

Elementary Derivation of the Multicomponent Diffusion Equation*

F. A. WILLIAMS†

Daniel and Florence Guggenheim Jet Propulsion Center, California Institute of Technology,
Pasadena, California

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It is demonstrated that the multicomponent diffusion equation can be derived from elementary kinetic-theory considerations without employing the results of the mathematical theory of nonuniform gases. By using the approach described by Furry, elementary expressions for the binary diffusion coefficients are also obtained. The advantage of the concept of the equivalence of partial pressure gradients and momentum gradients is thereby emphasized.

IT has been emphasized by Furry¹ that the usual elementary treatments of transport processes, which involve the concept of mean free path, lead to results which are qualitatively incorrect for diffusion. It has been demonstrated that if one uses the alternate viewpoint of calculating the diffusion velocities necessary to support specified concentration gradients, then the results are in quantitative agreement with results derived from the accurate kinetic theory of gases. In this note we use the approach suggested by Furry to derive the multicomponent diffusion equation from elementary considerations. Thermal diffusion is neglected, but the effects of pressure gradients and body forces are included. We also obtain approximate expressions for the binary diffusion coefficients.

The total momentum is conserved in molecular collisions. Hence the momentum of molecules of type i can be changed only by collisions with molecules of other types ($j \neq i$) and by body forces acting on species i . If \mathbf{V}_j is the diffusion velocity of component j and μ_{ij} is the reduced mass of the colliding molecules, then the average momentum transferred in a collision is, approximately, $\mu_{ij}(\mathbf{V}_j - \mathbf{V}_i)$, where $(\mathbf{V}_j - \mathbf{V}_i)$ is seen to be the average relative velocity of species i and j . The body force acting on the molecules of type i in a unit volume element is given by $\rho Y_i \mathbf{F}_i$, where ρ is the fluid density, Y_i represents the mass fraction of component i , and \mathbf{F}_i is the body force on a molecule of species i per unit molec-

ular mass. If the symbol Γ_i is used to denote the net rate of change of momentum of molecules of type i per unit volume, then

$$\Gamma_i = \sum_{j=1}^s \mu_{ij} \nu_{ij} (\mathbf{V}_j - \mathbf{V}_i) + \rho Y_i \mathbf{F}_i, \quad (1)$$

where ν_{ij} is the collision frequency and s denotes the total number of chemical components.

The change in momentum of molecules of species i includes changes in the random velocity and in the ordered velocity. The rate of change of the ordered momentum is $\rho Y_i D\mathbf{v}/Dt$, where \mathbf{v} is the mass average velocity of the fluid and D/Dt represents the substantial derivative with respect to time. Since the partial pressure p_i of species i is the momentum of random motion of molecules of type i transported per unit time across a unit surface area traveling with the mass average velocity of the fluid,² it follows that the gradient of p_i (∇p_i) is the rate of change of the momentum of random motion of molecules of type i per unit volume. The quantity Γ_i is therefore also given by the relation

$$\Gamma_i = \rho Y_i \frac{D\mathbf{v}}{Dt} + \nabla p_i. \quad (2)$$

Since the partial pressure of species i is related to the mole fraction X_i of species i and the total hydrostatic pressure p by the expression

$$p_i = X_i p, \quad (3)$$

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¹ W. H. Furry, *Am. J. Phys.* **16**, 63-78 (1948). References to earlier work on this subject may be found in the article by Furry.

² See, for example, J. Jeans, *The Dynamical Theory of Gases* (Cambridge University Press, London, 1925), Sec. 146, pp. 115-117; or G. N. Patterson, *Molecular Flow of Gases* (John Wiley and Sons, Inc., New York, 1956), Sec. 3.6, pp. 81-86.

Eq. (2) may be written in the form

$$\Gamma_i = \rho Y_i \frac{D\mathbf{v}}{Dt} + \rho \nabla X_i + X_i \nabla p. \quad (4)$$

To the order of approximation used here the nondiagonal elements of the pressure tensor are negligible.³ The conservation of total momentum is therefore given by the equation

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla p + \rho \sum_{j=1}^s Y_j \mathbf{F}_j.$$

If this relation is substituted into Eq. (4), then

$$\Gamma_i = \rho \nabla X_i + (X_i - Y_i) \nabla p + \rho Y_i \sum_{j=1}^s Y_j \mathbf{F}_j. \quad (5)$$

The desired diffusion equation is obtained by equating the values for Γ_i derived in Eqs. (1) and (5), *viz.*,

$$\nabla X_i = \sum_{j=1}^s \frac{\mu_{ij} \nu_{ij}}{\rho} (\mathbf{V}_j - \mathbf{V}_i) + (Y_i - X_i) \frac{\nabla p}{\rho} + \frac{\rho}{p} \sum_{j=1}^s Y_i Y_j (\mathbf{F}_i - \mathbf{F}_j), \quad (6)$$

where use has been made of the identity

$$\sum_{j=1}^s Y_j = 1.$$

The meaning of the product $\mu_{ij} \nu_{ij}$ may be found by considering the limiting case of a constant pressure process in a two-component system with no body forces. If we denote the two components by the subscripts 1 and 2, then Eq. (6) becomes

$$\nabla X_1 = \frac{\mu_{12} \nu_{12}}{\rho} (\mathbf{V}_2 - \mathbf{V}_1). \quad (7)$$

The diffusion velocity \mathbf{V}_1' of species 1 with respect to the number-weighted average velocity of the mixture, $(\mathbf{v} + \mathbf{V}_1)X_1 + (\mathbf{v} + \mathbf{V}_2)X_2$, is given by

$$\mathbf{V}_1' \equiv \mathbf{v} + \mathbf{V}_1 - (\mathbf{v} + \mathbf{V}_1)X_1 - (\mathbf{v} + \mathbf{V}_2)X_2.$$

³ See, for example, Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), Sec. 7.3c, pp. 468-469.

By using in this relation the identity $(1 - X_1) = X_2$, we obtain the expression

$$\mathbf{V}_1' = X_2 (\mathbf{V}_1 - \mathbf{V}_2). \quad (8)$$

The substitution of Eq. (8) into Eq. (7) leads to the result

$$\nabla X_1 = -\frac{\mu_{12} \nu_{12}}{X_2 \rho} \mathbf{V}_1'. \quad (9)$$

The binary diffusion coefficient D_{12} for species 1 and 2 is often defined by the equation

$$D_{12} \nabla X_1 = -X_1 \mathbf{V}_1'. \quad (10)$$

It is seen by comparing Eqs. (9) and (10) that

$$D_{12} = X_1 X_2 \rho / \mu_{12} \nu_{12},$$

which implies that, in general,

$$D_{ij} = X_i X_j \rho / \mu_{ij} \nu_{ij}. \quad (11)$$

An approximate expression for the binary diffusion coefficient D_{ij} can be obtained from Eq. (11). It is readily seen from elementary kinetic theory considerations⁴ that the collision frequency ν_{ij} is given by the relation

$$\nu_{ij} = X_i X_j n^2 \sigma_{ij} c_{ij}, \quad (12)$$

where σ_{ij} represents the collision cross section for molecules of types i and j , the quantity n is the total number of molecules per unit volume, and c_{ij} signifies the magnitude of the average relative velocity of the colliding molecules. If Eq. (12) and the ideal gas law,

$$p = nkT, \quad (13)$$

are substituted into Eq. (11), then the resulting equation for the diffusion coefficient is

$$D_{ij} = \frac{kT}{n \mu_{ij} \sigma_{ij} c_{ij}}. \quad (14)$$

Here T is the temperature and k represents the Boltzmann universal gas constant. The corresponding equation derived from the exact kinetic theory of gases⁵ differs from this prediction only by a constant factor of approximately $\frac{3}{4}$.

⁴ See, for example, J. Jeans, *The Dynamical Theory of Gases* (Cambridge University Press, London, 1925), Sec. 33, pp. 35-37.

⁵ See, for example, S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, London, 1952), Sec. 9.81, p. 165.

By substituting Eq. (11) into Eq. (6) we obtain the relation

$$\nabla X_i = \sum_{j=1}^s \frac{X_i X_j}{D_{ij}} (V_j - V_i) + (Y_i - X_i) \frac{\nabla p}{p} + \frac{p}{p} \sum_{j=1}^s Y_i Y_j (\mathbf{F}_i - \mathbf{F}_j). \quad (15)$$

It can be shown by the exact kinetic theory of gases that this diffusion equation is valid to first order in a Sonine polynomial expansion.⁶ This exercise demonstrates the obvious usefulness and great advantage of the point of view discussed by Furry.¹

⁶ See, for example, Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), Sec. 7.4 ei, pp. 485-488.

Writing Test Exercises in the Natural Sciences

LEO NEDELSKY

University of Chicago, Chicago, Illinois

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This paper is concerned with general principles to be used in writing test exercises, especially objective test exercises, in natural sciences. Most examples will be drawn from physics, the field in which the author feels most at home; the generalizations which these examples are to illustrate, however, should be applicable to any of the natural sciences.

EXERCISE VARIETY

IN these relatively enlightened times it may be safe to assume that the test writer has before him a list of clearly stated objectives, i.e., a description of the kinds of knowledge and abilities the test is to measure. It is well, however, to look into the origin of the list. The most important function of a science test, perhaps its only defensible function, is to predict the student's behavior when faced with a situation in which an understanding of science is useful and important. Such a situation, which we shall call a criterion situation, may occur in the student's academic career, his life as a citizen, or his work as a scientist.

One way to test the student's criterion competence, i.e., competence to deal with a criterion situation, is to present the student with realistic problems, i.e., with situations that closely resemble those he is likely to face in the future. A test of this "synthetic" sort is quite valid but also almost prohibitively cumbersome and expensive, for genuine problems facing a scientist or a citizen are usually very complex and not of the paper and pencil type. Further disadvantages of such a test lie in the difficulty of assembling an adequate sample of problems

and of communicating about the precise nature of the test and students' "scores."

Another way, is first to analyze the complex competence to solve genuine problems into its constituents and then to test for the more important but still tractable of these. Such an "analytic" test has all the usual shortcomings of an analytic representation of complex and incompletely understood phenomena: neither are all the constituents known nor do they add up to the whole. In addition, some of the more important constituents, such as habits of thought and attitudes, cannot be conveniently or accurately measured. Those shortcomings of an analytic test which result from the unavailability of a complete analysis of a complex competence are probably best alleviated by including in the test exercises that, in the aggregate, evoke in the student a great variety of mental processes in varied patterns.

We are here concerned with the analytic type of test. The list of objectives is the list of presumed constituents of the criterion competence. As has been suggested in the last paragraph, the test writer can in some respects transcend statements of objectives and come closer to the criterion competence by varying test exercises as widely as the limits of the formally stated