

A Numerical Solution Method for Boundary Value Problems Containing an Undetermined Parameter

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A number of physical problems can be described by a complex differential equation with an undetermined coefficient appearing as an explicit term. The problem is usually encountered in diffusion-reaction systems and in these cases the unknown parameter is the gradient at the diffusing interface. The problem is stiff and difficult to solve. This paper describes a new method for the solution of such problems. The procedure is based on the boundary integral element concepts where both the dependent variable and its gradient become the primary variables. This permits a direct iterative solution to this problem. Numerical studies presented here show that the proposed solution method is very accurate and rapidly convergent. Two cases studies involving gas absorption with chemical reaction are also presented. © 1992 Academic Press, Inc.

1. INTRODUCTION AND PROBLEM SPECIFICATION

The focus of this paper is to develop an efficient numerical solution method to a certain class of boundary value ordinary differential equations in which an undetermined parameter appears directly as a coefficient in the equation. This parameter is usually the derivative or the gradient of the dependent variable at one of the boundaries. This makes the numerical solution procedure a complicated task. A representative problem of this type will be first formulated and a new method using boundary integral concepts will be demonstrated for the numerical solution to the problem. A number of physical processes where such equations appear will be mentioned and two case studies presented for the system of absorption of a gas accompanied by fast reaction in a liquid containing a reactive species.

The differential equation considered here is of the form

$$\frac{d^2c}{dx^2} = f(c, x, p_1), \quad (1)$$

where c is the dependent variable, x is the independent variable, f is a nonlinear function of c and x while p_1 is the undetermined parameter defined as the derivative of c at

$x=0$. The variable p will be used here to denote the derivative or the gradient of the dependent variable:

$$p = \frac{dc}{dx} \quad (2)$$

and p_1 will denote the gradient at $x=0$,

$$p_1 = \left(\frac{dc}{dx} \right)_{x=0}, \quad (3)$$

where the subscript 1 (rather than zero) has been used in conformity with the notation to be used in later sections and arises due to the reason that $x=0$ will be denoted as nodal point 1 in the discretization scheme. Thus the differential Eq. (1) itself contains an undetermined parameter, p_1 , which can be obtained only after a solution satisfying the boundary conditions has been found to the problem.

The problem considered here is of a boundary value type. The range of variable x can be taken to be from 0 to 1 for illustration purposes without loss of generality and the boundary conditions may be stated in a general form as

$$\text{At } x=0, a_1 p + a_2 c - a_3 = 0 \quad (4)$$

and

$$\text{At } x=1, b_1 p + b_2 c - b_3 = 0, \quad (5)$$

where a_1, a_2, a_3 and b_1, b_2, b_3 are specified constants.

2. SCOPE AND SIGNIFICANCE

The above problem, although very specific, is representative of the class of problems where an undetermined parameter appears as an explicit term. The problem has direct physical significance in a variety of situations and a few examples will be mentioned here. The problem occurs

very often when one is dealing with diffusion-reaction problems with complex kinetics involving more than one species. The variable c will now represent the concentration of the diffusing species and this terminology will be used subsequently in the paper. The gradient p_1 is then directly proportional to the flux of the diffusing species and is very often the primary quantity of interest. An archetypical example is in gas absorption in a medium containing a reacting liquid (see Danckwerts [1], Doraiswamy and Sharma [2] for details of a large number of practical examples of processes of this type). For this case two examples will be presented in a later section where the developments leading to Eq. (1) will be presented in some detail in order to gain further understanding of this problem. The problem also finds applications in a variety of related areas such as transport phenomena in membranes containing reacting carriers (Roberts and Friedlander [3]), phase transfer catalysis (Melville and Goddard [4]; Melville and Yortsos [5]), carrier mediated transport (Goddard [6]; Schultz *et al.* [7]), and combustion processes.

Some comments on the nature of the solution for these types of problems for rapid reactions is in order here. The reaction will now be confined to a thin boundary layer usually near the interface. The reaction rate is close to zero elsewhere leading to a situation where equilibrium conditions can be assumed outside the boundary layer. The boundary layer associated with this problem is therefore often referred to as a non-equilibrium boundary layer (NEBL). The concentration and its gradient are rapidly changing within the NEBL leading to a stiff differential equation. The added complication is due to the undetermined parameter, p_1 . The region where the reaction is close to equilibrium is known as the outer region and here the concentration and/or the gradient would either change very modestly or remain constant. The above discussion provides some picture of the nature of the solution and also emphasizes the complexities associated with the numerical solution to the problem.

Further comments on an instantaneous asymptote for the case of fast reactions is useful here. If one assumes that the reaction is at equilibrium everywhere then the flux of the species diffusing into the system at the interface can be directly calculated without the need for solving the differential equation. The classical paper of Olander [8] is one example of such an approach and the resulting value of the gradient at the interface is known as the instantaneous reaction asymptote. The entire reaction is now assumed to take place right at the interface for reversible reaction or at a sharp reaction front for irreversible reactions. This asymptotic nature of the solution will be obtained in the limit of the reaction rate constant tending to infinity. In practice, however, the reaction takes place over a finite region of the domain and not at a sharp point. The deter-

mination of the region in which the reaction is taking place (the reaction zone) is of importance in the estimation of the kinetic rate constants for fast reactions by capillary flow techniques or other related methods. This will need an accurate resolution of the NEBL; otherwise the estimated rate constant is likely to be in error. One example is the reaction of sulfur dioxide in water which is a fast reaction; this problem being of direct practical importance in the fate of pollutants in the atmosphere and in the acid rain issue. The reported rate constant for the kinetics of the reaction differ by a factor of eight [3, 9]. An early paper by Friedlander and Keller [10] also refer to the difficulties associated with the calculation of the structure of the reaction zone for fast reaction and the present work can be considered to provide additional information for diffusion-controlled fast reactions.

Previous studies that account for fast reactions (but not at equilibrium at all points) have included perturbation analysis [3, 5] and very careful numerical shooting methods [11, 12]. Shooting methods can be used but have stability and convergence problems in general. The solution procedures based on finite difference or finite elements also are not straightforward and require an indirect iteration procedure based on a posteriori estimation of the term p_1 . This is an involved two-step procedure and could have convergence problems. Here a new direct one-step procedure is developed based on the boundary integral concepts. The boundary integral methods have several novel features which are useful to the problem under consideration. These are as follows: (1) The method leads to a fully integral formulation of the problem, thus avoiding the need for the approximation of the first and second derivatives in terms of the nodal values. (2) Both the concentration c and its derivative p are primary variables in this method and are, therefore, calculated as part of the solution technique here. Thus an estimated value of the unknown parameter p_1 is available at each stage of calculation and, hence, a direct iterative procedure is possible as shown in this paper. Previous papers by the author [13, 14] have shown the use of this method in connection with nonlinear boundary value problems of the standard type; i.e., those which do not contain any undetermined parameters. This paper applies this technique to problems containing an undetermined coefficient as formulated in Section 1 of this paper.

The scope of the remaining portion of this paper is as follows: In Section 3 the boundary integral method is developed in detail. Section 4 shows how one solves the resulting nonlinear algebraic-integral equations by the use of Newton-Raphson method. Section 5 shows the utility of the method by use of two case study problems. These study problems are chosen to be simple enough so that comparison with previous approximate analytical solutions are possible. Further, the solution of more complex problems and problems involving multiple reactions (i.e., multiple dif-

ferential equations) using the current method are worthy of further research but is not addressed here as the emphasis of this paper is to develop a new numerical method and demonstrate its accuracy.

3. BOUNDARY INTEGRAL REPRESENTATION

The interval 0 to 1 for x is divided into a number of subintervals or elements just as in the finite element or finite difference method. Consider N subintervals as the basis for the discretization. Then there are $N + 1$ nodes or positions at which the values of the dependent variable and its derivatives have to be calculated. Thus the unknowns are

$$p_1, c_1, p_2, c_2, \dots, p_{N+1}, c_{N+1},$$

where p_1 refers to p at $x = 0$ representing node 1 as defined earlier while the subscript $N + 1$ refers to $x = 1$. Thus we need to formulate $2(N + 1)$ equations for the evaluation of these quantities. The boundary conditions given by Eqs. (4) and (5) provide two such equations, leaving $2N$ equations to be developed by using boundary integral concepts. The details are discussed below.

Consider a subinterval between $x = a$ and $x = b$ ($a \geq 0$ and $b \leq 1$). The solution proceeds by forming a weighted residual formulation of Eq. (1) with weighting functions G which are yet to be specified. Thus multiplying Eq. (1) by G and integrating with respect to x from a to b , we have

$$\int_a^b G \frac{d^2c}{dx^2} dx = \int_a^b Gf(c, x, p_1) dx. \quad (6)$$

The first term on the LHS of Eq. (6) is now integrated by parts twice as

$$\int_a^b G \frac{d^2c}{dx^2} dx = \left[G \frac{dc}{dx} \right]_a^b - \left[\frac{dG}{dx} c \right]_a^b + \int_a^b c \frac{d^2G}{dx^2} dx. \quad (7)$$

The differential operator in the variable x in Eq. (7) (last term on RHS) can now be eliminated, provided one chooses weighting functions as the solution to the adjoint operator:

$$\frac{d^2G}{dx^2} = 0. \quad (8)$$

With this choice for G , Eqs. (6) and (7) can be combined, leading to the boundary integral element formulation of the problem

$$\left[G \frac{dc}{dx} \right]_a^b - \left[\frac{dG}{dx} c \right]_a^b - \int_a^b Gf(c, x, p_1) dx = 0. \quad (9)$$

Two weighting functions will be needed for each subinterval (since we need to develop two equations for each element) and these are chosen as two independent solutions to Eq. (8). Thus the weighting functions G_1 and G_2 are now specified as

$$G_1 = x \quad \text{with} \quad \frac{dG_1}{dx} = 1 \quad (10)$$

$$G_2 = 1 \quad \text{with} \quad \frac{dG_2}{dx} = 0. \quad (11)$$

With these simplifications Eq. (9) for $G = G_1$ and $G = G_2$ can be written as

$$-ap_a + c_a + bp_b - c_b - \int_a^b xf(c, x, p_1) dx = 0 \quad (12)$$

and

$$-p_a + p_b - \int_a^b f(c, x, p_1) dx = 0, \quad (13)$$

where the subscripts a and b refer to the values (of c and p) at $x = a$ and $x = b$ respectively.

Equations (12) and (13) are the discretization equations for each element or the subinterval and are akin to the element level equations in the finite element method. The complete problem is then obtained by combining all the element level equations, together with the boundary conditions at $x = 0$ and $x = 1$.

In addition, in order to handle terms containing c in Eqs. (12) and (13) we need to construct an approximating function for c for each subinterval. Note that in the current method the approximation for c is needed only for the numerical integration of the term containing $f(c)$ and not for the discretization of the first and second derivatives. The approximating function is used only within the integrals and hence is smoothed, providing a high measure of accuracy. Since the information on both the concentration and its derivative is expected to be available at all the nodal points, we can construct a cubic osculating polynomial for c for each subinterval. Such an osculating polynomial is then defined as

$$c = \phi_1(b-a) p_a + \phi_2 c_a + \phi_3(b-a) p_b + \phi_4 c_b. \quad (14)$$

Further, the osculating polynomials ϕ_i ($i = 1$ to 4) are defined with respect to a local coordinate system η ,

$$\eta = \frac{x-a}{b-a} \quad (15)$$

and are as follows:

$$\phi_1 = \eta - 2\eta^2 + \eta^3 \quad (16)$$

$$\phi_2 = 1 - 3\eta^2 + 2\eta^3 \quad (17)$$

$$\phi_3 = -\eta^2 + \eta^3 \quad (18)$$

$$\phi_4 = 3\eta^2 - 2\eta^3. \quad (19)$$

It may be noted here that other approximating functions for c can be used instead of the cubic shape functions defined by ϕ_i . For instance, c can be expanded in terms of rational functions, trigonometric or exponential functions, etc., if there are clear advantages for doing so. In this work a cubic polynomial is used for generality.

This completes the boundary integral representation or "discretization" of the problem. Note that the unknown parameter p_1 is now a primary variable appearing naturally in the discretization scheme and is directly determined as a part of the overall solution strategy. All that one needs now is to solve the set of non-linear algebraic-integral equations by the most efficient method. In this paper, Newton-Raphson iteration scheme is proposed and implemented.

4. NEWTON-RAPHSON METHOD

In this method it is necessary to construct a Jacobian matrix for the system. The Jacobian for the boundary conditions can be easily constructed: (1) by differentiating Eq. (4) with respect to p_1 and c_1 for $x=0$ and (2) by differentiating Eq. (5) with respect to p_{N+1} and c_{N+1} for $x=1$. The Jacobian terms corresponding to the element level equations can be constructed by differentiating under the integral sign using the chain rule. The details will be presented below:

Let the element level equations be represented by $F_1=0$ and $F_2=0$ corresponding to Eqs. (12) and (13). The element level variables are $p_a, c_a, p_b,$ and c_b . Further, all the element level equations contain the variable p_1 in the integral term (indirectly due to the dependency of f on p_1). Taking these features into consideration the element level Newton-Raphson formulation is therefore given by the pair of equations,

$$\begin{aligned} H_{10} \Delta p_1 + H_{11} \Delta p_a + H_{12} \Delta c_a \\ + H_{13} \Delta p_b + H_{14} \Delta c_b = -F_1 \end{aligned} \quad (20)$$

and

$$\begin{aligned} H_{20} \Delta p_1 + H_{21} \Delta p_a + H_{22} \Delta c_a \\ + H_{23} \Delta p_b + H_{24} \Delta c_b = -F_2, \end{aligned} \quad (21)$$

where $\Delta p_1, \Delta c_1, \Delta p_2,$ etc. are the corrections to $p_1, c_1, p_2,$

etc. to obtain the improved values for the next iteration. The coefficients of the Jacobian are given by the following expressions:

$$H_{10} = \frac{\partial F_1}{\partial p_1} = - \int_a^b x \frac{\partial f}{\partial p_1} dx \quad (22)$$

$$H_{20} = \frac{\partial F_2}{\partial p_1} = - \int_a^b \frac{\partial f}{\partial p_1} dx \quad (23)$$

$$H_{11} = \frac{\partial F_1}{\partial p_a} = -a - \int_a^b x \frac{\partial f}{\partial c} \phi_1(b-a) dx \quad (24)$$

$$H_{12} = \frac{\partial F_1}{\partial c_a} = 1 - \int_a^b x \frac{\partial f}{\partial c} \phi_2 dx \quad (25)$$

$$H_{13} = \frac{\partial F_1}{\partial p_b} = b - \int_a^b x \frac{\partial f}{\partial c} \phi_3(b-a) dx \quad (26)$$

$$H_{14} = \frac{\partial F_1}{\partial c_b} = -1 - \int_a^b x \frac{\partial f}{\partial c} \phi_4 dx \quad (27)$$

$$H_{21} = \frac{\partial F_2}{\partial p_a} = -1 - \int_a^b \frac{\partial f}{\partial c} \phi_1(b-a) dx \quad (28)$$

$$H_{22} = \frac{\partial F_2}{\partial c_a} = - \int_a^b \frac{\partial f}{\partial c} \phi_2 dx \quad (29)$$

$$H_{23} = \frac{\partial F_2}{\partial p_b} = 1 - \int_a^b \frac{\partial f}{\partial c} \phi_3(b-a) dx \quad (30)$$

$$H_{24} = \frac{\partial F_2}{\partial c_b} = - \int_a^b \frac{\partial f}{\partial c} \phi_4 dx. \quad (31)$$

The Jacobian elements listed above are constructed using the chain rule,

$$\frac{\partial f}{\partial * } = \frac{\partial f}{\partial c} \frac{\partial c}{\partial * } \quad (32)$$

with * representing any variable ($p_a, c_a,$ etc.).

The solution procedure is then as follows:

1. Assign trial values for the dependent variables c_i at the nodal points x_i and estimate the trial values of the gradient at these points.
2. Evaluate the coefficients of the Jacobian matrix and the functions F_1 and F_2 for all the elements using the current values of c_i and p_i . (The various integrals appearing in the Jacobian terms were evaluated in this work using a 10-point Gaussian quadrature.)
3. Assemble the element level Jacobians together with the Jacobians for the boundary conditions into an overall global matrix.

TABLE I
Global Matrix of the Final Assembled Equations
Shown Here for $N = 4$ for Illustration

		Variables										
		Δp_1	Δc_1	Δp_2	Δc_2	Δp_3	Δc_3	Δp_4	Δc_4	Δp_5	Δc_5	RHS
B. C at $x = 0$		a_1	a_2	0	0	0	0	0	0	0	0	-Eq. (4)
Element 1,	1	H_{10}	H_{12}	H_{13}	H_{14}	0	0	0	0	0	0	$-F_1(1)$
	2	$+H_{11}$	H_{20}	H_{22}	H_{23}	H_{24}	0	0	0	0	0	$-F_2(1)$
			$+H_{21}$									
Element 2,	1	H_{10}	0	H_{11}	H_{12}	H_{13}	H_{14}	0	0	0	0	$-F_1(2)$
	2	H_{20}	0	H_{21}	H_{22}	H_{23}	H_{24}	0	0	0	0	$-F_2(2)$
Element 3,	1	H_{10}	0	0	0	H_{11}	H_{12}	H_{13}	H_{14}	0	0	$-F_1(3)$
	2	H_{20}	0	0	0	H_{21}	H_{22}	H_{23}	H_{24}	0	0	$-F_2(3)$
Element 4,	1	H_{10}	0	0	0	0	H_{11}	H_{12}	H_{13}	H_{14}		$-F_1(4)$
	2	H_{20}	0	0	0	0	H_{21}	H_{22}	H_{23}	H_{24}		$-F_2(4)$
B. C at $x = 1$		0	0	0	0	0	0	0	0	b_1	b_2	-Eq. (5)

Note. $H_{10}, H_{11}, H_{21},$ etc., are different for each element.

4. Solve this matrix using any linear equation solver for the unknowns: $\Delta p_1, \Delta c_1, \Delta p_2, \Delta c_2, \dots, \Delta c_{N+1}$.

5. Use these values to update the primary variables, c_i and p_i , at the nodes, for the next iteration.

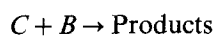
6. Continue the process until convergence is obtained.

It may be useful to discuss briefly here the structure of the global matrix obtained by assembling the Newton-Raphson equations. This matrix is very sparse as shown in Table I. For an efficient solution of the resulting linear equations the sparsity of the matrix should be effectively utilized.

5. CASE STUDIES: GAS ABSORPTION PROBLEMS

5.1. Second-Order Irreversible Reaction

Consider a gas C absorbing and reacting into a liquid containing a dissolved reactant B according to a reaction scheme represented by



with the rate of chemical reaction represented by an irreversible second-order kinetics:

$$\text{Rate} = kCB.$$

The problem can be modeled by the set of differential equations,

$$D_C \frac{d^2 C}{dy^2} = kCB, \quad (33)$$

$$D_B \frac{d^2 B}{dy^2} = kCB, \quad (34)$$

where D is the diffusion coefficient of the subscripted species and y is a distance parameter measured from the interface.

The following boundary conditions will be used here: At the

$$\text{gas-liquid interface, } y = 0, C = C^*, dB/dy = 0 \quad (35)$$

and

$$\text{end of diffusion film, } y = \delta, C = 0, B = B_l. \quad (36)$$

Here δ represents the thickness of the diffusion boundary layer or the Nernst's diffusion film, C^* is the saturation solubility of the gas at the interface, B_l is the concentration of the liquid phase reactant in the bulk liquid. The boundary condition for B in Eq. (35) is valid for a non-volatile liquid phase reactant.

Using the following dimensionless variables

$$c = \frac{C}{C^*}, \quad b^* = \frac{B}{B_l}, \quad x = \frac{y}{\delta},$$

the equations can be put into a dimensionless form,

$$\frac{d^2 c}{dx^2} = Mcb^* \quad (37)$$

$$\frac{d^2 b^*}{dx^2} = qMcb^*, \quad (38)$$

where M is the ratio of the time constant for diffusion to the time constant for reaction:

$$M = \frac{kB_l}{D_C} \delta^2 \quad (39)$$

and

$$q = \frac{C^* D_C}{B_l D_B}. \quad (40)$$

Equations (37) and (38) can be combined to yield

$$\frac{d^2 b^*}{dx^2} = q \frac{d^2 c}{dx^2}. \quad (41)$$

Equation (41) can be integrated with the above boundary conditions to give an equation relating b^* to c ,

$$b^* = 1 + qc - qp_1(x - 1). \quad (42)$$

Substituting for b^* in Eq. (37) yields our equation containing an undetermined parameter,

$$\frac{d^2c}{dx^2} = Mc[1 + qc - qp_1(x - 1)]. \quad (43)$$

The boundary conditions in terms of the dimensionless variable c can be expressed now in the form similar to Eqs. (4) and (5). Thus now

$$\begin{aligned} a_1 = 0, & \quad a_2 = 1, & \quad a_3 = 1 \\ b_1 = 0, & \quad b_2 = 1, & \quad b_3 = 0. \end{aligned}$$

The above discussion shows an illustrative and practical problem where an undetermined coefficient appears in the differential equation. Many other complex cases will be governed by a similar type of differential equation and hence the present work provides an important contribution in the numerical solution of such problems. The numerical procedure developed in this work will now be tested on this problem and the results compared to the numerical solutions to this problem available in the literature (DeSantiago and Farina [11], Sen [12]). Further, approximate analytical solutions of sufficient accuracy for engineering design purposes are available for this problem and these are summarized in the excellent book by Cussler [15]. This provides an additional method for the comparison of the accuracy of the numerical method.

The first case studied was for $\sqrt{M} = 10$ and $q = 0.1$. The starting profiles for the concentration was unity at all the nodal points and hence the assumed value for p_1 was zero. Five elements ($N = 5$) were used and the nodes were unevenly spaced at $x = 0.0, 0.01, 0.05, 0.1, 0.3, 0.5,$ and 1.0 . The iterations converged in five trials within five-digit accuracy. The approach to the converged value of the parameter p_1 is shown in Table II. It is seen that the system is rapidly convergent with the value for p_1 approaching within 1.6% of the final value in just two iterations. Further results were generated for $\sqrt{M} = 100$ and 1000 for various values of q and the results are shown in Table III. For the case of $\sqrt{M} = 100$, six elements were used rather than five due to the expected steepness of the profiles. The additional node was placed at $x = 0.005$. Similarly for $\sqrt{M} = 1000$, an extra node was placed at $x = 0.001$. The results are in exact agreement with the earlier numerical studies (11, 12). Table III also presents some results using $N = 12$ for $\sqrt{M} = 100$ and $N = 14$ for $\sqrt{M} = 1000$. The mesh refinements improves the value of p_1 by only about 1%

TABLE II

Approach to Converged Solution for p_1 for the Case of $M = 100, q = 0.1$ for Irreversible Second-Order Reaction

Iteration	Value of p_1
0	0.0000
1	-5.4854
2	-6.5717
3	-6.6816
4	-6.6829
5	-6.6829

showing that discretization requirements for the method are not very tight. This is due to the integral nature of the problem. Further the computational efforts are minimum, each iteration taking about 10 s on an ordinary IBM-PC. The program developed did not use the sparse nature of the matrix; if this is done the computational efficiency would improve further.

For large values of \sqrt{M} and moderate values of q the equilibrium assumption has been used in prior studies (see, for instance, 1, 2, 15). For an irreversible reaction the reaction is then confined to a reaction plane, since the species C and B cannot coexist in the liquid for very rapid reaction. The results obtained by using this assumption are generally known as the instantaneous reaction asymptote as already discussed in Section 2. For this case the asymptotic value of p_1 is given by setting $b^* = 0$ at $x = 0$ in Eq. (42). Thus

$$p_1(\text{Asymptotic } \sqrt{M} \rightarrow \infty) = -\frac{1+q}{q}. \quad (44)$$

The location of the reaction plane x^* at which the all the reaction is assumed occur in the asymptotic model is then

TABLE III

Gradient at the Diffusing Surface for a Second-Order Irreversible Reaction

\sqrt{M}	N	q	p_1
10	5	0.001	-9.94
		0.01	-9.56
		0.1	-6.68
		0.5	-2.90
		1.0	-1.99
100	6	0.001	-94.38
		0.1	-10.94
		1.0	-2.00
1000	12	0.001	-95.09
	7	0.001	-605.67
		1.0	-2.00
		0.001	-616.96

given by the intersection of the X -axis with the line of slope equal to p_1 and passing through $(0, 1)$,

$$x^* = \frac{q}{1+q}. \quad (45)$$

In order to compare the present numerical results with this asymptotic approach, a case of $\sqrt{M} = 1000$ and $q = 1.0$ can be chosen. The earlier studies have shown that the instantaneous asymptote is a good approximation for this case. Here the numerical value of p_1 was found to be -2.0 , in exact agreement with the asymptotic value. Detailed concentration profiles for this case are plotted in Fig. 1. It is seen that the predicted concentration profiles are in excellent agreement with the instantaneous reaction asymptote but numerical results show that the concentration does not drop to zero sharply at $x = x^*$ but decays smoothly to zero near that point. The concentration gradient also is not discontinuous in the numerical solution in contrast to that predicted by the instantaneous asymptotic solution.

5.2. First-Order Reversible Reaction

Consider now a case of gas absorption with a first-order reversible reaction represented by



with the rate given

$$\text{Rate} = k(C - B/K),$$

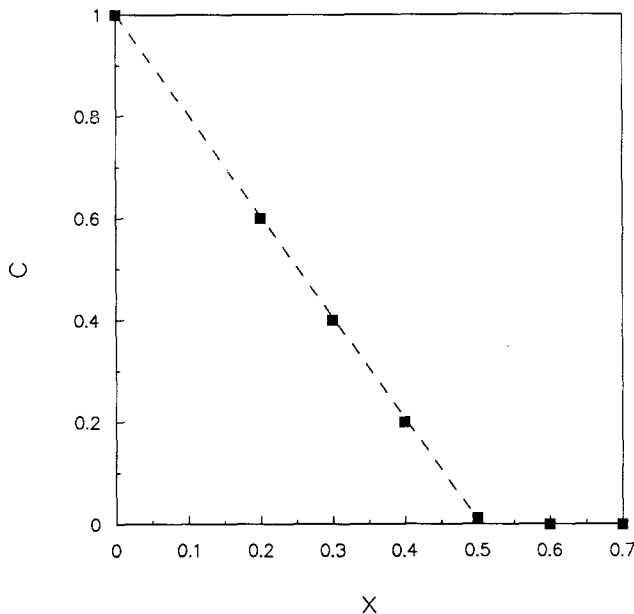


FIG. 1. Concentration profiles as a function of distance parameter for $\sqrt{M} = 1000$ and $q = 1.0$. Solid points are the numerical results while the dashed line shows the profiles corresponding to the instantaneous reaction asymptote; $N = 7$.

where k is the first-order rate constant and K is the equilibrium constant for the reaction.

This case study was chosen for two reasons: (1) A simple analytical solution is available for comparison purposes; (2) The problem is representative of the class of diffusion-reaction problems with a boundary layer of constant gradient type as opposed to conventional problems of constant concentration type.

The problem can be modeled by

$$D_C \frac{d^2 C}{dy^2} = k(C - B/K) = -D_B \frac{d^2 B}{dy^2}. \quad (46)$$

The boundary conditions will be assumed to be the same as given by Eqs. (35) and (36) with the modification that at $y = \delta$, $C = C_l$. If one focuses attention on fast reactions which are complete in the diffusion film itself then the equilibrium requirement dictates that

$$B_l = KC_l \quad (47)$$

and this condition also will be used here. Further, for simplicity, equal diffusion coefficients for C and B will be used. Thus $D_C = D_B$. Integration of the first and the last pair of equations in (46) and the use of the boundary conditions listed above provide a relationship for B in terms of C . This can be expressed in terms of dimensionless concentration as:

$$b^* = c_l(1 + K) - c + p_1(x - 1), \quad (48)$$

where b^* is now defined as B/C^* .

Equation (48), when substituted into the first pair of equations in (46) yields the differential equation with the unknown coefficient. The equation in terms of dimensionless variables then is

$$\frac{d^2 c}{dx^2} = \beta^2 [c - c_l - p_1(x - 1)/(1 + K)], \quad (49)$$

where

$$\beta^2 = M \left(\frac{1 + K}{K} \right) \quad (50)$$

and M now is given by $k\delta^2/D_C$.

The equation can be solved analytically to yield the following equations for the concentration distribution and the gradient at the gas-liquid interface:

$$c = c_l + \left(1 - c_l + \frac{p_1}{K + 1} \right) \frac{\sinh[\beta(1 - x)]}{\sinh \beta} + \frac{p_1}{K + 1} (x - 1) \quad (51)$$

$$p_1 = - \frac{(1 - c_l)(1 + K)}{1 + (K/\beta) \tanh \beta}. \quad (52)$$

TABLE IV
Gradient at the Diffusing Surface for a Reversible
First-Order Reaction

\sqrt{M}	c_i	K	p_1
10	0.5	0.1	-0.5483
		1.0	-9.9339
		10.0	-2.8153
10	0.0	0.1	-1.0966
		1.0	-1.8679
		10.0	-5.6307
100	0.0	0.1	-1.09966
		1.0	-1.9859
		10.0	-10.0414
1000	0.0	0.1	-1.09996
		1.0	-1.9986
		10.0	-10.8951
		100.0	-91.782

Note. $N = 13$.

These equations can be used to compare the numerical results obtained using the procedure described in this work.

The numerical solutions were generated for various values of \sqrt{M} , c_i , and K and compared with the analytical solution. The results are presented in Table IV for the values of p_1 for various combinations of the parameters. These results were generated with $N = 13$ with the nodal points shown in Table V. The numerical results are in very close agreement with the analytical solution, the errors in the value of p_1 being only 1 to 2%. It may be noted here that only two iterations were needed to obtain convergence in view of the quasi-linear nature of the rate term.

For large values of M the solution is of a boundary layer type. The boundary layer exists in a region close to $x = 0$

TABLE V

Detailed Concentration (c) and Gradient (p) Profiles for a Reversible First-Order Case

x	c	p
0.0	1.0000	-91.782
0.001	0.9422	-33.266
0.005	0.9058	-2.327
0.01	0.8997	-0.952
0.03	0.8815	-0.915
0.05	0.8623	-0.909
0.075	0.8406	-0.909
0.1	0.8178	-0.909
0.2	0.7269	-0.909
0.3	0.6361	-0.909
0.4	0.5452	-0.909
0.5	0.4543	-0.909
0.7	0.2726	-0.909
1.0	0.0000	-0.909

Note. $M = 10^6$, $K = 100$.

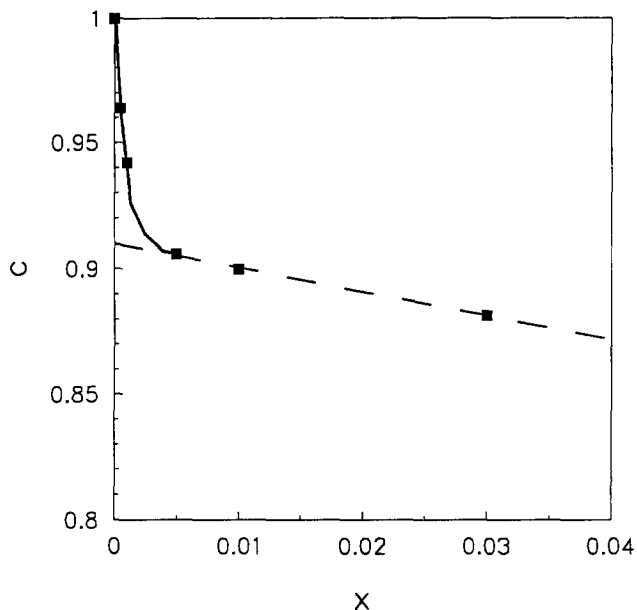


FIG. 2. Concentration profiles for c for $\sqrt{M} = 1000$ and $K = 100$. for a reversible reaction; $N = 13$. Solid line and points are the numerical results while the dashed line shows the profiles corresponding to the outer solution.

where both c and p are rapidly changing. For the region outside the boundary layer, the nature of the solution can be examined by equating the term under the square bracket in Eq. (49) to zero. Thus the outer solution in the region, where the concentration is not rapidly changing, is given by

$$c^0 - c_i - p_1(x - 1)/(1 + K) = 0, \quad (53)$$

where the superscript 0 is used to indicate that this is the outer solution, valid outside the boundary layer. The gradient of c in the outer region denoted as p^0 is obtained by differentiating Eq. (53),

$$p^0 = p_1/(K + 1). \quad (54)$$

Equation (54) shows that the gradient is constant in the outer region and hence the outer solution is of constant gradient type and not one with a constant value of c . This was pointed out in an earlier paper by Melville and Yortsos [5] as well. In order to ascertain whether the numerical solutions have the same features, it is appropriate to present the detailed c and p profiles as a function of x for one such case. This is shown in Table V for $M = 1 \times 10^6$ and $K = 100$. A region of constant p is obtained for the large part of the domain (for values of x greater than 0.01, which is also the approximate thickness of the boundary layer). The value of p shown in Table V also matches exactly the

analytical value given by Eq. (54). Thus the current method gives accurate solutions, both within the boundary layer as well as for the region outside the boundary layer. The results of the solution for this case are shown in Fig. 2. Note that the numerical results show the correct boundary layer behavior and, in addition, predict the exact results for the outer region as well.

6. CLOSING REMARKS

The above case studies illustrate that the numerical procedure developed in this work is an accurate, efficient, and robust method for the solution of boundary value problems containing an undetermined parameter. Application to problems with a more complex kinetics and to systems governed by multiple differential equations should prove to be useful for practical applications and should be addressed in future studies.

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