TABLE 1. COMPARISON OF COLUMN REACTOR WITH PLUG-FLOW REACTOR

Mole ratio in feed water to oxide	Selectivity*	
	Column	Plug flow
1.0	0.881	0.382
2.33	0.917	0.668
9.0	0.886	0.900
20	0.900	0.960

* Selectivity is defined as moles of monoethylene glycol/total moles of glycol.

higher and lower relative volatilities were used.

The convergence was measured by taking a material balance over the column for each component. When a material balance closure was within 1%, the solution was accepted. The relative rate constant κ was obtained from data in the literature (*2*).

The results of this analysis are shown in Table 1 where they are compared with the results to be expected in a plug-flow and in a continuous stirred-tank reactor. It can be seen from Table 1 that at mole ratios of water to oxide greater than 2:1 (mole fraction of B greater than 0.7 in Table 1), the plug-flow reactor gives superior performance, and at mole ratios of 9:1 or greater, both the plug-flow and the continuous stirred-tank reactor give superior performance. The distillation column is superior only at low feed mole ratios.

At first it might be assumed that the greater the relative volatilities among the components of the system, the better the distillation column would work. However, this is not the case. Let us consider the extreme cases in a qualitative manner. If all four components had the same volatilities, there would be no separation at all in the column, the composition on all plates would be the same, and the system would tend to behave like a continuous stirred-tank reactor.

In the opposite case of infinite relative volatility, there would be immediate separation and the components could contact each other only on the feed tray. The system would behave as a single continuous stirred-tank reactor. The patent is concerned with only intermediate cases.

The relative volatilities were calculated by taking the ratio of the vapor pressure of each pure component at 40°C. to the vapor pressure of B at 40°C. The use of relative volatilities eliminates the need to know the pressures and temperatures in the distillation column to make the separation calculations, since it is assumed that relative volatility is independent of pressure and temperature. It was also assumed, in order to simplify the calculations, that the reaction rate constants were independent of temperature and pressure. In all cases only three theoretical trays were required because of the high relative volatilities.

Simulation of a distillation column reactor on a 7094 computer has shown that it will not exceed the performance of a tubular or continuous stirred-tank reactor operating at high ratios of water to ethylene oxide in the feed.

LITERATURE CITED

1. Parker, Almon S., U. S. Pat. 2,839,588 (June 17, 1958).
2. Sonawala, S. K., "Report on Kinetics of Ethylene Oxide-Water Reaction," Ohio State Univ., Columbus.

The Use of Green's Functions in the Solution of a Convective Diffusion Equation: Application to a Fuel Cell Battery

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The diffusion equation with a constant mass flow term to account for bulk transport of heat or chemical species occurs in many practical problems, such as in heat transfer in fuel cell batteries, in chromatographic work with appreciable diffusion in the direction of flow, and in dispersion studies in fluids with and without reaction. The methods of solving these problems include the classical separation of variables method, the Laplace and Fourier transform operational methods, and the moving source technique discussed by Carslaw and Jaeger (*1*). The complexity of some of these problems, especially those in three dimensions, is such that it is desirable to have additional simplifying techniques.

The principal simplifying technique for the usual diffusion equation widely used in heat transfer is the product theorem due to Newman (*1, 2*). Recently the construction of three-dimensional solutions from one- and two-dimensional problems was extended by Goldenberg (*3*). For the case of the diffusion equation with a linear term, for example, for diffusion with a first-order reaction, the transformation of Danckwerts is useful (*1, 4*). In this paper it is shown how a change of the dependent variable, similar to that employed in the Danckwerts method, together with the tabulated Green's functions for the simple diffusion equation, can rapidly lead to many new solutions of the convective diffusion equation with a constant velocity. Then various product properties useful for analytical and graphical representations of two- and three-dimensional problems are established for the general, second-order, parabolic partial differential equation with constant coefficients. To call attention to its utility, the method will be illustrated with examples having practical importance in heat transfer in fuel cell batteries.

REDUCTION TO THE DIFFUSION EQUATION

The partial differential equation for the temperature distribution in a rectangular fuel cell battery has been derived by Gidaspow and Baker (5). For the purpose of this paper it will be written in a somewhat different dimensionless form (6). The coordinates are chosen to correspond to those for Green's function given in paragraph 14.3 in reference 1. The unsteady state energy balance for a constant rate of heat generation becomes

$$\frac{\partial \tilde{T}}{\partial t} = \frac{\partial^2 \tilde{T}}{\partial x^2} + \frac{\partial^2 \tilde{T}}{\partial y^2} + \frac{\partial^2 \tilde{T}}{\partial z^2} - N_{Pe}\frac{\partial \tilde{T}}{\partial z} + 8 \quad (1)$$

To solve boundary value problems by Green's functions, let

$$\tilde{T}(t, x, y, z) = v(t, x, y, z) \exp\left[\frac{1}{2} N_{Pe} z - \frac{1}{4} N_{Pe}^2 t\right] \quad (2)$$

Simple differentiation shows that the partial differential equation for v becomes the diffusion equation with a time- and position-dependent source.

$$\frac{\partial v}{\partial t} = \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 v}{\partial z^2} + 8 \exp\left[-\frac{1}{2} N_{Pe} z + \frac{1}{4} N_{Pe}^2 t\right] \quad (3)$$

The transformed boundary conditions remain of the same type and homogeneous in v, except for the boundary condition given by Equation (4). In this boundary condition the nonhomogeneous term is $-N_{Pe} \tilde{T}_A \exp[\frac{1}{4} N_{Pe}^2 t]$. The solution for v by the method of Green's functions (1, 7) can be written for zero initial temperature distribution as

$$v = 8 \int_0^t dt' \int_0^1 \int_0^{a_2} \int_0^{a_1} \exp\left[-\frac{1}{2} N_{Pe} z' + \frac{1}{4} N_{Pe}^2 t'\right] \cdot G(x, y, z; x', y', z', t-t') dx' dy' dz' + N_{Pe} \tilde{T}_A \int_0^t dt' \int_0^{a_2} \int_0^{a_1} \exp\left[\frac{1}{4} N_{Pe}^2 t'\right] \cdot G(x, y, z; x', y', 0, t-t') dx' dy' \quad (7)$$

The Green's function G is given as a product of the Green's functions given by Equations (2) and (5) in reference 1, p. 360. It can be written as

$$G(x, y, z; x', y', z', t-t') = G_1(x; x', t-t') \cdot G_2(y; y', t-t') \cdot G_3(z; z', t-t') \quad (8)$$

This product property of the Green's functions makes the integration simple and leads to the possibility of expressing certain multidimensional problems in terms of one-dimensional problems. Since the solution to the boundary value problem has been reduced to simple integration and since the final formula is quite long, only the limiting case of infinite Biot numbers and zero $\tilde{T}_A$ will be explicitly shown here. With all six faces at zero reduced temperature, the Green's function, G in Equation (7), is given explicitly in reference 1 in paragraph 14.5 by Equation (1). Integration and rearrangement yield the following relatively simple expression for the temperature:

$$\tilde{T} = \frac{256\, e^{\frac{1}{2} N_{Pe} z}}{\pi} \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{(2n+1) \sin \frac{(2l+1)\pi x}{a_1} \sin \frac{(2m+1)\pi y}{a_2} \sin (2n+1)\pi z}{\left[(2n+1)^2 \pi^2 + \frac{1}{4} N_{Pe}^2\right] (2m+1)(2l+1)\left(\alpha_{l,m,n} + \frac{1}{4} N_{Pe}^2\right)} \cdot [1 - (-1)^{2n+1} e^{-\frac{1}{2} N_{Pe}}][1 - e^{-(\alpha_{l,m,n} + \frac{1}{4} N_{Pe}^2) t}] \quad (9)$$

Now it is clear that this partial differential equation can be solved by the standard method of Green's functions (1, 7). The Green's functions are tabulated in reference 1 for the three basic types of Sturm-Liouville boundary conditions for the rectangular parallelipiped and for the cylinder.

To illustrate the technique, consider a specific example of importance in fuel cell heat transfer. If the inlet temperature of the gases entering the battery at its bottom face is varied, the top face loses heat by convection with a finite resistance to heat transfer to surroundings at T_w and the other four walls are at T_w, the boundary conditions expressed in dimensionless form are:

$$\frac{\partial \tilde{T}}{\partial z} = (N_{Bib} + N_{Pe}) \tilde{T} - N_{Pe} \tilde{T}_A \quad \text{at} \quad z = 0 \quad (4)$$

$$\frac{\partial \tilde{T}}{\partial z} = -N_{Bit} \tilde{T} \quad \text{at} \quad z = 1 \quad (5)$$

$$\tilde{T} = 0 \text{ at } x = 0 \text{ and } a_1,\ y = 0 \text{ and } a_2 \quad (6)$$

where

$$\alpha_{l,m,n} = \pi^2 \left[\frac{(2l+1)^2}{a_1^2} + \frac{(2m+1)^2}{a_2^2} + (2n+1)^2\right] \quad (10)$$

For $N_{Pe} = 0$ Equation (9) reduces itself to Equation (5) in reference 1, p. 363. The steady state temperature distribution is obtained by letting t approach infinity which yields Equation (9) with the exponential involving time set equal to zero. The expression thus obtained is somewhat easier to program for a digital computer than the previous expression obtained by Gidaspow and Baker (5), even though it involves a triple series in place of double series. The main advantage of this method, however, is the relative ease with which this technique yields expressions for temperature distributions. It should be emphasized that it was much easier to solve the unsteady problem and then reduce it to the steady state than it was to obtain the steady state solution directly.

If the unsteady temperature distribution is desired after a change of the electrical load of the battery and if the initial distribution was $f(x, y, z)$, then the temperature will be that given by Equation (9) plus an expression of the type given in reference *1*, p. 362, Equation (2) with $f(x', y', z')$ multiplied by $\exp[-\frac{1}{2} N_{Pe}(z'-z)]$.

THREE-DIMENSIONAL FROM ONE- AND TWO-DIMENSIONAL PROBLEMS—WITH SOURCE

A further advantage of the use of Green's functions for solution of problems of this type emerges from their product property. The temperature distribution in the parallelepiped with a constant rate of heat generation and zero reduced wall temperatures or zero ambient temperature can be expressed as follows:

$$\tilde{T} = 8 \int_0^t dt' \int_0^1 \exp\left[\frac{1}{2} N_{Pe}(z-z') - \frac{1}{4} N_{Pe}^2(t-t') \right] G_3(z; z', t-t')\, dz' \cdot \int_0^{a_2} G_2(y; y', t-t')\, dy' \int_0^{a_1} G_1(x; x', t-t')\, dx' \quad (11)$$

It can now be observed that each integral over a spatial coordinate represents a solution to a homogeneous one-dimensional boundary value problem with a unit initial temperature distribution. The solution to

$$\frac{\partial \phi_1}{\partial t} = \frac{\partial^2 \phi_1}{\partial x^2} \quad (12)$$

with

$$\phi_1(0, t) = 0,\ \phi_1(a_1, t) = 0 \text{ and } \phi_1(x, 0) = 1 \quad (13)$$

is

$$\phi_1(x, t) = \int_0^{a_1} G_1(x; x', t)\, dx' \quad (14)$$

Similarly, the integral over y' in Equation (11) represents the solution to the one-dimensional diffusion equation for ϕ_2 with homogeneous boundary conditions and with unit initial temperature.

$$\phi_2(y, t) = \int_0^{a_2} G_2(y; y', t)\, dy' \quad (15)$$

The solution to the one-dimensional convective diffusion equation

$$\frac{\partial \phi_3}{\partial t} = \frac{\partial^2 \phi_3}{\partial z^2} - N_{Pe} \frac{\partial \phi_3}{\partial z} \quad (16)$$

with

$$\phi_3(0, t) = 0,\ \phi_3(1, t) = 0 \text{ and } \phi_3(z, 0) = 1 \quad (17)$$

is

$$\phi_3(z, t) = \int_0^1 \exp\left[\frac{1}{2} N_{Pe}(z-z') - \frac{1}{4} N_{Pe}^2(t) \right] G_3(z; z', t)\, dz' \quad (18)$$

Therefore the temperature distribution in the rectangular parallelepiped with a constant rate of heat generation and with zero surface temperatures can be expressed as the integral of the product of the one-dimensional problems given above.

$$\tilde{T} = 8 \int_0^t \phi_1(x, t-t') \cdot \phi_2(y, t-t') \cdot \phi_3(z, t-t')\, dt' \quad (19)$$

It is evident that this representation is valid for $N_{Pe} = 0$. The author is unaware that it had ever been given in the literature even for this reduced case, that is, for heat generation with pure conduction. It is also clear that each ϕ_i can satisfy a more general linear partial differential equation. This will be illustrated in a later section of this paper. Furthermore, the representation of the type given by Equation (19) is valid for time-dependent heat generation, as seen by inspection of Equation (11). The time-dependent function simply multiplies the ϕ_i's under the integral sign in Equation (19). Thus, for example, if ϕ_4 is the solution to the cooling problem of a right infinite cylinder with an arbitrary cross section from an initial temperature of unity and with boundaries held at zero, the solution to the heat generation problem for the finite cylinder becomes

$$\tilde{T} = 8 \int_0^t g(t')\ \phi_3(z, t-t')\ \phi_4(\xi, \eta, t-t')\, dt' \quad (20)$$

where $g(t')$ is the normalized time-dependent heat generation rate. Such solutions may be useful in cylindrical flow reactors.

WITH NONHOMOGENEOUS BOUNDARY CONDITIONS

To make representations of the type given by Equation (19) most useful it is necessary to extend them to nonzero surface or ambient temperatures. If an integral representation in terms of simpler problems is given for the homogeneous equation with all but one face at a nonzero surface temperature, then an application of the superposition principle will give the solution to the completely nonhomogeneous boundary value problem. This was illustrated in the previous section for the case of one ambient temperature equal to a nonzero value. By referring to that example it can be seen that $\tilde{T}$ can be written as follows:

$$\tilde{T}_2 = N_{Pe} \tilde{T}_A \int_0^t \exp\left[\frac{1}{2} N_{Pe} z - \frac{1}{4} N_{Pe}^2(t-t') \right] G_3(z; 0, t-t')\, dt' \cdot \int_0^{a_2} G_2(y; y', t-t')\, dy' \int_0^{a_1} G_1(x; x', t-t')\, dx' \quad (21)$$

It can be seen from Equations (14) and (15) that the second and third integrals in the above equation are simply ϕ_2 and ϕ_1, respectively.

Let Φ be the solution to the boundary value problem governed by the one-dimensional convective diffusion equation, Equation (16) and the boundary conditions of the type given by Equations (4) and (5) with a zero initial temperature distribution. The solution for Φ is expressed by

$$\Phi(z, t) = N_{Pe} \tilde{T}_A \int_0^t \exp\left[\frac{1}{2} N_{Pe} z - \frac{1}{4} N_{Pe}^2(t-t') \right] G_3(z; 0, t-t')\, dt' \quad (22)$$

The time derivative of this expression is the quantity under the integral sign over t' in Equation (21). This is easy to see by noting the form of G_3. Only an exponential of time is integrated in Equation (22). Therefore T_2 can be expressed as follows:

$$\tilde{T}_2 = \int_0^t \frac{\partial \Phi(z, t-t')}{\partial t} \cdot \phi_1(x, t-t') \cdot \phi_2(y, t-t')\, dt' \quad (23)$$

This representation is valid for the nonhomogeneous boundary condition of either Dirichlet or convection type. A similar result for the case of the simple diffusion equation was derived by operational methods by Goldenberg (*3*). Again this type of representation is valid for a general parabolic partial differential equation with constant coefficients and for cylindrical regions in the sense discussed in the previous section.

WITH INITIAL TEMPERATURE OF PRODUCT TYPE

The solution to the homogeneous convective diffusion equation with homogeneous boundary conditions but with an initial temperature distribution given by $f(x, y, z)$ can be expressed by

$$\tilde{T} = \exp\left[\frac{1}{2}N_{Pe}z - \frac{1}{4}N_{Pe}^2 t\right] \cdot \int_0^1 \int_0^{a_2} \int_0^{a_1} f(x', y', z') \exp\left[-\frac{1}{2}N_{Pe}z'\right] G(x, y, z; x', y', z', t)\,dx'\,dy'\,dz' \quad (24)$$

The Green's functions are factorable into a product of three functions of x', y', and z' for the basic three Sturm-Liouville boundary conditions. Then if and only if

$$f(x, y, z) = f_1(x) \cdot f_2(y) \cdot f_3(z) \quad (25)$$

$\tilde{T}$ can be expressed as the product of three integrals shown below.

$$\tilde{T} = \int_0^1 f_3(z') \exp\left[\frac{1}{2}N_{Pe}(z - z') - \frac{1}{4}N_{Pe}^2 t\right] G_3(z; z', t)\,dz' \cdot \int_0^{a_2} f_2(y')\,G_2(y; y', t)\,dy' \cdot \int_0^{a_1} f_1(x')\,G_1(x; x', t)\,dx' \quad (26)$$

The first integral is the solution to the homogeneous convective diffusion equation with homogeneous boundary conditions and with an initial temperature distribution given by $f_3(z)$. The second and third integrals are the solutions to the corresponding simple one-dimensional diffusion equations with initial distributions given by $f_2(y)$ and $f_1(x)$, respectively.

The existence of such a product solution for the simple diffusion equation was first pointed out by Newman (2) and is derived in reference 1, pp. 33-35, by a different method. The Green's function method used here permits one to make generalizations more readily. For example, the product solution for a finite cylindrical region holds for convective flow in the z direction. The product property can be used in both analytical and numerical work. To use this property numerically it is necessary to construct charts for the one-dimensional convective diffusion equation with, for example, a unit initial temperature. These can then be used in the usual manner to obtain temperatures with conduction and convection in two or three directions.

MORE GENERAL PARTIAL DIFFERENTIAL EQUATIONS

The change of the dependent variable used in the Danckwerts transformation, together with that given by Equation (2), shows that the more general parabolic second-order partial differential equation with constant coefficients can be transformed into a diffusion equation. Thus

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial z^2} - N_{Pe}\frac{\partial u}{\partial z} + Au \quad (27)$$

is transformed into

$$\frac{\partial w}{\partial t} = \frac{\partial^2 w}{\partial z^2} \quad (28)$$

by means of

$$u = w \exp\left[\frac{1}{2}N_{Pe}z - \left(\frac{1}{4}N_{Pe}^2 - A\right)t\right] \quad (29)$$

Equation (29) makes it clear that the Green's function techniques and the integral representations of two- and three-dimensional solutions in terms of simpler problems can be applied to the two- and three-dimensional versions of Equation (27). This is clear from the fact that $\frac{1}{4}N_{Pe}^2$ needs merely to be replaced by $\frac{1}{4}N_{Pe}^2 - A$. It is therefore possible to obtain quickly many solutions to

$$\frac{\partial u}{\partial t} = \nabla^2 u - \sum_{i=1}^{n} P_i \frac{\partial u}{\partial x_i} + nA \quad (30)$$

where P_i and A are constants, any of which may be zero, and n is the number of dimensions. The recent widespread use of computers in engineering work has made these apparently complex solutions practical.

NOTATION

a_1 = $\frac{a_{1A}}{a_{3A}}$; $a_2 = \frac{a_{2A}}{a_{3A}}\sqrt{\frac{k}{k_r}}$, dimensionless

a_{1A}, a_{2A}, a_{3A} = actual thickness, width and height of battery, ft.

C_p = heat capacity of gases at constant pressure, B.t.u./(lb.) (°F.)

C_{pB} = heat capacity of the battery, B.t.u./(lb.) (°F.)

G = Green's function; also mass flow rate per unit of total area, lb./(hr.) (sq.ft.) when used in defining N_{Pe}

h = heat transfer coefficient, B.t.u./(hr.) (sq.ft.) (°F.)

k = effective thermal conductivity of the fuel cell battery in the direction of flow, B.t.u./(hr.) (ft.) (°F.)

k_r = effective thermal conductivity in the direction perpendicular to cells, B.t.u./(hr.) (ft.) (°F.)

N_{Pe} = Peclet number = $\frac{GC_p\,a_{3A}}{k}$, dimensionless

N_{Bib}, N_{Bit} = Biot number at bottom and top = $\frac{h_b a_{3A}}{k}$, $\frac{h_t a_{3A}}{k}$

S = surface

T = temperature, °F.

T_w = wall temperature, °F.

$\tilde{T}$ = dimensionless temperature = $(T - T_w) \Big/ \frac{\psi a_{3A}^2}{8k}$

t = dimensionless time = $\frac{k\tau}{\rho_B C_{pB} a_{3A}^2}$

V = volume

x, y, z = dimensionless space coordinates = x_A/a_{3A}, $\frac{y_A}{a_{3A}}\sqrt{\frac{k}{k_r}}$, $\frac{z_A}{a_{3A}}$, respectively

x_A, y_A, z_A = space coordinates, ft.

ψ = rate of heat generation per unit volume of battery, B.t.u./(hr.) (cu.ft.)

ρ_B = density of the battery, lb./cu.ft.

τ = time, hr.

$'$ = dimensionless source coordinates

LITERATURE CITED

1. Carslaw, H. S., and J. C. Jaeger, "Conduction of Heat in Solids," Oxford Univ. Press, London (1959).
2. Newman, A. B., *Ind. Eng. Chem.*, **28**, 545-548 (1936).
3. Goldenberg, H., *Quart. J. Mech. Appl. Math*, **XVI**, Pt. 4, 483-505 (1963).
4. Crank, J., "The Mathematics of Diffusion," Oxford Univ. Press, London (1956).
5. Gidaspow, Dimitri, and B. S. Baker, *AIChE J.*, **11**, No. 5, 825-831 (1965).
6. ———, B. C. Jee, and F. Oliva, paper presented at 17 meeting C.I.T.C.E., Tokyo, abstr. C-513 (Sept. 5-13, 1966).
7. Morse, P. M., and H. Feshbach, "Methods of Theoretical Physics," Pt. I, Chap. 7, McGraw-Hill, New York (1953).