Unsteady Diffusion with a First-Order Homogeneous Reaction

J. S. Vrentas, C. M. Vrentas
Department of Chemical Engineering
Pennsylvania State University
University Park, PA 16802

Introduction

In the mathematical analysis of transport processes, it is sometimes possible to formulate a solution to a complex problem in terms of a solution to a simpler transport problem. For example, it has been shown (Danckwerts, 1951; Crank, 1956; Bird et al., 1960; Lightfoot, 1964) that the solution for a problem with unsteady diffusion and a first-order homogeneous reaction can be derived by utilizing the solution to the corresponding diffusion problem without chemical reaction. These results are valid for mass transfer problems where the nonhomogeneous parts of the surface boundary conditions are independent of time. However, as will be evident below, it is possible to formulate solutions to a wider class of problems than is implied in the previous investigations cited above.

Carslaw and Jaeger (1959) have shown that a general procedure of obtaining solutions to unsteady diffusion problems with a first-order chemical reaction can be developed by combining a simple transformation of the dependent variable with Duhamel's theorem for the parabolic diffusion equation. The purpose of this note is to develop a generalized version of the Carslaw and Jaeger method that makes it possible to solve unsteady diffusion-reaction problems with time-dependent surface boundary conditions and that thus provides a generalization of previous results for this problem.

Formulation of Solution

We consider the absorption, diffusion, and reaction of component A in a liquid phase under isothermal conditions. It is assumed that A is present in such a small concentration that all physical properties of the system (total mass density, viscosity, and mutual diffusion coefficient) are essentially constant. Furthermore, it is assumed that component A is depleted according to an irreversible first-order reaction and that there is a time-independent velocity field for the system. A mass transfer problem of this type can be described by the following set of equations for diffusion in a phase of volume V:

$$\frac{\partial c_A}{\partial t} + \underline{v} \cdot \nabla c_A = D\nabla^2 c_A - kc_A \tag{1}$$

$$c_A(\xi, 0) = q(\xi) \quad \xi \in V \tag{2}$$

$$c_A(\xi, t) = h_1(\xi, t) \quad \xi \in \partial V_D \tag{3}$$

$$\frac{\partial c_A}{\partial n} + Kc_A = h_2(\xi, t) \quad \xi \in \partial V_R \tag{4}$$

$$\underline{v} = \underline{v}(\xi) \tag{5}$$

$$K = K(\xi) \tag{6}$$

The volume V is bounded by two types of surfaces, ∂V_D and ∂V_R; Dirichlet boundary conditions are imposed on ∂V_D and Robin boundary conditions on ∂V_R.

A second, simpler problem for the dependent variable $w(\xi, \lambda, t)$ obeys the following set of equations:

$$\frac{\partial w}{\partial t} + \underline{v} \cdot \nabla w = D\nabla^2 w \tag{7}$$

$$w(\xi, 0) = q(\xi)e^{-k\lambda} \quad \xi \in V \tag{8}$$

$$w(\xi, t) = h_1(\xi, \lambda) \quad \xi \in \partial V_D \tag{9}$$

$$\frac{\partial w}{\partial n} + Kw = h_2(\xi, \lambda) \quad \xi \in \partial V_R \tag{10}$$

The problem for w is derived from the original problem for c_A by deleting the reaction term from the species continuity equation, by using time-independent nonhomogeneous terms in the surface boundary conditions by evaluating these terms at time λ, and by multiplying the original initial condition by the constant $e^{-k\lambda}$.

Correspondence concerning this paper should be addressed to J. S. Vrentas.

By generalizing the procedure suggested by Carslaw and Jaeger (1959), it is possible to develop a solution, $c_A(\xi, t)$, to the original set of equations in terms of the solution $w(\xi, \lambda, t)$. The solution for $c_A(\xi, t)$ can be expressed as

$$c_A = e^{-kt} \frac{\partial}{\partial t} \int_0^t w(\xi, \lambda, t - \lambda) e^{k\lambda} \, d\lambda \tag{11}$$

or, equivalently, as

$$c_A = q(\xi) e^{-kt} + e^{-kt} \int_0^t \frac{\partial w(\xi, \lambda, t - \lambda)}{\partial t} e^{k\lambda} \, d\lambda \tag{12}$$

Consequently, a solution, $c_A(\xi, t)$, to an unsteady diffusion problem with first-order reaction, nonzero initial condition, and surface boundary conditions with time-dependent nonhomogeneous terms can be derived by solving a simpler problem for $w(\xi, \lambda, t)$ if the velocity field is independent of time. The solution c_A to Eqs. 1–4 can thus be derived by substituting the solution to the simpler problem, Eqs. 7–10, into either Eq. 11 or Eq. 12. Finally, we note that it is easy to show that previous solutions to problems of this type, which have been nicely summarized by Slattery (1972), are special cases of Eq. 11 or Eq. 12.

Acknowledgment

This study was supported by funds provided by the Dow Chemical Company.

Notation

c_A = molar density of component A
D = mutual diffusion coefficient
h_1 = function in surface boundary condition, Eq. 3
h_2 = function in surface boundary condition, Eq. 4
k = first-order reaction rate constant
K = function in surface boundary condition, Eqs. 4 and 6
n = outward normal direction for volume of phase
q = initial concentration distribution of component A, Eq. 2
t = time
$\underline{v}$ = velocity vector of fluid
$\bar{V}$ = volume of phase
w = function that is a solution of Eqs. 7–10
λ = specified value of time variable
ξ = point in space characterized by the three independent distance variables

Literature cited

Bird, R. B., W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York, 621 (1960).

Carslaw, H. S., and J. C. Jaeger, *Conduction of Heat in Solids*, Oxford, London, 2nd ed., 144 (1959).

Crank, J., *The Mathematics of Diffusion*, Oxford, London, 124 (1956).

Danckwerts, P. V., "Absorption by Simultaneous Diffusion and Chemical Reaction into Particles of Various Shapes and into Falling Drops," *Trans. Faraday Soc.*, **47**, 1014 (1951).

Lightfoot, E. N., "Unsteady Diffusion with First-Order Reaction," *AIChE J.*, **10**, 278 (1964).

Slattery, J. C., *Momentum, Energy, and Mass Transfer in Continua*, McGraw-Hill, New York, 512 (1972).

Manuscript received May 9, 1986, and revision received Aug. 14, 1986.