polyethylene and polypropylene samples of different types yielded essentially the same diffusivity and solubility data.

CONCLUSIONS

1. A technique has been developed for the simultaneous measurement of diffusivities and solubilities or gases in softened and molten polymers.
2. Henry's law was found to hold in such systems up to 20 atm.
3. Henry's law constants were determined for nitrogen, carbon dioxide, argon, and helium in polyethylene, polypropylene, polyisobutylene, and polymethylmethacrylate, as well as for neon, krypton, and monochlorodifluoromethane in some of these polymers.
4. Diffusion coefficients of gases in softened or molten polymers were found to be fairly independent of pressure up to 20 atm.
5. Diffusion coefficients of gases were determined for nitrogen, carbon dioxide, argon, and helium in polyethylene, polypropylene, and polyisobutylene as well as for monochlorodiflouromethane (except for polyisobutylene.)

NOTATION

c = cc. (STP)/g. of polymer
c^* = cc. (STP)/g. of polymer at saturation in experiment under consideration
$\bar{c}$ = average concentration of gas in polymer at time t
c_o = cc. (STP)/g. of polymer at saturation in previous experiment
D = diffusion coefficient, sq. cm./sec.
L = height of polymer sample, cm.
P' = absolute pressure at time t, atm.
P_f = final equilibrium pressure, atm.
Pi = initial pressure, atm.
t = time, sec.
z = axial position, cm.

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Upper and Lower Bounds for Solutions to the Transport Equation

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The collocation method and a maximum principle are used to generate pointwise, improvable upper and lower bounds for solutions of the transport equation. This new method of analysis is applicable to the unsteady state transport equation with a specified velocity field as well as to other problems which have a maximum principle. An application to unsteady state transfer to a fluid in ideal stagnation flow illustrates the method.

Because analytical solutions of the equations of change for realistic mathematical models are so rare, the engineer must of course rely often on approximate solutions in analyzing transport phenomena. The method of weighted residuals (*1* to *3*) is a very general class of error-distribution approximating schemes with features the engineer finds attractive; but, unfortunately, the method suffers from the deficiency that usually no error bounds can be placed on the approximate solution. In a succession of approximate solutions there may be no stage at which it is possible to state how good the approximation is, even though a proof of ultimate convergence may be available. This paper outlines a method of approximate solution which combines the collocation method, which is one version of the method of weighted residuals, with a maximum principle to provide *pointwise, improvable upper and lower bounds* for a scalar field such as temperature or concentration. The method is limited to those problems for which a maximum principle has been proved, but these include a large class of problems of concern to the chemical engineer—in particular, the unsteady state transport equation with a known velocity field.

The idea of combining an approximation method with a maximum principle has been applied previously by

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Nickel (4) and by Collatz (5). Nickel proved a maximum principle for the laminar flow of an incompressible fluid in a two-dimensional boundary layer. He then constructed comparison functions which are lower bounds on the velocity, but he was unable to provide upper bounds on the velocity for this nonlinear, steady state problem. Collatz (5) used a maximum principle for elliptic partial differential equations to obtain upper and lower bounds for the solution of Poisson's equation. He used trial solutions which contained two adjustable parameters and there was no way to improve the results systematically. The procedure presented here differs from that of Collatz in that: (1) the construction of comparison functions is systematic, (2) any number of parameters may be used, and (3) the results are systematically improved with successive approximations.† A noteworthy feature is the optimization of bounds by solving linear programming problems.

Following a brief statement of the underlying theorems, the method is outlined and then applied to a specific problem. Finally, the general merits of the method are discussed along with areas for future research. An appendix gives detailed statements of the pertinent theorems.

OUTLINE OF METHOD

Maximum Principle

Consider the following initial value problem:

$$L(u) \equiv \sum_{i,j=1}^{3} a_{ij}(\mathbf{x}, t) \frac{\partial^2 u}{\partial x_i \partial x_j} + \sum_{i=1}^{3} b_i(\mathbf{x}, t) \frac{\partial u}{\partial x_i} + c(\mathbf{x}, t) - \frac{\partial u}{\partial t} = f(\mathbf{x}, t) \quad (1)$$

and

$$u(\mathbf{x}, t = 0) = \phi(\mathbf{x}) \quad (2)$$

in some region of physical space V and

$$u(\mathbf{x}, t) = \psi(\mathbf{x}_s, t) \quad (3)$$

on S, the boundary of V. This problem includes as a special case, which is treated below, the unsteady state transport equation with a known velocity field. The dependent variable u is then interpreted as either temperature or concentration. The maximum principle for this problem, due to Il'in et al. (6), states in essence‡ that if for some function $w(\mathbf{x}, t)$

$$\begin{aligned} L(w) &\leq 0, \ \mathbf{x} \text{ in } V, \ t > 0 \\ w(\mathbf{x}, t = 0) &\geq 0, \ \mathbf{x} \text{ in } V \end{aligned} \quad (4)$$

and

$$w \geq 0 \quad \mathbf{x} \text{ on } S \quad (5)$$

then

$$w(\mathbf{x}, t) \geq 0 \quad \mathbf{x} \text{ in } V, \quad t > 0 \quad (6)$$

Suppose there is a function v which satisfies the following conditions:

$$\begin{aligned} L(v) - f &\leq 0 && \mathbf{x} \text{ in } V, \quad t > 0 \\ v(\mathbf{x}, t = 0) &= \phi && \mathbf{x} \text{ in } V \\ v(\mathbf{x}, t) &= \psi && \mathbf{x} \text{ on } S, \quad t > 0 \end{aligned} \quad (7)$$

Then the new function $w \equiv v - u$, where u is the unknown solution to Equations (1), (2), and (3), satisfies the conditions of the theorem [Equations (4) and (5)] and hence

$$w \geq 0 \quad \mathbf{x} \text{ in } V, \quad t > 0 \quad (8)$$

Then

$$v \geq u \quad \mathbf{x} \text{ in } V, \quad t > 0 \quad (9)$$

and v is a pointwise upper bound on u. Clearly, the solution u need not be known. The conditions on v in Equation (7) are sufficient to make v an upper bound on u, and Equation (7) does not involve the solution u. What the maximum principle does not reveal is how to obtain a function v which satisfies Conditions (7); that is the job of the engineer.

It should be noted that the maximum principle remains valid if each inequality is reversed in Equations (4) and (5). Consequently, if a function is found that satisfies Conditions (7) with the inequality reversed, then that function is a lower bound on u. Moreover, at any point where the upper and lower bounds coincide (and hence the exact value of u is known), the respective first derivatives are also upper and lower bounds for the first derivatives of the exact solution (this is shown in the Appendix). For example, if the comparison functions satisfy the boundary conditions as in Conditions (7), then the flux at the boundary can be bounded above and below. This feature is exploited in the example treated below. The flux at the boundary is often of primary concern in practice, of course.

Construction of Comparison Functions

Approximate methods provide a source of comparison functions for use in establishing the bounds mentioned in the preceding section. Any approximate solution can be tested, and if Conditions (7) hold at each position and time, then the approximate solution is an upper bound. On the other hand, if similar conditions hold but with the inequality reversed, that is, if the residual $L(v) - f$ is everywhere non-negative, then the approximate solution is a lower bound. The following method ensures that Conditions (7) are satisfied (and likewise for the case in which the inequality is reversed).

One assumes a trial solution of the form

$$u^* = u_o + \sum_{i=1}^{N} c_i u_i \quad (10)$$

and forms the residual (1 to 3)

$$R[u^*] \equiv L[u^*] - f = R_o + \sum_{i=1}^{N} c_i R_i \quad (11)$$

where R_o and R_i depend on the u_o, u_i, and L. If the original problem is solved by the collocation method, one has

$$R_o + \sum_{i=1}^{N} c_i R_i = 0 \quad \text{at}$$

$$(\mathbf{x}, t) = (\mathbf{x}_j, t_j), \ j = 1, 2, \ldots, N \quad (12)$$

This is a system of N equations for the N unknown constants c_i. When they are obtained the values of c_i determine the approximate solution given by Equation (10). If Equation (12) is satisfied, the residual as a function of position oscillates around zero, taking on positive and negative values in the neighborhood of the collocation points. But then Conditions (7) are not satisfied, and so the approximate solution is not necessarily either an upper or lower bound.

To rectify this situation, one rewrites Equation (12), replacing zero by a small negative number $-\epsilon$ on the

† Of course the method used here is applicable to more general equations than are treated by Collatz. Unsteady situations are considered here and there are no restrictions on the velocity field other than it be known.

‡ See the Appendix for a rigorous statement of the theorem. The maximum principle for this problem was first proved in a slightly different form by Nirenberg (8).

right-hand side:

$$R_o + \sum_{i=1}^{N} c_i R_i = -\epsilon$$

$$(\mathbf{x}, t) = (\mathbf{x}_j, t_j),\ j = 1, 2, \ldots, N \qquad (13)$$

Now if Equation (13) is satisfied, the residual as a function of position oscillates around $-\epsilon$ and might conceivably be negative at all positions and time. Were this true, one would have

$$R_o + \sum_{i=1}^{N} c_i R_i \leq 0, \quad \mathbf{x} \text{ in } V, \quad t > 0 \qquad (14)$$

and Equations (7), (8), and (9) would ensure that the approximate solution is an upper bound on the actual solution. A lower bound might be found in similar fashion. Whether the possibility is realized depends on the magnitude of ϵ and the location of the collocation points, which are both arbitrary matters of choice. While this implies a need to hunt for fruitful choices, the effort and potential frustration of an uncoordinated search can be avoided by a stratagem that is a novel and important part of the new method.

Rather than insisting that the residual have a fixed value $-\epsilon$ at N collocation points, one requires only that it be no greater (in the algebraic sense) than $-\epsilon$ at a number of positions and times:

$$R_o + \sum_{i=1}^{N} c_i R_i \leq -\epsilon \quad \text{at}$$

$$(\mathbf{x}, t) = (\mathbf{x}_j, t_j),\ j = 1, 2, \ldots M \qquad (15)$$

This represents a system of linear constraints on the constants c_i. Such restrictions remind one of linear programming problems, and it turns out that a similarity exists which can be exploited to good advantage.

Indeed, there is a linear programming problem which corresponds to *minimizing the upper bound* (and another corresponding to maximizing the lower bound, as is clear by analogy): minimize the so-called profit function

$$Q = \sum_{i=1}^{N} c_i u_i(\mathbf{x}_o, t_o) \qquad (16)$$

while satisfying the constraints, Inequalities (15). The signs of the c_i are unrestricted, but one can express these constants in terms of a doubled set:

$$c_i = c_i' - c_i'', \quad c_i' \geq 0, \quad c_i'' \geq 0 \qquad (17)$$

There are now twice as many constants, but they are all positive. The solution to this linear programming problem minimizes the approximate solution at the point $(\mathbf{x}_o, t_o)$. If the residual satisfies Inequalities (14), the approximate solution is an upper bound. In this way one arrives at the best set of c_i which satisfies Inequalities (15), instead of blindly solving Equation (13).

The procedure, then, is to maximize the "profit function" Q for a given ϵ, subject to Inequalities (15). The result is then tested at all points $(\mathbf{x}, t)$; if $R[u^*] \leq 0$ everywhere in V for $t > 0$, then u^* is a comparison function. Furthermore, u^* is so constituted that it is the "best" comparison function in that it is better than any other approximate solution of the form of Equation (10), as long as u_o, u_j, ϵ, and the collocation points are the same. As the number N of approximating functions increases, one knows that the upper bound (at the point $\mathbf{x}_o$, t_o) can never increase, because the $(N-1)^{\text{th}}$ approximation is contained within the N^{th} approximation for $c_N = 0$. In this way, one can construct a "best" comparison function, and can systematically improve the results.

Naturally the results depend on the value of ϵ. It can be shown (3) that the profit function Q is a monotone function of ϵ; consequently ϵ should be as small as possible. However, if it is made too small, and $\epsilon = 0$ is obviously too small, no upper bound results, as indicated in the discussion following Equations (12) and (13). The method is to find a value of ϵ that leads to a comparison function and then to decrease ϵ as much as possible. The feasibility of doing this is demonstrated below.

APPLICATION

As a test problem, consider the following unsteady state convective transport problem, which has already been solved by several versions of the method of weighted residuals by use of various criteria (2). A liquid in potential flow and initially at temperature T_o impinges upon a flat free interface. At time zero, the temperature of the interface is raised to T_1; the flow field remains the same. The problem is to predict the unsteady state temperature distribution and heat flux at the interface (or similar quantities for the equivalent mass transfer problem).

The velocity field is taken as

$$\mathbf{u} = a(x\mathbf{i} - z\mathbf{k}) \qquad (18)$$

where a is the stagnation flow parameter. The dimensionless transport equation and boundary and initial conditions are (2, 3)

$$L[T] = \nabla^2 T - N_{Pe}\, \mathbf{u} \cdot \nabla T - \frac{\partial T}{\partial t} = 0$$

$$T(\mathbf{x}, 0) = 0$$

$$T(z = 0, t) = 1 \qquad (19)$$

$$T \text{ is bounded for large } \mathbf{x}$$

The physical situation should be examined carefully for guidance in the choice of approximating function. It is clear that immediately after the step change in interfacial temperature, the region in which the temperature has changed significantly is confined to a small region adjacent to the interface—a thermal boundary layer. As time proceeds, this region of influence becomes larger. Within it, the temperature decreases in value monotonically from unity at the interface to substantially zero at the edge of the thermal boundary layer. Commonly used polynomial functions with variable "boundary-layer thickness," or thermal penetration depth are suitable here. The particular forms of trial solutions used below resemble closely those employed earlier in solving the same problem by means of various versions of the method of weighted residuals (2).

Upper Bound

For the upper bound on heat flux, the trial solution is

$$T^*(z, t) = \begin{cases} 1 + \sum_{i=1}^{N} a_i \left[\frac{z}{\delta(t)}\right]^i, & \frac{z}{\delta} < \kappa \\ 0, & \frac{z}{\delta} > \kappa \end{cases} \qquad (20)$$

The restrictions

$$1 + \Sigma a_i\, \kappa^i = 0, \quad \delta(0) = 0 \qquad (21)$$

ensure that T^* satisfies the boundary and initial conditions, while the equations

$$\sum_{i=1}^{N} i\ a_i\ \kappa^i = 0,\quad \sum_{i=1}^{N} i\ (i-1) a_i\ \kappa^i = 0 \qquad (22)$$

ensure that the derivatives in the differential equation are continuous at $z = \kappa\ \delta$; these derivatives are then continuous for $z > 0$, $t > 0$. The function $\delta(t)$ is chosen to satisfy

$$\frac{d\delta^2}{dt} + 4N_{Pe}\ \delta^2 = \alpha \qquad (23)$$

with α a constant as yet undetermined; this choice is suggested by previous work (2). The residual is

$$2\delta^2 R[T^*] = 2\delta^2 L[T^*] =$$

$$\begin{cases} \sum_{i=1}^{N} \left[\alpha \left(\frac{z}{\delta}\right)^2 + 2(i-1)\right] i\ a_i \left(\frac{z}{\delta}\right)^{i-2}, & z < \kappa\ \delta \\ 0, & z \geq \kappa\ \delta \end{cases} \qquad (24)$$

and the heat flux at the interface is

$$N_{Nu}[T^*] = -\frac{2a_1}{\sqrt{\alpha}} N_{Pe}^{1/2}\ [1 - \exp\ (-4N_{Pe}t)\ ]^{-1/2} \qquad (25)$$

T^* is bounded above by $1 + \kappa^N \sum_{i=1}^{N} |a_i|$. If α, κ, and a_i are so chosen that

$$R[T^*] \geq 0,\quad z \geq 0,\quad t > 0 \qquad (26)$$

then all the hypotheses of Theorem 4 (Appendix) are fulfilled; therefore, T^* is a lower bound for the exact solution T and, furthermore, the approximation to the heat flux at the interface is an upper bound on the exact value. The independent variables in Equation (24) appear only in the combination $u = z/\delta$; consequently Equation (26) must be satisfied as a function of only one variable, u, rather than two, z and t. It follows that the collocation maximum principle method is simply

$$\text{minimize } Q = -\frac{2a_1}{\sqrt{\alpha}} \qquad (27)$$

subject to the conditions at M points $u = u_j$

$$A_j = \sum_{i=1}^{N} [\alpha u_j^2 + 2(i-1)]\ i a_j u_j^i \geq \epsilon,$$

$$0 \leq u_j \leq \kappa,\quad j = 1, 2, \ldots, M \qquad (28)$$

as well as Equations (21) and (22). For simplicity the M collocation points are distributed evenly between zero and κ. To ensure essential continuity the residual at $u = \kappa$ must be zero, rather than ϵ; then the additional condition

$$dA/du \leq -\epsilon \text{ at } u = \kappa \qquad (29)$$

guarantees that Equation (28) holds in the left-hand neighborhood of $u = \kappa$.

Calculations were performed on the Control Data 1604 computer at the University of Minnesota. For a given set of parameters (α, κ, ϵ, N, M), the linear programming problem was formulated, solved, and the results tested to see whether Inequality 26 was satisfied. If it was, ϵ was decreased and the calculations were repeated; if not, ϵ was increased before further calculations. In this way the lowest value of ϵ was found for which the corresponding solution is a pointwise lower bound on temperature.

Lower Bound

To obtain upper bounds for temperature, two different trial solutions can be used:

$$T_1^* = \sum_{i=1}^{N} a_i e^{-iz/\delta(t)} \qquad (30)$$

or

$$T_2^* = \sum_{i=1}^{N} a_i e^{-(i+1)z/\delta(t)} \qquad (31)$$

with

$$\sum_{i=1}^{N} a_i = 1 \qquad (32)$$

The function $\delta(t)$ is again chosen to satisfy Equation (23) and the condition $\delta(0) = 0$, with α to be determined. The residuals are again functions of $u = z/\delta$ alone. The heat flux at the interface is

$$N_{Nu_1} = \sqrt{\frac{4N_{Pe}}{\alpha}} \sum_{i=1}^{N} i a_i\ [1 - \exp\ (-4N_{Pe}t)\ ]^{-1/2} \qquad (33)$$

$$N_{Nu_2} = \sqrt{\frac{4N_{Pe}}{\alpha}} \sum_{i=1}^{N} (i+1) a_i\ [1 - \exp\ (-4N_{Pe}t)\ ]^{-1/2} \qquad (34)$$

The values of α and the a_i must be so chosen that

$$R[T_i^*] \leq 0 \quad i = 1 \text{ or } 2 \qquad (35)$$

for all positive u. Inasmuch as T_i^* is bounded below by $-\Sigma|a_i|$ for $u \geq 0$, the conditions of Theorem 4 are satisfied and T_i^* is an upper bound for the temperature; the approximate heat flux at the interface is then a lower bound on the exact value. The problem is to maximize

$$Q = \sum_{i=1}^{N} i a_i \quad \text{or} \quad Q = \sum_{i=1}^{N} (i+1) a_i \qquad (36)$$

subject to the constraint in Condition (35) and to Inequalities (37).

Condition (35) must be satisfied on the semi-infinite interval $0 \leq u \leq \infty$. It is not practicable, however, to distribute collocation points on such an interval. But it is possible to ensure that $R[T_i^*(u)] \leq 0$ for all values of u greater than a certain cut-off value u^*; in this way the distribution of collocation points can be restricted to a finite interval. As proved elsewhere (3) the linear restrictions

$$\sum_{i=j}^{N} (i+1) a_i \leq -\epsilon,\ j = 2, 3, \ldots, N;\ \sum_{i=1}^{N} (i+1) a_i \geq \epsilon \qquad (37)$$

do ensure that $R[T_2^*(u)] \leq 0$ for $u \geq u^*$, where

$$u^* = \underset{1 \leq j \leq N}{\text{maximum}} \left\{ \frac{2 \sum_{i=j}^{N} (i+1)^2 a_i}{\alpha \sum_{i=j}^{N} (i+1)\ a_i} \right\} \qquad (38)$$

(A similar result applies to T_1^*.) The value of u^* depends on the solution a_i of the linear programming problem. Trial and error can be avoided if the M collocation points turn out to have been spread over a range running from $u = 0$ to a value greater than u^*. In this example $u^* = 2(N+1)/\alpha$ was usually satisfactory as a working cut-off value.

For a given set of parameters (α, ϵ, N, M) the linear programming problem and the problem of refining ϵ were handled in the same way as above.

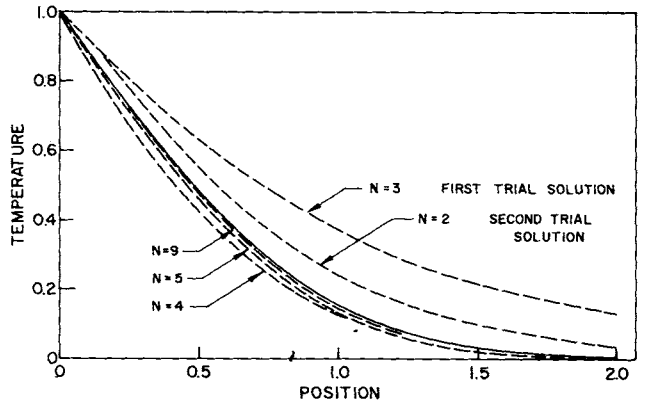

Fig. 1. Upper and lower bounds on temperature, $\alpha = 4$.

Results

The upper and lower bounds for temperature are presented graphically in Figure 1. Complete numerical results are available in tabular form elsewhere (3). The best estimates obtained for heat flux at the interface are

$$0.864\,N_{Pe}^{1/2}\,[1-\exp(-4N_{Pe}t)]^{-1/2} \leq N_{Nu} \leq 1.145\,N_{Pe}^{1/2}\,[1-\exp(-4N_{Pe}t)]^{-1/2} \qquad (39)$$

or

$$N_{Nu} = (1.00 \pm 0.15)N_{Pe}^{1/2}\,[1-\exp(-4N_{Pe}t)]^{-1/2} \qquad (40)$$

From Chan's solution the exact value of the constant multiplier is known to be 1.128 (2). Typical estimates for the temperature are

$$\begin{aligned} T &= 0.748 \pm 0.030 \text{ at } z = \delta/4 \\ T &= 0.512 \pm 0.040 \text{ at } z = \delta/2 \\ T &= 0.195 \pm 0.050 \text{ at } z = \delta \end{aligned} \qquad (41)$$

In fact the relative error varies from $\pm$ 4% at $z = \delta/4$ to $\pm$ 25% at $z = \delta$ (the percentage increasing still more with depth). These estimates for temperature could probably be improved by using the value of temperature at the desired point as the profit function, Q, rather than the interface heat flux, as was done in this investigation; actually the temperature estimates are incidental here.

Discussion of Results

The results presented are more extensive than would usually be required, but interesting conclusions can be drawn which might simplify or shorten the computations in other applications of the collocation maximum principle method.

Epsilon. The effect of epsilon on the heat flux estimate, shown in Figure 2, obeys the theoretical prediction: the interface heat flux is a monotone function of ϵ. More sophisticated procedures for locating the minimum admissible value of ϵ could be used (3).

Table 1. Heat Flux Dependence on the Number of Approximating Functions

N	M	$-2a_1/\alpha$
$\alpha = 4,$	$\kappa = 2,$	$\epsilon = 0.125$
4	4	1.6251
5	4	1.2148
8	7	1.1924
$\alpha = 4,$	$\kappa = 2,$	$\epsilon = 0.0156$
8	12	1.1490
9	12	1.1477

Number of approximating functions. The upper bound on flux decreases as N increases, as is shown in Table 1.

The situation is more complicated when exponentials are used in the trial function. The N^{th} restriction in Inequalities (37) is

$$(N+1)a_N \leq -\epsilon \qquad (42)$$

so that $a_N = 0$ is not allowed. Consequently, the N^{th} approximation is not contained within the $(N-1)^{\text{th}}$ approximation; accordingly the flux may possibly decrease as N increases, thereby giving a less desirable lower bound. When the foregoing restriction is replaced by $a_N \leq 0$, the best solution occurs when $a_N = 0$. In addition, if N is too large, Inequalities (37) become incompatible with Inequalities (35). This is unfortunate, because it limits the trial solutions to two or three terms, at least in this case, and the dramatic improvement obtained in the upper bound on flux evidently cannot be duplicated for the lower bound.

Residual. Figure 3 illustrates the oscillatory dependence of the residual on relative position u. The collocation points are marked to show that the minimum of the residual occurs at roughly the midpoint between two collocation points.

Computer time. As a rough indication of the amount of computation time needed for this method, sixty-four different functions T^* were generated and tested within 1 min. on the Control Data 1604 machine with a Fortran program. Some of these functions proved not to be comparison functions, but it obviously does not take long to generate a great many solutions.

These results suggest that the collocation maximum principle method is a reasonably efficient means for constructing upper and lower bounds for solutions to the unsteady state transport equations. The limitations of the method are discussed in the following section.

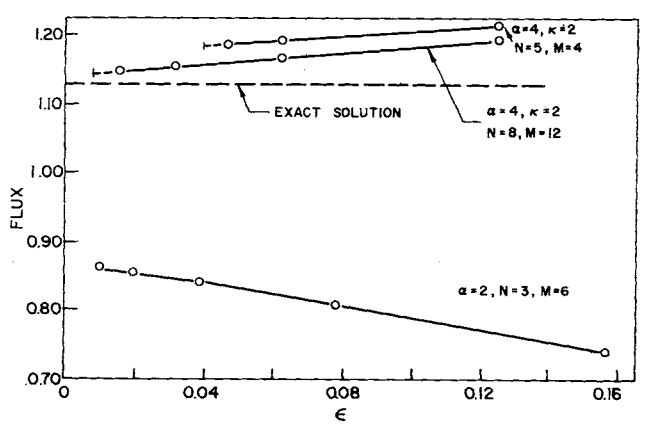

Fig. 2. Dependence of flux value on epsilon.

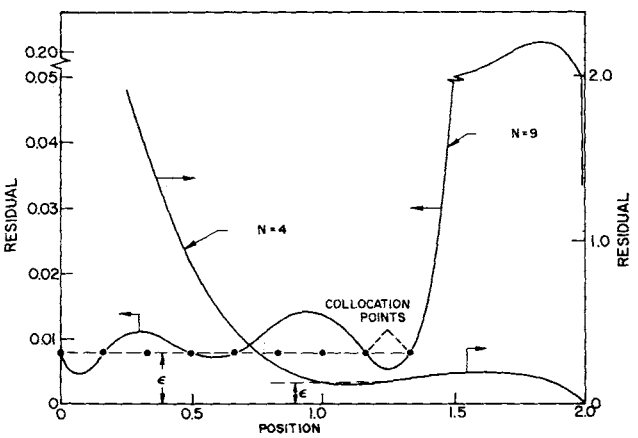

Fig. 3. Dependence on residual on position.

CONCLUDING REMARKS

The maximum principle (Theorems 1 to 4 in the Appendix) has some interesting consequences which are not related to any approximate solution. For the unsteady state mass transport equation with a first-order chemical reaction, namely

$$-L_2[c] = \frac{\partial c}{\partial t} + \nabla\cdot(\mathbf{u}c) - \nabla\cdot D\,\nabla c - Kc = 0,\ K < 0 \tag{43}$$

the solution can be compared to that without chemical reaction. If

$$-L[c'] = \frac{\partial c'}{\partial t} + \nabla\cdot(\mathbf{u}c') - \nabla\cdot D\ \nabla c' = 0 \tag{44}$$

then the solution without reaction c' is an upper bound on that with reaction c. Because

$$L_2[c - c'] = -Kc' \tag{45}$$

and $c' \geq 0$, the right-hand side is always positive. The maximum principle states that if

$$L_2[c - c'] \geq 0 \tag{46}$$

then

$$c - c' \leq 0 \tag{47}$$

Consequently, the concentration is everywhere less than it would be without the chemical reaction. This result holds irrespective of the relative importance of the convective, diffusive, and reaction processes.

The collocation maximum principle method requires three important items: (1) a maximum principle, (2) methods for maximizing a quantity subject to certain constraints, and (3) methods for proving that a function is positive in the entire space-time domain. The first item limits application to those problems for which a maximum principle has been proved. This includes many practically important unsteady state transport problems, but only first-order chemical reactions can be included and the boundary conditions must be of the first kind (Dirichlet problem). However, a zero-order generation term can be handled. For the second item the simplex method of linear programming provides an efficient and well-established procedure for solving the maximization problem. The third item probably limits the usefulness of the method to a few dimensions, for as the number of dimensions increases, it becomes more difficult to prove that the residual is positive at every position and time. Numerical searching schemes can be used, but computation time multiplies rapidly with the number of dimensions. But since only one good solution is needed, this might be acceptable in some circumstances. The calculations presented here also suggest that better results are obtained for finite domains than for infinite domains. The requirement that the residual be negative for all $z > 0$ introduces restrictions that limit improvement of successive approximations. The choice of functional form of trial functions remains an open matter; choices other than those made here might yield better results than have been presented.

Future research might well include attempts to (1) prove a maximum principle which allows nonlinear chemical reaction terms, (2) to improve the choice of trial solutions for semi-infinite and two-dimensional domains, and (3) to apply the same procedure to the conventional boundary-layer equations—possibly the most important area. Nickel (*4*), who proved a maximum principle for the boundary-layer equations for velocity, constructed lower bounds on velocity, but there is no evident way to improve his results nor as yet to obtain an upper bound. The same ideas presented here, combined with Nickel's maximum principle and nonlinear programming, might lead to such an upper bound with a possibility of systematically improving the results. Further research is suggested to explore this possibility. For one thing, any information on the reliability of the commonly used von Kármán-Pohlhausen approximation scheme (method of moments) is likely to be valuable. In general, as the engineer with each successive generation of high-speed computers attempts to get approximate solutions to more and more difficult flow and transport problems, the potential value to him of information about error bounds increases. In some cases it may pay for him to look thoroughly into the subject while still in a planning stage.

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NOTATION

a = stagnation flow parameter
a_i = undetermined constants
A_j = defined by Equation (28)
c_i = adjustable constants (or functions)
c = concentration
D = molecular diffusivity
$\mathbf{i}$ = unit vector parallel to interface
$\mathbf{k}$ = unit vector perpendicular to interface
K = first-order reaction rate constant
L = general differential operator
M = number of collocation points
N = number of approximating functions
N_{Nu} = Nusselt number
N_{Pe} = Peclet number
Q = profit function; see Equation (16)
R = residual
S = boundary of V
T = temperature
t = time
u = dummy dependent variable; also z/δ
$\mathbf{u}$ = velocity
V = domain of physical space
w = dummy comparison function
$\mathbf{x}$ = position (x, y, z)
x = distance in direction of $\mathbf{i}$
z = distance in direction of $\mathbf{k}$

Greek Letters

α = parameter in trial solution; see Equation (23)
δ = thermal penetration depth
ϵ = positive number
κ = parameter in trial solution
ϕ = known initial condition
ψ = known boundary condition

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APPENDIX

A maximum principle for parabolic partial differential equations has been proved by Il'in, Kalashnikov, and Oleinik (6). The pertinent theorems are repeated here; the notation, while complicated, is necessary for the correct statement of the theorems. Let

D = a bounded domain in an $(n+1)$ dimensional Euclidean space, contained between the planes $t=0$ and $t=T$

$\overline{D}$ = closure of D

D_o = intersection of $\overline{D}$ with the plane $t=0$

$\overline{S}$ = closure of the set of boundary points of D, for which $t \neq 0$ and $t \neq T$

S = points of $\overline{S}$ that do not belong to $t=0$

Γ = union of S and D_o

H = all points of an $(n+1)$ dimensional Euclidean space for which $0 < t \leq T$

$\overline{H}$ = closure of H

G = semi-infinite domain in an $(n+1)$ dimensional Euclidean space for which $0 < t \leq T$ and which is partially bounded by S_2

$\overline{G}$ = closure of G

G_o = intersection of $\overline{G}$ with the plane $t=0$

$\overline{S}_2$ = closure of the set of boundary points of G for which $t \neq 0$ and $t \neq T$

S_2 = points of $\overline{S}_2$ that do not belong to $t=0$

Γ_2 = union of S_2 and G_o

x = (x_1, x_2, x_3).

Suppose that a_{ij}, b_i, c, f are real and take finite values, and that

$$a_{ij} = a_{ji}, \sum_{j=1}^{N} a_{ij}\alpha_i\alpha_j > 0 \text{ if } \sum_{i=1}^{N} \alpha_i^2 > 0$$

Finally, the function $u(x,t)$ is said to be a solution of

$$L(u) = f \qquad (A1)$$

at (x,t) if $u(x,t)$ is continuous and has continuous derivatives $\partial u/\partial x_i$, $\partial u/\partial t$, $\partial^2 u/\partial x_i \partial x_j$ $(i,j = 1,2,3)$ satisfying (A1).

Maximum Principle

The maximum principle for parabolic differential equations is (6):

Theorem 1: Suppose that the function $u(x,t)$ is continuous in $\overline{D}$, that those of its derivatives which enter into the operator L are continuous, and that it satisfies the inequality $L(u) \leq 0$ in $\overline{D} - \Gamma$, where $c(x,t) < M$ and M is some constant. Then $u(x,t) \geq 0$ in $\overline{D}$ if $u(x,t) \geq 0$ on Γ.

The theorem for infinite domains is similar (6):

Theorem 2: Let $u(x,t)$ be continuous and bounded below in $\overline{H}$: $u(x,t) > -m$, $m > 0$. Suppose that the function $u(x,t)$ has continuous derivatives in H as far as they occur in the operator L and that $L(u) \leq 0$. Let a_{ij}, b_i, c satisfy the following relations:

$$|a_{ij}(x,t)| < M(r^2+1),\ |b_i(x,t)| < M\sqrt{r^2+1},\ c(x,t) < M \qquad (A2)$$

where $r^2 = \sum_{i=1}^{3} x_i^2$ and M is a positive constant. Then $u(x,t) \geq 0$ everywhere in H if $u \geq 0$ for $t = 0$.

Now, as might be anticipated, a similar theorem holds for a semi-infinite domain:

Theorem 3: Let $u(x,t)$ be continuous and bounded below in $\overline{G}$: $u(x,t) > -m$, $m > 0$. Suppose that the function $u(x,t)$ has continuous derivatives in G as far as they occur in the operator L and that $L(u) \leq 0$ in $\overline{G} - \Gamma_2$. Let a_{ij}, b_i, c satisfy Equation (A2). If $u(x,t) \geq 0$ on Γ_2, then $u(x,t) \geq 0$ in $\overline{G}$.

This theorem can be proved in exactly the same way that Theorem 2 is proved. The semi-infinite domain is replaced by an arbitrarily large one and Theorem 1 is applied.

Consider the problem

$$\begin{aligned} L(u) &= f(x,t) \text{ in } G \\ u(x, t=0) &= \phi(x) \text{ in } G \\ u(x,t) &= \psi(x,t) \text{ in } S \end{aligned} \qquad (A3)$$

where ϕ and ψ are given continuous functions and $|a_{ij}| < M(r^2+1)$, $|b_i| < M(r^2+1)^{1/2}$, and $c < M$, where M is a positive constant. The function $u(x,t)$ is said to be a solution if it satisfies Equation (A3), if it is continuous, and if it has continuous derivatives $\partial u/\partial x_i$, $\partial u/\partial t$, $\partial^2 u/\partial x_i \partial x_j$ $(i, j = 1, 2, 3)$ in $\overline{G}$; in addition u must be bounded above and below in $\overline{G}$. A function $v(x,t)$ is said to be a comparison function if it satisfies the same requirements as u except that Equation (A3) is replaced by either

$$\begin{cases} L(v_u) \leq f \\ v_u(x,0) = \phi \\ v_u(x,t) = \psi \\ v_u \text{ is bounded below} \end{cases} \text{ or } \begin{cases} L(v_l) \geq f \\ v_l(x,0) = \phi \\ v_l(x_s,t) = \psi \\ v_l \text{ is bounded above} \end{cases} \begin{matrix} \text{in } G \\ \\ \text{on } S \end{matrix} \qquad (A4)$$

Theorem 4: The function v_l is a lower bound and v_u is an upper bound for the solution of Equation (A3). If $v_l = v_u$ at any point (x_o, t_o) in $\overline{G}$, then the first derivatives of v_l and v_u are lower and upper bounds, respectively, for the first derivatives of u.

Proof: Consider $w_u = v_u - u$, $w_l = u - v_l$. Then

$$\begin{cases} L(w_u) \leq 0 \\ w_u(x,0) = 0 \\ w_u(x_s,t) = 0 \end{cases} \quad \begin{cases} L(w_l) \leq 0 \\ w_l(x,0) = 0 \\ w_l(x_s,t) = 0 \end{cases} \begin{matrix} \text{in } G \\ \\ \text{on } S_2 \end{matrix} \qquad (A5)$$

The functions w_u and w_l are continuous in G and have continuous derivatives in G as far as they occur in L, since w_u and w_l are the differences of functions with these properties. The functions w_u and w_l are continuous on S as well as for x in G, $t = 0$. Even though u, v_u, and v_l are not necessarily continuous at $t = 0$, x on S [since $\phi(x_s)$ may not equal $\psi(x_s, 0)$], their differences are continuous at $t = 0$, x on S. Consequently, w_u and w_l are continuous in $\overline{G}$. The functions w_u and w_l are bounded below in $\overline{G}$ so all the conditions of the theorem are satisfied. Consequently

$$\begin{matrix} w_u \geq 0 & w_l \geq 0 & \text{in } G; \\ v_u \geq u & u \geq v_l & \end{matrix} \qquad (A6)$$

hence

and v_u is an upper bound for u, whereas v_l is a lower bound for u. If $v_l = v_u$ at (x_o, t_o), then $u = v_l = v_u$ at (x_o, t_o), Hence

$$u(x_o, t_o + \Delta t) - u(x_o, t_o) \geq v_l(x_o, t_o + \Delta t) - v_l(x_o, t_o) \qquad (A7)$$

Since u and v_l are continuous in $\overline{G}$, this inequality holds uniformly with respect to t at (x_o, t_o). Hence

$$\left.\frac{\partial u}{\partial t}\right|_{x_o,t_o} = \lim_{\Delta t \to 0} \frac{u(x_o, t_o + \Delta t) - u(x_o, t_o)}{\Delta t} \geq \lim_{\Delta t \to 0} \frac{v_l(x_o, t_o + \Delta t) - v_l(x_o, t_o)}{\Delta t} = \left.\frac{\partial v_l}{\partial t}\right|_{x_o,t_o} \qquad (A8)$$

Similar results hold for spatial first derivatives.

As a result of Theorem 4, the functions v_u and v_l provide pointwise error bounds for u, that is

$$\left| u - \frac{1}{2}(v_u + v_l) \right| < \frac{1}{2}(v_u - v_l) \qquad \text{in } G \qquad (A9)$$

The method described above provides these comparison functions, v_u and v_l.

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