Multicomponent Diffusion in Capillaries

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A useful expression for diffusivity of counter-diffusing binary gases in straight, uniform capillaries has been recently presented in these pages by Scott and Dullien (*1*). The expression is restricted to constant pressure and assumes that bulk flow proceeds without a radial velocity gradient in the capillary. The purpose of this note is to show that the Scott and Dullien expression may be extended to multicomponent gas mixtures if a mean diffusivity defined by Hsu and Bird (*2*) is substituted for the binary bulk diffusivity. A diffusion term which may be used with an axial pressure gradient is also given.

In the absence of both a total pressure gradient along the capillary axis, and a radial velocity gradient, a momentum balance for a differential section yields in terms of species *A*

$$-\pi r^2\, dp_A = \left(\frac{n_A m_A u_A \bar{v}_A}{4\delta}\right) 2\pi r dz + \pi r^2 dz \sum_{i=A}^{\nu} \frac{n_A n_i (u_A - u_i) kT}{n\, D_{Ai}} \tag{1}$$

where δ is a correlation factor related to accommodation for which Carman (*3*) reports values of 0.6 to 0.9. When Equation (1) is rewritten in terms of molecular flux, *G*, mole fraction, *y*, Knudsen and bulk diffusivities, D_{kA}, D_{Ai} and $\delta = 0.85$ typical value for ceramic materials

$$G_A = \frac{-\dfrac{1}{kT}\dfrac{dp_A}{dz}}{\dfrac{1}{D_{kA}} + \sum\limits_{i=A}^{\nu} \dfrac{y_i}{D_{Ai}} - \dfrac{y_A}{G_A} \sum\limits_{i=A}^{\nu} \dfrac{G_i}{D_{Ai}}} \tag{2}$$

Hsu and Bird (*2*) define a mean diffusivity for bulk diffusion under constant total pressure as

$$D_{mA} = \frac{1 - \Xi\, y_A}{\sum\limits_{i=A}^{\nu} \dfrac{y_i}{D_{Ai}} - \dfrac{y_A}{G_A} \sum\limits_{i=A}^{\nu} \dfrac{G_i}{D_{Ai}}} \tag{3}$$

where

$$\Xi = \frac{1}{G_A} \sum_{i=A}^{\nu} G_i$$

Thus

$$G_A = \frac{-\dfrac{1}{kT}\dfrac{dp_A}{dz}}{\dfrac{1}{D_{kA}} + \dfrac{1 - \Xi\, y_A}{D_{mA}}} \tag{4}$$

For a binary mixture, Equation (4) reduces to the Scott and Dullien expression.

To apply Equation (4), information on the relative fluxes of each species in the mixture must be obtained. For a constant pressure system, it may be shown (*5*, *6*) that

$$\sum_{i=A}^{\nu} G_i \sqrt{m_i} = 0 \tag{5}$$

This relation provides sufficient information only for a binary system. For multicomponent systems, $\nu - 1$ boundary conditions are needed where ν is the number of species in the system. To calculate flux in a given system, Equation (4) must be integrated for each of $\nu - 1$ species and the integrated forms solved simultaneously. Analytical integration of Equation (4), however, is probably no longer practical, in contrast to the binary case, because of the strong variation of D_{mA} with concentration.

Where one or more of the species is formed or disappears at the end or at a point in the diffusion path, stoichiometry provides additional information so that fewer boundary conditions are necessary. If all but one species takes part in a reaction, only a single boundary condition must be known. However, if all species take part, the system is over determined by just one boundary condition. In such a case, the constant pressure assumption is no longer valid and Equation (5) can no longer be used. In the latter case where the relative flux of all species is fixed by stoichiometry, integration of Equation (4) between boundaries to give the fluxes in the system is permissible only if the pressure gradient is small, that is if hydrodynamic flow is negligible.

If chemical reaction involving the diffusing species occurs along the diffusion path as in porous catalytic solids, Equation (4) describes the flux across a capillary cross section for constant total pressure. To meet this condition, there must be an inert species or, if this is not the case, the reaction must be at least closely equimolar. Nonequimolar reactions, and for that matter nonisothermal reactions, result in axial pressure gradients.

An expression for binary diffusion in the presence of an axial pressure gradient has been derived recently by Evans, Watson and Mason (*4*) for porous solids. An analogous relation for multicomponent systems may be obtained from Equation (1) by forming separate diffusion and flow terms

$$G_A = -\frac{D_{eA}}{kT}\frac{dp_A}{dz} + y_A\, D_{eA} \sum_{i=B}^{\nu} \frac{G_i}{D_{Ai}} \tag{6}$$

The first term on the right is a diffusion term which does not depend on flux. The second term allows for bulk and hydrodynamic flow. Work is now underway on the nature of this term and how it varies with the total pressure gradient. The diffusivity parameter D_{eA} is defined by

$$\frac{1}{D_{eA}} = \frac{1}{D_{kA}} + \sum_{i=B}^{\nu} \frac{y_i}{D_{Ai}} \tag{7}$$

Although D_{eA} does not depend upon flux in contrast to an effective diffusivity defined by the denominator of the right-hand side of Equation (4), it depends upon concentration, making integration difficult again. Once information on the bulk and hydrodynamic flow term in Equation (6) becomes available, it should prove to be valuable since pressure differences in the pore diffusion system are difficult to avoid and probably occur often in porous catalysts.

NOTATION

D_{AB}, D_{Ai} = binary bulk diffusion coefficients, that is for species A and B, sq. cm./sec.
D_{kA} = Knudsen diffusion coefficient for species A, sq. cm./sec.
D_{mA} = mean bulk diffusion coefficient for species A, sq. cm./sec.
D_{eA} = effective diffusion coefficient for species A, sq. cm./sec.
G = molecular flux with respect to fixed coordinates, molec./(sec.)(sq. cm.)
k = Boltzmann constant
m = molecular mass
n = molecular concentration, molec./cc.
p = partial pressure
r = capillary radius
T = temperature—°K.
u = axial velocity with respect to fixed coordinates, cm./sec.
$\bar{v}$ = average molecular velocity
y = mole fraction
δ = correction factor
$\Xi = \dfrac{1}{G_A}\sum_{i=A}^{\nu} G_i$
ν = number of diffusing species in the system

Subscripts

i = property of species i
k = Knudsen diffusivity
AB, Ai = binary bulk diffusivity of species A and i or A and B
m = Hsu and Bird (*2*) mean diffusivity
e = effective diffusivity

LITERATURE CITED

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4. Evans, R. B., G. M. Watson, and E. A. Mason, *J. Chem. Phys.*, **36**, 1894 (1962).
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situation to a considerable extent. Its scope is considerably wider than that of its predecessors, and it is also clearly and logically written so that it can easily be followed as a text.

The describing function is given the greatest attention and, is treated in considerable detail in four of the ten chapters. Since the describing-function method is probably one of the simplest and most convenient techniques for analyzing and synthesizing nonlinear control systems, it does not seem unreasonable to devote almost half of the book to a thorough treatment of it. The authors derive the describing function for a large number of commonly encountered nonlinearities and present curves not only for the fundamental but also some harmonic outputs. There is also a chapter on the describing function of nonlinear elements excited by random functions with Gaussian distribution.

Phase-plane methods, particularly as applied to piecewise linear systems and switched systems, take up most of the remainder of the book. Here again the treatment is quite thorough and a number of specific results, such as the phase-plane equation for typical linear systems, are worked out in complete detail. There is also a chapter on optimum-switched systems and a short section on Liapunov's second method with two rather interesting examples.

Although at the time of its publication the book was probably the best text available on the subject of nonlinear control, it does have a number of shortcomings. One of the most important of these is the rather brief treatment of Liapunov's second method. This method has received a great deal of attention in recent years and a number of fairly useful results have been developed that should certainly be included in the next book written about nonlinear control systems. Also, despite the fact that almost half of the book deals with describing functions, a number of important topics, such as the effect of two or more inputs, the closed-loop response and the inverse describing function problem, are completely absent. Some of the simpler analytic methods for solving nonlinear equations as well as a discussion of adaptive systems and their peculiar problems are also missing. Finally, the usefulness of the book as a text is reduced by the complete lack of problems.

However, the advantages of the book outweigh the shortcomings, and it should be especially useful to the student seeking an introduction to the subject of nonlinear control.

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A Course in Process Design, Thomas K. Sherwood, Massachusetts Institute of Technology Press, Cambridge, Mass. (1963). 256 pages. $6.00.

This book is one of the results of the Ford Foundation grant to Massachusetts Institute of Technology for a study of improved methods in engineering education. Its main purpose is to illustrate the types of process-design problems which are especially suited to an undergraduate design course in the senior year. It achieves its purpose by analyzing nine processes or cases selected to cover a wide range of processes. Most of the problems are slanted toward chemical engineering, but at least two of them and probably four are equally suitable for mechanical engineering students.

There are ten chapters and an appendix. The first chapter includes a discussion of the principles and philosophy of design and some general remarks on the design method with examples. The following nine chapters are devoted to the detailed analysis of nine design problems. The chapter headings reveal the wide range of coverage of subjects such as the liquefaction of methane, the desulfurization of petroleum naphtha, gas transmission line, the use of thermocouples for refrigeration, water desalination by hydrate formation, fresh water from sea water, solvent recovery, pigment washing and the production of hydrogen by steam reforming of methane and butane.

The appendix describes a short-cut method of optimizing a quantity, such as a cost, which is a function of several variables. The method has certain limitations on its generality but there are many practicable cases where it is applicable and involves less labor than conventional methods.

Design problems of this general type have been used in the senior design course in many schools, and the annual student chapter contest problem of American Institute of Chemical Engineers which is now in its 30th edition is closely related. Nevertheless, this book is unique in its assemblage of a variety of very carefully worked out cases with each step and assumption clearly explained. Each chapter shows the results of the thought and effort that has gone into presenting each problem in a clear and logical manner. All the material has been well organized so that it is easy to follow and comprehend.

All engineering teachers who are concerned with process design (and this should include practically all process-engineering teachers since design is the very essence of engineering) should find this book a very useful guide in the development of their own design problems for undergraduates. As a textbook illustrating typical undergraduate problems in process design, it should prove useful to students working on design problems even though their own problem is quite different in content. This is true because the general methods of approach to the problems and many of the procedures are common to most process-design problems.

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