DETERMINATION OF EFFECTIVE DIFFUSION COEFFICIENTS IN A LAMINAR MULTICOMPONENT BOUNDARY LAYER

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Abstract

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DETERMINATION OF EFFECTIVE DIFFUSION COEFFICIENTS IN A LAMINAR MULTICOMPONENT BOUNDARY LAYER

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In multicomponent gas mixtures the diffusion-velocity vectors $\mathbf{V}_i = \mathbf{v}_i - \mathbf{v}$ are related to the concentration gradients by $N-1$ independent Stefan-Maxwell relations (^{1}), which, after passage to mass concentrations c_i, take the form

$$\nabla c_i = \sum_{j=1}^{N} \frac{c_i x_j}{D_{ij}} (\mathbf{V}_j - \mathbf{V}_i) - \sum_{k=1}^{N} c_k \sum_{j=1}^{N} \frac{c_i x_j}{D_{kj}} (\mathbf{V}_j - \mathbf{V}_k) \quad (i = 1, \dots, N), \tag{1}$$

$$c_i = \frac{m_i}{m} x_i, \qquad m^{-1} = \sum_{k=1}^{N} \frac{c_k}{m_k}, \qquad \mathbf{J}_i = \rho_i (\mathbf{v}_i - \mathbf{v}) = \rho_i \mathbf{V}_i,$$

where x_i is the molar concentration, m_i is the molecular weight of the i-th component, m is the mean molecular weight of the mixture, D_{ij} is the coefficient of binary diffusion, $\mathbf{J}_i$ is the vector of the mass diffusion flux, and N is the number of components.

Starting from relations (1), one can introduce a definition of effective diffusion coefficients in a multicomponent gas mixture.

I. Since in the boundary-layer theory approximation only the projections of the diffusion vectors $\mathbf{J}_i$ on the normal to the body surface, for example on the y-axis, are required, in what follows we shall operate only with these projections and denote them by the same letters, but in lightface type. Then relations (1) can be represented in the form of Fick' s laws

$$J_i = \rho_i (v_i - v) = \rho_i V_i = -\rho D_i \frac{\partial c_i}{\partial y} \quad (i = 1, \dots, N), \tag{2}$$

where the effective diffusion coefficients D_i are determined from the expressions

$$\frac{1}{D_i} = \sum_{j=1}^{N} \frac{x_j}{D_{ij}} \frac{v_i - v_j}{v_i - v} + \sum_{k=1}^{N} c_k \sum_{j=1}^{N} \frac{x_j}{D_{kj}} \frac{v_j - v_k}{v_i - v} \quad (i = 1, \dots, N). \tag{3}$$

In the general case the coefficients D_i can be calculated only after solving the diffusion equations and will depend, generally speaking, on the determining parameters of the particular problem.

II. Let us now consider a method for calculating effective diffusion coefficients in the boundary layer for a given particular gas mixture. Suppose that a mixture is given in which all binary diffusion coefficients can be divided into three groups: $D_{ij} = D$ $(i, j = \mathrm{O_2}, \mathrm{N_2}, \mathrm{NO}, \mathrm{CO}, \mathrm{CN})$, D_{ia} $(a = \mathrm{O}, \mathrm{N})$, where in each group the binary coefficients are equal or close. From definition (3), taking into account the closeness of the molecular weights of all components except atoms, we obtain

$$\frac{1}{D_O} = \frac{1}{D_{ia}} + B\left(x_N - \frac{m}{m_a}\frac{c_N V_N}{c_O V_O} c_O\right), \qquad \frac{1}{D_N} = \frac{1}{D_{ia}} + B\left(x_O - \frac{m}{m_a}\frac{c_O V_O}{c_N V_N} c_N\right),$$

$$\frac{1}{D_i} = \frac{1 - x_O^* - x_N}{D_{ij}} + \frac{x_O + x_N}{D_{ia}} + \left(\frac{1}{D_{ij}} - \frac{1}{D_{ia}}\right)\frac{m}{m_i}\frac{c_O V_O + c_N V_N}{c_{iV} i} c_i \quad (i = \mathrm{O_2}, \mathrm{NO}, \mathrm{CO}, \mathrm{CN}),$$

$$\frac{m}{m_i} = \frac{1 - x_O - x_N}{1 - c_O - c_N}, \qquad B = \frac{1}{D_{aa}} - \frac{1}{D_{ia}}, \qquad \frac{1}{D_{ij}} - \frac{1}{D_{ia}} = \frac{0.285}{D_{ij}} = \frac{0.400}{D_{ia}}. \tag{4}$$

The ratios of the mass diffusion fluxes entering the right-hand sides of expressions (4) are found from the solution of the diffusion equations. For definiteness, let us consider the flow in the neighborhood of a critical point (line) in the presence of heterogeneous reactions on the surface. The boundary-value problem for the diffusion equation in this case will be (^{2})

$$[l S_i^{-1} c_i'(\eta)]' + n\varphi(\eta) c_i'(\eta) = 0, \qquad c_i(0) = c_{i0}, \qquad c_i(\infty) = c_{ie}, \qquad l = \frac{\mu\rho}{\mu_0\rho_0},$$

$$S_i = \frac{\mu}{\rho D_i}, \qquad \psi(x, y) = \sqrt{\beta\mu_0\rho_0}\,\frac{x^2}{2}\, n\varphi(\eta), \qquad \eta = \left(\frac{\beta}{\mu_0\rho_0}\right)^{1/2}\int_0^y \rho\, dy, \tag{5}$$

where the subscript 0 refers to the values of the parameters at the wall, and the subscript e to the values at the outer boundary of the boundary layer.

From problem (5) the required value of the mass-transfer coefficient will be

$$\frac{c_i'(0)}{c_{ie} - c_{i0}} = \frac{S_{i0}}{\omega(\infty, S_i)}, \qquad \omega(\infty, S_i) = \omega(S_i) = \int_0^\infty \frac{S_i}{l}\exp\left(-n\int_0^\lambda \varphi\frac{S_i}{l}\, dt\right) d\lambda. \tag{6}$$

The Laplace-type integral $\omega(S_i)$, by passing to the new independent variable of integration $\eta_i = \int_0^\eta \frac{S_i}{l}\, d\eta$ (we assume that $S_i > 0$), takes the form

$$\omega(S_i) = \int_0^\infty \exp\left(-n\int_0^\lambda \varphi_i(t_i)\, dt_i\right) d\lambda, \qquad \varphi_i(\eta_i) = \varphi[\eta(\eta_i)].$$

Assuming the parameter S_i (or n) sufficiently large, and the value of the function $\varphi_i(0) = \varphi(0) = a < 0$ sufficiently small, $-an \sim S_{i0}^{-1}$, we obtain, analogously to how this was done in work (2), the following asymptotic expression for $\omega(S_i)$:

$$\omega(S_i) = \frac{1}{3}\left(\frac{6S_{i0}^2}{\tau n}\right)^{1/3}\Gamma\left(\frac{1}{3}\right)\left\{1 - \left(\frac{6S_{i0}^2}{\tau n}\right)^{1/3}\left[n\alpha + \varphi_i'''(0)\frac{S_{i0}^2}{6\tau}\right]\frac{\Gamma(2/3)}{\Gamma(1/3)} + \dots\right\}, \qquad \tau = \varphi''(0). \tag{7}$$

The ratio of the mass-transfer coefficients (6), using the asymptotics (7) with two terms retained, is calculated especially simply:

$$\frac{c_i'(0)}{c_j'(0)} = \frac{c_{ie} - c_{i0}}{c_{je} - c_{j0}}\,\frac{S_{i0}}{S_{j0}}\,\frac{\omega(S_j)}{\omega(S_i)} = \frac{c_{ie} - c_{i0}}{c_{je} - c_{j0}}\left(\frac{S_{i0}}{S_{j0}}\right)^{1/3} I(S_{i0}, S_{j0}),$$

$$I(S_{i0}, S_{j0}) = 1 + 0.506\left(\frac{6}{\tau n}\right)^{1/3}\left\{n\alpha\left(S_{i0}^{2/3} - S_{j0}^{2/3}\right) + \right. \tag{8}$$

$$\left. + \frac{1}{2}\left[S_{i0}^{2/3}\left(\frac{l}{S_i}\right)_0' - S_{j0}^{2/3}\left(\frac{l}{S_j}\right)_0'\right] - \frac{1}{6\tau}\left(\frac{\rho_e}{\rho_0} + n\alpha\tau + \tau l_0'\right)\left(S_{i0}^{-1/3} - S_{j0}^{-1/3}\right) + \dots\right\}.$$

Since in most practical cases $S_{i0} \sim 1$ (see below), the accuracy of formula (8) was checked by comparison with numerous numerical solutions obtained for a binary mixture when six different gases were blown into air. One such comparison for the flat case with helium blowing is given in Table 1. For moderate blowing $-n\alpha = 0.2$–0.6 and $0.3 < S_{i0}, S_{j0} < 3$, formula (8), as well as the numerical solutions, shows that the complex $(S_{i0}/S_{j0})^{1/3} I(S_{i0}, S_{j0}) \approx 1$. In the absence of blowing, however, for $0.25 < S_{i0}, S_{j0} < 5$, this complex is approximated sufficiently accurately by the expression $(S_{i0}/S_{j0})^{1/3} I(S_{i0}, S_{j0}) = (S_{i0}/S_{j0})^{0.4}$.

Thus, in the absence of supply of substance from the surface, the ratios of the mass diffusion fluxes at the wall will be equal to

Table 1

$n = 1, \quad S_j = 1, \quad T_0/T_e = 0.5$

α	$\tau = \varphi''(0)$	S_{i0}	ρ_e/ρ_0	l_0	$(l/S_i)'_0$	c_{i0}	$S_{i0}^{1/3} \times I(S_{i0}, 1)$	Formula (8)
−0.2	1.1401	0.379	0.971	0.1706	0.9947	0.1510	0.884	0.90
−0.3	1.1242	0.473	1.210	0.2506	1.1270	0.2276	0.989	1.08
−0.4	1.3289	0.564	1.442	0.3146	1.620	0.3019	1.067	1.18
−0.5	1.4041	0.625	1.665	0.3591	1.378	0.3736	1.117	1.26

$$\left(\frac{c_{iV} i}{c_{jV} j}\right)_0 = \left[\frac{\rho D_i c_i'(0)}{\rho D_j c_j'(0)}\right]_0 = \frac{c_{ie} - c_{i0}}{c_{je} - c_{j0}} \left(\frac{D_{i0}}{D_{j0}}\right)^{0.6}. \qquad (9)$$

With moderate supply of substance from the surface,

$$\left(\frac{c_{iV} i}{c_{jV} j}\right)_0 = \frac{c_{ie} - c_{i0}}{c_{je} - c_{j0}} \frac{D_{i0}}{D_{j0}}. \qquad (10)$$

With intensive blowing, close to the flow-separation regime ($-n\alpha \approx 1$, $0.6 < S_{i0}, S_{j0} < 1.4$), in (10) the ratio D_{i0}/D_{j0} should be replaced by $(D_{i0}/D_{j0})^2$.

For case (4), using relations (10) and the boundary conditions

$$(c_O)_0 = (c_N)_0 = (c_{O_2})_0 = (c_{\mathrm{NO}})_0 = 0, \qquad (c_{\mathrm{CO}})_e = (c_{\mathrm{CN}})_e = 0,$$

$$(c_O V_O)_0 < \infty, \qquad |c_N V_N|_0 < \infty, \qquad |c_{O_2} V_{O_2}|_0 < \infty, \qquad |c_N V_{\mathrm{NO}}|_0 < \infty \qquad (11)$$

we obtain for the effective diffusion coefficients at the wall the expressions

$$D_O = D_N = D_a = D_{ia}, \qquad D_{O_2} = D_{N_2} = D_{ij},$$

$$D_i = D_{ij} \left[1 + \left(\frac{D_{ia}}{D_{ij}} - 1\right) c_{ae}\right], \qquad c_{ae} = (c_O)_e + (c_N)_e. \qquad (12)$$

The effective diffusion coefficient for molecular nitrogen need not be calculated, since one of the components can always be found from the identity $\sum_{k=1}^{N} c_k = 1$, and the diffusion equation for N_2 can be omitted.

It follows from the structure of formulas (12) that the effective diffusion coefficients at the wall are equal to the corresponding binary coefficients multiplied by known functions of the degree of dissociation. This result is physically clear and justifies the introduction of the concept of effective diffusion coefficients in a multicomponent gas mixture. In an analogous way, effective diffusion coefficients can be calculated for more complex gas mixtures.

Table 2

	O	O_2	N_2	O	O_2	N	N_2	NO
c_{ie}	0,227	0,004	0,769	0,210	0,003	0,034	0,719	0,034
c_{i0}	0	0,279(0,273)	0,721(0,727)	0	0,259(0,267)	0	0,741(0,733)	0
$\left(\dfrac{D_O}{D_{O_2}}\right)_0$	1,38(1,36)			1,37(1,35)				

III. Let us consider, as an example, the problem of determining the composition of air on an impermeable catalytic wall in the vicinity of the critical point; for simplicity of exposition we shall assume that $c_{\mathrm{NO}} = 0$ ($c_{\mathrm{NO}} < 0.05$). The conservation law for the element O on an impermeable wall can be written in the form

$$\rho D_O \frac{\partial c_O}{\partial y} + \rho D_{O_2} \frac{\partial c_{O_2}}{\partial y} = 0, \qquad (c_O)_0 = (c_N)_0 = 0. \tag{13}$$

Using relations (6) and (9), condition (13) takes the form

$$(c_O)_0 = (c_{O_2})_e + (c_O)_e \, (D_O/D_{O_2})_0^{0.6}. \tag{14}$$

Calculating the ratio $(D_O/D_{O_2})_0$ from (4), using the boundary conditions (13) and the analogy (9), we obtain ($D_{\mathrm{OO2}}/D_{O_2 \mathrm{N}_2} = 1.53$)

$$(c_{O_2})_0 = (c_{O_2})_e + 1.29 \, (c_O)_e \left[1 - 0.347 \, c_{ae} \frac{(c_{O_2})_0}{(c_O)_e}\right]^{0.6},$$

$$\left(\frac{D_O}{D_{O_2}}\right)_0 = 1.53 \left[1 - 0.347 \, c_{ae} \frac{(c_{O_2})_0}{(c_O)_e}\right],$$

whence it follows that when $(c_O)_e = 0$, $(c_{O_2})_0 = (c_{O_2})_e$, and there is no change in the concentration of the element O at the wall. The maximum value of the O_2 concentration at the wall, equal to 0.280, will occur at $(c_O)_e = 0.231$, i.e., when all the oxygen at the outer boundary of the boundary layer is dissociated. As $c_{ae} \to 1$, the separating effect will decrease and tend to zero.

Comparison of the formulas obtained with two numerical solutions of work (^{3}), given in Table 2 (the numerical results are given in parentheses), shows a sufficiently high accuracy of the method.

Fig. 1

Figure 1: Fig. 1

IV. To justify the validity of deriving formula (7), it is sufficient to require that the generalized Schmidt numbers S_i be positive throughout the entire thickness of the boundary layer. The positivity of the corresponding numbers S_i in each specific case can be proved. For example, for the mixture considered in Sec. II, from formulas (4) it follows that $S_O > 0$ and $S_N > 0$, since the quantities $c_O V_O$ and $c_N V_N$ have the same sign. To determine the numbers S_i $(i = \mathrm{CO}, \mathrm{CN})$, when $(c_{\mathrm{CO}})_e = (c_{\mathrm{CN}})_e = 0$, from (4) and (5) we obtain the system of equations $(l = 1)$

Fig. 1

$$Z_i' = a(\eta)X_i - b(\eta)(1 - Z_i), \qquad Z_i(0) = 0, \qquad Z_i(\infty) = 1,$$

$$X_i' + n\varphi(\eta)a(\eta)X_i = -\,n\varphi(\eta)b(\eta)(1 - Z_i),$$

where

$$c_i = c_{i0}(1 - Z_i), \qquad X_i = \frac{J_i}{c_{i0}\sqrt{\beta\mu_0\rho_0}}, \qquad S_{ij} = \frac{\mu}{\rho D_{ij}} = \frac{\mu}{\rho D}, \qquad a(\eta) = S_{ij}\,[1- \tag{15}$$

$$-\,0.285(x_O + x_N)] > 0, \qquad b(\eta) = -\,0.285\,S_{ij}\frac{m}{m_i}(X_O + X_N) > 0,$$

$$S_i \equiv \frac{Z_i'}{X_i} = S_{ij}[1 - 0.285(x_O + x_N)] + 0.285\,S_{ij}\frac{m}{m_i}\frac{X_O + X_N}{X_i}(1 - Z_i). \tag{16}$$

The function X_i takes a positive value at $\eta = 0$ by virtue of the boundary conditions of conservation of mass of the i-th component $(i = \mathrm{CO}, \mathrm{CN})$ and tends to zero as $\eta \to \infty$ (Fig. 1). At the same time, X_i cannot vanish. To prove this, we use the following elementary lemma. Let the equation $u' + f(x)u = g(x)$ be given. If $f(x)$ and $g(x)$ are continuous for $x_0 < x < x_1$ and if $g(x) \neq 0$, then the integral curve passing through the point (x_0, y_0) can have no more than one common point with the x-axis. The role of the function $g(x)$ in the second equation of system (15) is played by the function $g(\eta) = -\eta\varphi(\eta)b(\eta)(1 - Z_i)$, which first assumes a positive value, then becomes zero at a certain value η_0, and for $\eta > \eta_0$ remains negative, since the function $\varphi(\eta)$ is monotone and becomes zero at $\eta = \eta_0$ (see Fig. 1). Then the integral curve for the second equation of system (15), passing through the point $(\eta_0, X_i(\eta_0))$, will satisfy the conditions of the lemma. Moreover, if the integral curve crosses the η-axis, then, by virtue of its monotonicity as $\eta \to \infty$, X_i will tend to $-\infty$, which will contradict the boundary condition at infinity, since the diffusion flux X_i as $\eta \to \infty$ must be bounded and positive. Consequently, the function X_i remains positive throughout the entire thickness of the boundary layer. It is similarly proved, with the aid of the first equation of system (15), that the function $Z_i(\eta)$ is monotone and $Z_i' > 0$ on the interval $(0, \infty)$. Then from (16) it will follow that the Schmidt numbers S_i are positive throughout the entire thickness of the boundary layer.

For O_2, NO, satisfying the boundary conditions $(c_{O_2})_0 = (c_{\mathrm{NO}})_0 = 0$, the proof of the positivity of the generalized Schmidt numbers is analogous.

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