_{x_k} \quad \text{and} \quad C_{ji} = \sum_{k=1}^{n+1} W_k A_{kj} A_{ki} \quad (40)$$

For a symmetric problem the relationship between the matrices, Eq (24), reduces to:

$$C_{ji} = \delta_{j,n+1} A_{n+1,i} - W_j B_{ji} \quad (41)$$

For symmetric problems, Eq. (41) is valid for both Gauss and Lobatto points, whereas for nonsymmetric problems Eq. (24) is valid only for Lobatto points.

Constant Diffusion: With these definitions, the orthogonal collocation approximation for a constant diffusion coefficient is:

$$D \sum_{i=1}^{n+1} B_{ji} \tilde{y}_i + r(\tilde{y}_j) = 0 \quad (42)$$

for $j = 1, \dots, n$. For a constant diffusion coefficient, Eq. (39) reduces to the symmetric equation:

$$\delta_{j,n+1} Bi \tilde{y}_{n+1} + D \sum_{i=1}^{n+1} C_{ji} \tilde{y}_i - W_j r(\tilde{y}_j) = 0 \quad (43)$$

Using the relationships, Eqs. (40) and (41), it is apparent that Eqs. (42) and (43) are equivalent at the interior points. With Gaussian quadrature, Eq. (43) with $j = n + 1$ reduces to boundary collocation, Eq. (37). However, with Lobatto quadrature Eq. (43) is different from boundary collocation. With Lobatto points, the treatment of boundary fluxes is the same as in the previous example, Eq. (31).

Long ago, poor results were found using Eq. (37) together with orthogonal collocation at Lobatto points. It was discovered that good results were achieved if the right hand side of Eq. (28) is used instead for the flux in the boundary condition, Eq. (33). By summing Eq. (39) or (43) for all j , the identical condition is obtained:

$$Bi y_{n+1} = \sum_{j=1}^{n+1} W_j r(\tilde{y}_j) \quad (44)$$

so Eq. (43) is equivalent to this superior method for treating the boundary condition. Eq. (43) is simpler, since the nonlinear reaction terms appear only on the diagonal of every equation, whereas Eq. (44) contains all of the nonlinear terms, i.e. in every column. Eq. (43) is also symmetric, whereas with the normal orthogonal collocation approach, Eq. (42), the equations are equivalent, but not symmetric. Also, for a nonsymmetric problem with a different flux condition on each end, Eq. (28) cannot be used to approximate both boundary conditions.

We will now consider an example with a constant diffusion coefficient, but nonlinear reaction rate. First, we summarize the findings from the previous paragraphs. For constant D , Eq. (42) and (43) are equivalent and either may be used at the interior points. For collocation at Gauss points, boundary collocation, Eq. (37), should be used. For collocation at Lobatto points, either Eq. (44) or (43) with $j = n + 1$ should be used for the boundary condition.

Example – Nonlinear r : For this example a value of $Bi = 100$ is used. With regard to geometry, since there are no fundamental differences in solution procedure planar geometry is used. The nonlinear equations are solved with a Newton-Raphson method, but in some cases modifications were required to achieve convergence to the desired solution.

The reaction rate expression considered in the example is:

$$r = \phi^2 \frac{1-y}{(1-0.95y)^2} \quad (45)$$

With this rate expression the reaction rate initially increases with conversion, y . This form of rate expression can lead to multiple solutions to Eq. (33). This is easily illustrated by considering the approximation with a single term, $n = 1$. The approximation with a single Gauss point is:

$$a \frac{\tilde{y}_1}{\phi^2} = \frac{1-\tilde{y}_1}{(1-0.95\tilde{y}_1)^2} \quad (46)$$

where $a = 2.913$. With a single Lobatto point, the approximation is complicated by the dependence on the reaction rate at the boundary in Eq. (43) or (44). However, this

dependence is very weak, so Eq. (45) with $a = 2.449$ is an accurate approximation. Fig. 6 is a plot of Eq. (45). It is apparent that between the indicated slopes, there are three solutions. The intermediate solution is thermodynamically unstable, so only the lowest and highest solution can occur in practice. Using the calculated values for parameter a , the predicted range of multiple solutions is $0.722 < \phi < 0.900$ for a single Gauss point and $0.662 < \phi < 0.825$ for a single Lobatto point. It is also apparent from Fig. 6 that the rate expression is mildly nonlinear for small y , but extremely nonlinear as the conversion increases. We will find that with an accurate approximation, multiple solutions occur for $0.71 < \phi < 0.80$, so the equation with $n = 1$ are only approximate. However, a simple representation like Eq. (46) and Fig. 6 is very helpful for understanding the multiple solution phenomena.

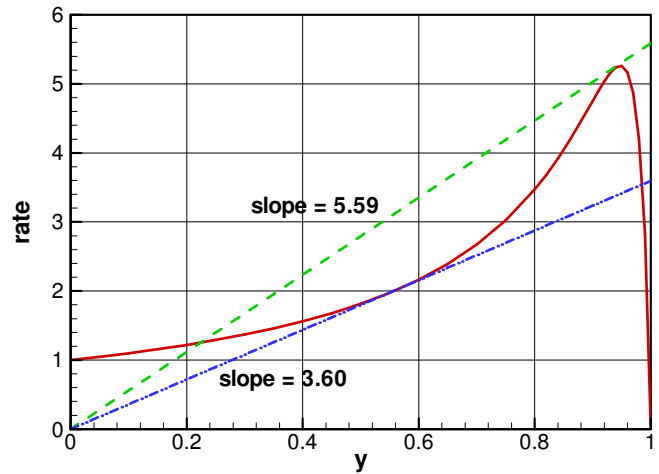


Fig. 6 Graphical solution nonlinear reaction with $n = 1$

For $\phi = 0.75$, Fig. 7 shows calculated conversion profiles for some low order approximations together with an accurate profile (Lobatto, $n = 6$). There are two stable profiles at this condition. The lower profile is accurately approximated with $n = 1$ or 2, whereas the higher profile requires more terms to achieve an accurate solution. Even though the profile is relatively smooth, a larger number of points is required to get an accurate solution. The nonlinearity of the reaction rate (see Fig. 6) makes the problem more difficult for larger conversion. The low order approximations predict nonphysical conversion values greater than unity. Generally, for $y > 1$ it is better to use a linear extrapolation of the reaction rate rather than setting $r = 0$.

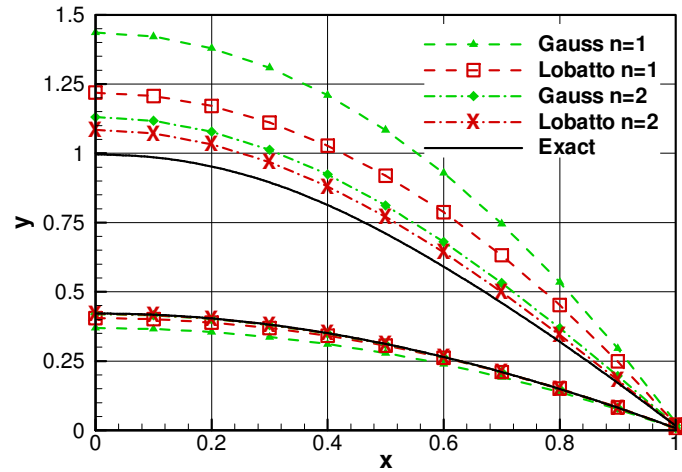


Fig. 7 Profiles for nonlinear rate, Eq. (45) $\phi = 0.75$

Fig. 8 shows the residual of the solution for several approximations. At low values of x the magnitude of the residual becomes very large and negative due to the nonlinearity of the reaction rate at large y . These errors contribute to the errors observed in Fig. 7. The overall error in the effectiveness factor, defined by Eq. (26), is shown in Fig. 9. To achieve an accuracy of 0.1% only $n = 2$ is needed for the lower solution, while $n = 8$ is required for the upper solution. The uneven convergence of the upper solution can be attributed to the nonlinearity of the reaction rate, Eq. (44) and Fig. 6. As with the previous example, see

Fig. 5, the solution with Lobatto points is generally more accurate than when using Gauss points.

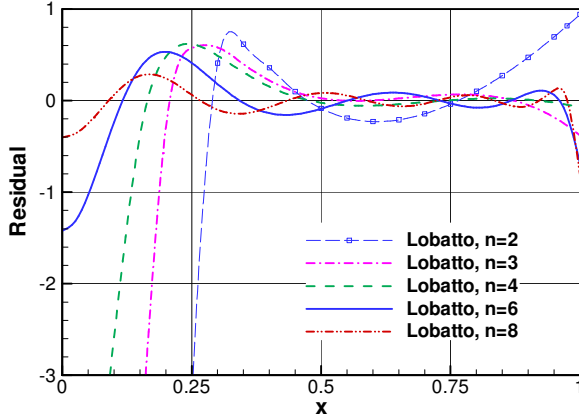


Fig. 8 Residual of upper solution, $\phi = 0.75$

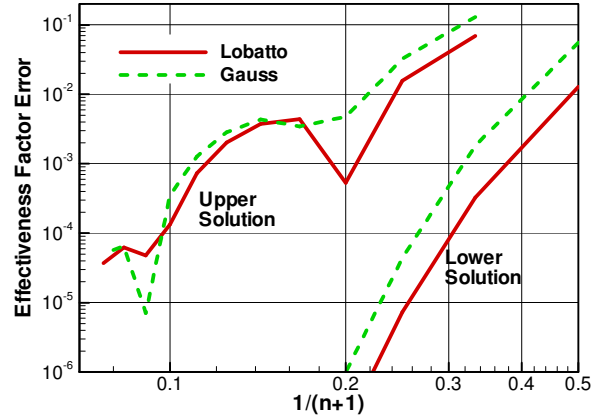


Fig. 9 Error vs n for nonlinear solutions, $\phi = 0.75$

Fig. 10 shows the effectiveness factor as a function of the Thiele modulus, ϕ . The solution with $n = 12$ is exact for practical purposes. It shows that two solutions exist for $0.71 < \phi < 0.80$. The low order solutions are accurate for the lower solution, but show considerable error for the upper one. With $n = 4$ the accuracy is much better with a maximum error of about 5%. With $n = 6$, the entire curve is matched within approximately one percent. Rapid convergence is one characteristic of the method. This problem is difficult due to the strong nonlinearity.

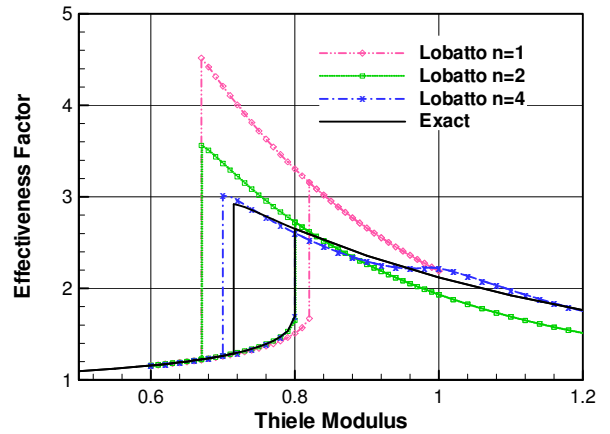


Fig. 10 Effectiveness factor for nonlinear reaction

Consequently, an unusually large number of collocation points are required.

Nonlinear Diffusion: We now consider diffusion problems with a variable or composition dependent diffusion coefficient. There are several options for treating these problems. For Lobatto points, Eq. (39) should be used since it is a Galerkin method. Eq. (39) is also valid for Gauss points.

Another possible method is to differentiate the diffusion term using the chain rule:

$$D(y) \frac{1}{x^\gamma} \frac{d}{dx} \left(x^\gamma \frac{dy}{dx} \right) + \left(\frac{dD(y)}{dx} \right) \left(\frac{dy}{dx} \right) + r(y) = 0 \quad (47)$$

The equation is then discretized using the **B** operator for the Laplacian, like Eq. (42), and the **A** operator for the first derivatives:

$$D \sum_{i=1}^{n+1} B_{ji} \tilde{y}_i + \left(\sum_{i=1}^{n+1} A_{ji} D_i \right) \left(\sum_{i=1}^{n+1} A_{ji} \tilde{y}_i \right) + r(\tilde{y}_j) = 0 \quad (48)$$

The boundary condition, Eq. (37), remains unchanged. As a variation on this method, the spatial derivative of D can be further differentiated, to give its derivative with respect to y multiplied by the square of the spatial derivative of y . With this approach, the approximation no longer preserves mass and the accuracy is not improved. Eq. (48) does

not give the best approximation and it is only suitable for use with Gauss points because Eq. (37) is not appropriate for Lobatto points.

Another method with Gauss points is to use Eq. (36) with weight functions for the moments method, like those used for the nonsymmetric problem, Eq. (17). Then, after application of the quadrature, Eq. (36) reduces to:

$$W_j \sum_{i=1}^{n+1} \tilde{y}_i \frac{1}{x_j^\gamma} \frac{d}{dx} \left[D(\tilde{y}) x^\gamma \frac{d\ell_i}{dx} \right]_{x_j} + W_j r(\tilde{y}_j) = 0 \quad (49)$$

For a symmetric problem, care must be taken when differentiating the diffusion term of Eq. (49). Since the interpolating polynomials are even, their first derivatives are odd, so the normal \mathbf{A} operator cannot be used for the term in brackets. As described in the appendix, a special derivative operator can be developed for odd functions:

$$A_{ij}^* = \frac{1}{x_i^\gamma} \frac{d}{dx} \left[x^\gamma \widehat{\ell}_j \right]_{x_i} \quad (50)$$

where $\widehat{\ell}$ is the interpolating polynomial for an odd function. Since $\mathbf{B} = \mathbf{A}^* \mathbf{A}$, this operator effectively splits the \mathbf{B} matrix in order to approximate the variable diffusion coefficient. Eq. (49) reduces to:

$$W_j \sum_{i=1}^{n+1} \sum_{k=1}^{n+1} A_{jk}^* D(\tilde{y}_k) A_{ki} \tilde{y}_i + W_j r(\tilde{y}_j) = 0 \quad (51)$$

which is simply the residual multiplied by the quadrature weight, W_j . Eq. (51) is an accurate approximation of the moments method. For constant D , Eq. (51) is equivalent to Eqs. (42) and (43). For variable D , Eq. (51) gives a different approximation from Eq. (39).

In summary, for a variable diffusion coefficient, Eq. (39) should be used with Lobatto points. With Gauss points, there are three choices which correspond to different methods of averaging D :

1. Galerkin type approximation, Eq. (39)
2. Moments type approximation, Eq. (51)
3. Equation reduction using the chain rule, Eq. (48)

Example – Nonlinear D: We now consider the case of a composition dependent diffusion coefficient as follows:

$$D = 4 - 3(1 - y)^2 \quad (52)$$

The coefficient is strongly nonlinear, varying by a factor of 4 from 1 at $y = 0$ to 4 at $y = 1$. A linear first order reaction is used:

$$r = \phi^2 (1 - y) \quad (53)$$

For this example we have chosen to use spherical geometry and $Bi = 100$.

Fig. 11 shows a graph of several solutions with $\phi = 10$. The two profiles with constant D correspond to the extremes of Eq. (52). By comparing these profiles, the effect of the nonlinear D is readily apparent. For constant D , the effectiveness factor for $\phi = 10$ is 0.248, 0.343 and 0.462 for $D = 1, 2$ and 4 respectively. For variable D , the effectiveness factor is 0.362.

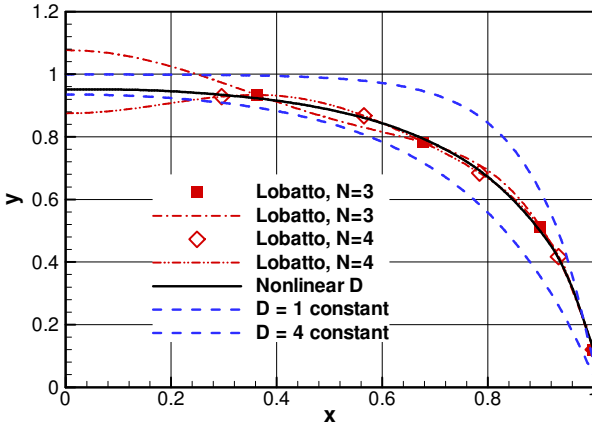


Fig. 11 Profiles with nonlinear and constant D

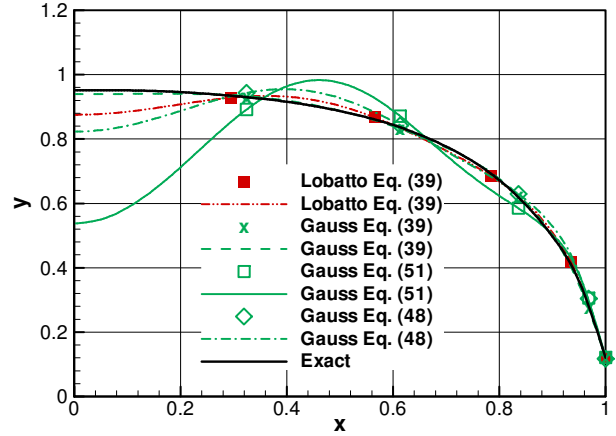


Fig. 12 Nonlinear diffusion approximations with $n = 4$

The approximate solutions in Fig. 11 for small n are accurate at the collocation points but tend to deviate near the center of the sphere. The solution near the center is relatively less important because of the smaller volume. Despite the obvious errors in the solution, the effectiveness factors are accurate to 0.5% and 0.2% for $n = 3$ and 4, respectively. Fig. 12 shows solutions for different approximations all with $n = 4$. Gauss points with Eq. (51) consistently produce the greatest errors in the profiles. The effectiveness factors calculated are more accurate than would be expected considering the deviations in Fig. 12. Fig. 13 shows the errors in effectiveness factor for the various methods. Gauss points with Eq. (48) give considerably more error than the other methods. Approximately three additional points are needed with Eq. (48) to achieve accuracy similar to either type of points with Eq. (39). Lobatto points provide the greatest accuracy for the effectiveness factor, but Gauss points with Eq. (39) gives the most accurate profiles (see Fig. 12).

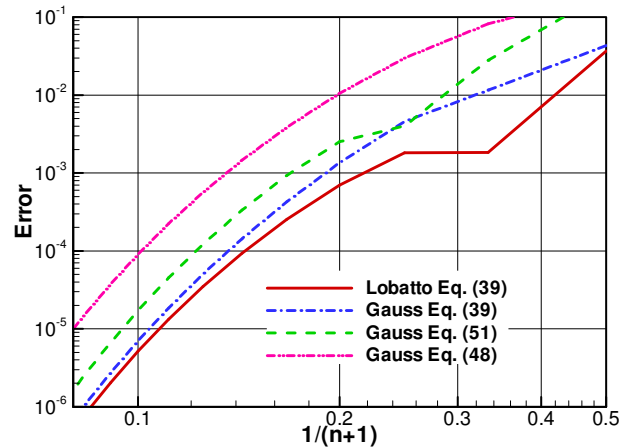


Fig. 13 Nonlinear diffusion, effectiveness factor error

Unfortunately, the use of Gauss points with Eq. (39) is only valid for symmetric problems. For nonsymmetric problems a similar approach is not valid because Gaussian quadrature is not accurate enough to integrate the diffusion term exactly even when D is constant. Consequently, the integration by parts is not exact, so Eq. (24) is not valid and Eq. (23) is not equivalent to Eq. (14) even when the diffusion coefficient is constant.