CALCULATING THE EFFECTIVE DIFFUSION COEFFICIENTS IN A LAMINAR DISSOCIATED MULTICOMPONENT BOUNDARY LAYER

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We derive expressions for the effective diffusion coefficients D_i $(i = 1, \ldots, N)$ defined in [1,2] in terms of the ratios of the mass diffusion fluxes for an arbitrary N-component mixture in a boundary layer. Sufficient conditions for the identity of the concentrations, diffusion fluxes, and generalized Schmidt numbers $S_i = \mu / (\rho D_i)$ across the "frozen" boundary layer are obtained. Using a generalization of the analogy between mass transfer coefficients based on the analytical and numerical solutions of the diffusion equations in the "frozen" boundary layer, we reduce the determination of the coefficients D_i for an arbitrary N-component medium at the wall to the solution of algebraic equations with and without blow-in. We solve this system approximately and obtain explicit expressions for D_{iw} for typical mixtures which appear in the boundary layer (at the surface) of thermoplastics based on phenol-formaldehyde resin, which decompose in a dissociated air stream in planetary atmospheres. Using the asymptotic form of solution of the boundary layer equations at the outer edge of the layer, we derive exact analytic formulas for the effective diffusion coefficients $D_{i\infty}$ in an arbitrary N-component system. The behavior of the corresponding generalized Schmidt numbers S_i is described qualitatively and their approximate (exact at the boundaries) values across the boundary layer are given. These results simplify appreciably the numerical and analytical solution of the equations for an arbitrary multicomponent dissociated boundary layer at the surface of a heat-insulating coating which disintegrates under the action of heat [3]. This in turn enables us to automatically extend various solutions, in particular the correlation formulas for the heat and mass transfer coefficients obtained in the "binary" boundary layer approximation, to a multicomponent layer. We can accomplish this simply by introducing the appropriate effective diffusion coefficients into these solutions [4]. Diffusion in specific multicomponent mixtures is also dealt with in an approximate manner in [5].

1. In the thin asymptotic boundary layer approximation the normal components of the mass diffusion fluxes $J_i = \rho_i (v_i - v) = \rho_i V_i$ in a multicomponent gas mixture flowing past a surface are related to the gradients of the molar (numerical) concentrations x_i by the Stefan-Maxwell equations [6] (we neglect thermal diffusion which is a second-order effect [7]; the barodiffusion effect and the influence of the viscous impulse transfer [8] are negligible by virtue of the boundary-layer-theory approximation)

$$\frac{\partial x_i}{\partial y} = \sum_{j=1}^{N} \frac{x_i x_j}{D_{ij}} \left(\frac{J_i}{\rho_j} - \frac{J_i}{\rho_i} \right) \qquad (i = 1, \ldots, N-1) \tag{1.1}$$

where

$$x_i = \frac{n_i}{n}, \qquad n = \sum_{j=1}^{N} n_j, \qquad v = \sum_{j=1}^{N} c_j v_j, \qquad c_i = \frac{m_i}{m} x_i$$
$$m = \sum_{j=1}^{N} x_j m_j, \qquad \sum_{j=1}^{N} J_j \equiv 0 \tag{1.2}$$

Here D_{ij} are the binary diffusion coefficients, ρ_i density, n_i the number of moles (particles) of the i-th component per unit volume, n the total number of moles per unit volume, v_i the mean statistical velocity of the i-th component, v the mean mass flow rate of the mixture, V_i the rate of diffusion of the i-th component, c_i mass concentration, m_i the molecular weight of the i-th component, m the molecular weight of the mixture, and y the coordinate normal to the surface. Relations (11) are preferable to

$$J_i = \frac{n^2}{\rho} \sum_{j=1}^{N} D^{*}_{ij} \frac{\partial x_j}{\partial y_i} \qquad (i = 1, \ldots, N) \tag{1.3}$$

for the diffusion fluxes [9] obtained from (1.1) by solving them for J_i. This is because (1.1) contain only the binary diffusion coefficients which are available from literature [9] for many component pairs, while (1.3) contain the multicomponent diffusion coefficients D^{*}_{ij} which are defined as the ratios of complicated N-th order determinants and depend on the composition of the mixture and on $\frac{1}{2} N (N - 1)$ binary diffusion coefficients D_{ij}. Moreover, substitution of (1.3) into the diffusion equations yields a system of equations for the concentrations which have not solved in the case of higher-order derivatives. This leads to great difficulties in obtaining the actual solutions even for the simplest problems of diffusion in stationary media [10]. Using (1.2) to convert from $\partial x_i / \partial y$ to $\partial c_i / \partial y$ in (1.1), we obtain

$$J_i \sum_{j=1}^{N} \frac{x_j}{D_{ij}} + \sum_{j=1}^{N} \left[\sum_{k=1}^{N} \left(\frac{m}{m_j} - \frac{m}{m_k} \right) \frac{c_k}{D_{kj}} - \frac{m}{m_j} \frac{1}{D_{ij}} \right] J_j c_i = -\rho \frac{\partial c_i}{\partial y} \tag{1.4}$$

$$(i = 1, \ldots, N)$$

Equation (1.4) implies that in the case of multicomponent mixtures with unequal binary diffusion coefficients, the diffusive flux J_i of the i-th component cannot, in general, be expressed in terms of the gradient of concentration alone. Some particular cases where the flux J_i can be expressed in terms of the concentration c_i only are dealt with in [9].

Our purpose in the present paper is to introduce a definition of the effective diffusion coefficients based on exact expression (1.4), and to compute these coefficients across the frozen boundary layer (when all reactions take place on the surface) for an arbitrary N-component mixture.

Relations (1.4) can be written formally in the form of Fick's laws,

$$J_i = \rho_i V_i = -\rho D_i \frac{\partial c_i}{\partial y} \quad (i = 1, \ldots, N) \tag{1.5}$$

where the effective diffusion coefficients D_i introduced in this manner can be obtained from the following $N - 1$ independent relations

$$\frac{1}{D_i} = \sum_{j-1}^{N} \frac{x_j}{D_{ij}} + \sum_{j=1}^{N} \left[\sum_{k=1}^{N} \left(\frac{m}{m_j} - \frac{m}{m_k} \right) \frac{c_k}{D_{kj}} - \frac{m}{m_j} \frac{1}{D_{ij}} \right] \frac{J_j}{J_i} c_i \tag{1.6}$$

$$(i = 1, \ldots, N)$$

These expressions indicate that in the general case of arbitrary diffusion properties of the components the effective diffusion coefficients can only be found from a known solution of a given problem; they therefore depend on the defining parameters of each specific problem. However, we shall see later that in the boundary layer the coefficients D_i depend only on the limiting concentrations at the wall and at the outer edge of the boundary layer, and on the binary diffusion coefficients, and that they are practically independent of the blow-in intensity and of other defining parameters of the problem. In other words, as far as their properties are concerned, the effective diffusion coefficients D_i behave just like binary diffusion coefficients with boundary values of the concentrations. (The corrections are necessitated by the cross-influence of the diffusion of other components.)

2. First let us consider the behavior of the effective diffusion coefficients for certain gas mixtures. Although obtained for particular mixtures, our findings will also hold for multicomponent boundary layers at the surfaces of thermally disintegrating thermoplastics. The binary diffusion coefficients are usually nearly equal [3] for components with close (equal) molecular weights. We call the components M and M′ "components with similar (equal) diffusive properties" if (*)

$$m(\mathrm{M}) \approx m(\mathrm{M}') \qquad (m(\mathrm{M}) = m(\mathrm{M}')) \tag{2.1}$$

$$D(\mathrm{M}, i) \approx D(\mathrm{M}' i) \qquad (D(\mathrm{M}, i) = D(\mathrm{M}', i))$$

Theorem 2.1. If a group of components with equal diffusion properties can be isolated in a gas mixture, then the effective diffusion coefficients (1.6) for all the components are not explicitly dependent on the diffusion fluxes of the components belonging to this group.

For a one-component group this theorem obviously follows from (1.6). In the general case we split the second sum over j in (1.6) into two parts: the first part ranging from $j = 1$ to N' and the second part from $j = N' + 1$ to N, where $N - N'$ is the number of components with equal diffusion properties; we then apply identity (1.2) for the diffusion fluxes to (1.6) to obtain

$$\frac{1}{D_i} = \sum_{j=1}^{N} \frac{x_j}{D_{ij}} + \sum_{j=1}^{N'} \left\{ \sum_{k=1}^{N} \left[\left(\frac{m}{m_j} - \frac{m}{m_k} \right) \frac{c_k}{D_{kj}} - \left(\frac{m}{m(\mathrm{M})} - \frac{m}{m_k} \right) \frac{c_k}{D(k, \mathrm{M})} \right] + \right.$$
$$\left. + \frac{m}{m(\mathrm{M})} \frac{1}{D(i, \mathrm{M})} - \frac{m}{m_j} \frac{1}{D_{ij}} \right\} \frac{J_j}{J_i} \qquad (i = 1, \ldots, N) \tag{2.2}$$

Corollary. If the mixture under consideration consists of a group of components with similar diffusion properties (index M) and a single additional component i, then the effective diffusion coefficient for this component is

$$D_i = D(i, \mathrm{M}) \tag{2.3}$$

The effective diffusion coefficients for the remaining components are in this case given by

$$\frac{1}{D(\mathrm{M})} = \frac{1}{D(\mathrm{M}, \mathrm{M})} + \left(\frac{1}{D(\mathrm{M}, i)} - \frac{1}{D(\mathrm{M}, \mathrm{M})} \right) \left(x_i - \frac{J_i}{J(\mathrm{M})} x(\mathrm{M}) \right)$$
$$(\mathrm{M} = 1, \ldots, N - 1) \tag{2.4}$$

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*) When a chemical symbol or a capital letter such as A or M has to be used as a subscript, it will be inclosed in parantheses, e.g. $D_{\mathrm{M}i} = D(\mathrm{M}, i)$ or $D_{\mathrm{A}} = D(\mathrm{A})$ etc.

If the group M consists of a single component (i.e. if the mixture is binary), then (2.4) implies directly that $D(\mathrm{M}) = D(\mathrm{M}, i)$, as expected. The above theorem is of practical value, e.g. it can be applied to mixtures generated in a high-enthalpy air or CO_2 flow in the boundary layer (at the surface) of a thermally disintegrating plastic based on phenol-formaldehyde resin [9].

Even though components such as O_2, N_2, NO, CO, CN, HCN, and C_3 appearing during this process do not strictly satisfy the conditions (2.1), nevertheless the assumption of equality of their diffusion properties does not introduce large errors into the calculation of the effective diffusion coefficients using (2.2) instead of (1.6). This is confirmed by the following values of the ratios of the binary diffusion coefficients for these components at $T = 2000°$ K (these ratios are practically independent of temperature):

$$\frac{D(\mathrm{CN}, \mathrm{CO})}{D(\mathrm{N_2}, \mathrm{CN})} = 1.005, \quad \frac{D(\mathrm{CN}, \mathrm{CO})}{D(\mathrm{N_2}, \mathrm{C_3})} = 1.006, \quad \frac{D(\mathrm{CN}, \mathrm{CO})}{D(\mathrm{C_3}, \mathrm{CO})} = 0.995 \quad \text{etc.}$$

The differences of the molecular weight ratios $m / m_j - m / m(\mathrm{M})$ $(j = 1, \ldots, N - N')$ for these components do not exceed 0.05 to 0.08. Consequently, if the terms in square brackets in (1.6) referring to the components with similar diffusion properties are replaced by the corresponding terms in which the subscript j is replaced by M, then the resulting error of estimating D_i from (2.2) instead of (1.6) will not exceed 10%, and will in fact be much smaller [11].

Equating the diffusion properties of just the two components CO and N_2, which together constitute the major portion of many interesting mixtures, we obtain

$$m(\mathrm{CO}) = m(\mathrm{N_2}) = 28, \qquad \frac{D(i, \mathrm{CO})}{D(i, \mathrm{N_2})} = 1 \pm 0.005 \qquad (i = 1, \ldots, N)$$

Formula (2.2) in this case entails an error not exceeding 1%.

3. Equations of diffusion of the components are required for investigating the properties of the coefficients D_i, concentration fields, and diffusion fluxes across the boundary layer. These equations in the boundary-layer approximation for a two-dimensional flow are given by

$$\rho\left(u \frac{\partial c_i}{\partial x} + v \frac{\partial c_i}{\partial y}\right) + \frac{\partial}{\partial y} J_i = 0 \qquad (i = 1, \ldots, N) \tag{3.1}$$

where x and y are the coordinates tangent and normal to the surface of the body respectively; u and v denote the corresponding components of the velocity vector.

New independent coordinates are convenient in actual solution and qualitative analysis. They are given by

$$\xi = \int_0^x \mu_e \rho_e U_e(x) r^{2k} dx, \qquad \eta = U_e(x) r^k \left(\frac{l_e}{2\xi}\right)^{1/2} \int_0^y \rho dy, \qquad l_e = \frac{\mu_e \rho_e}{\mu_w \rho_w} \tag{3.2}$$

where μ is the viscosity coefficient, $U_e(x)$ the velocity of nonviscous flow at the surface of the body, $r(x)$ the radius of the cross section of the solid of revolution ($k = 0$ and $k = 1$ for the plane-parallel and axisymmetric problems, respectively); e are the conditions at the outer boundary; w is the condition at the wall.

We shall attempt to find the velocities u and v and the diffusion fluxes in the form

$$u = U_e \frac{\partial f(\xi, \eta)}{\partial \eta}, \qquad -\rho v r^k = \frac{\xi_x}{(2\xi l_e)^{1/2}} \varphi(\xi, \eta) + \left(\frac{2\xi}{l_e}\right)^{1/2} \frac{\partial f}{\partial \eta} \eta_x \tag{3.3}$$

$$J_i = U_e r^k (\mu_w \rho_w \mu_e \rho_e)^{1/2} (2\xi)^{-1/2} X_i \qquad (i = 1, \ldots, N)$$

$$\varphi(\xi, \eta) = f(\xi, \eta) + 2\xi \left(\frac{\partial f}{\partial \xi} - \frac{1}{2} f \frac{d \ln l_e}{d\xi} \right) \tag{3.4}$$

Inserting u and v into the equation of continuity, we find that the latter is satisfied identically, that the impulse equation projected on the x-axis yields a certain equation for the function f which we omit giving here, that the heat influx equation is not required, and that equations (3.1) of the diffusion of the components become

$$-\frac{\partial X_i}{\partial \eta} + \varphi(\xi, \eta) \frac{\partial c_i}{\partial \eta} = 2\xi \frac{\partial f}{\partial \eta} \frac{\partial c_i}{\partial \xi} \qquad (i = 1, \ldots, N) \tag{3.5}$$

Stefan-Maxwell equations (1.4) in these variables are

$$-l \frac{\partial c_i}{\partial \eta} = X_i \sum_{j=1}^{N} x_j S_{ij} + c_i \sum_{j=1}^{N} A_{ij} X_j \qquad (i = 1, \ldots, N), \qquad l = \frac{\mu\rho}{\mu_w \rho_w} \tag{3.6}$$

where

$$A_{ij} = \sum_{k=1}^{N} \left(\frac{m}{m_j} - \frac{m}{m_k} \right) c_k S_{kj} - \frac{m}{m_j} S_{ij}, \quad S_{ij} = \frac{\mu}{\rho D_{ij}} \qquad (i, j = 1, \ldots, N) \tag{3.7}$$

If we replace derivatives $\partial c_i / \partial \eta$ in (3.5) by their expressions in (3.6), then the fluxes are given by the following system in partial derivatives:

$$-l \frac{\partial X_i}{\partial \eta} = \varphi X_i \sum_{j=1}^{N} x_j S_{ij} + \varphi c_i \sum_{j=1}^{N} A_{ij} X_j + 2\xi l \frac{\partial f}{\partial \eta} \frac{\partial c_i}{\partial \xi} \qquad (i = 1, \ldots, N) \tag{3.8}$$

Equations (3.6) and (3.8) with the boundary conditions for the concentrations (*) $c_i(\xi, 0) = c_{iw}(\xi)$, $c_i(\xi, \infty) = c_{ie} =$ const $(i = 1, \ldots, N)$, the initial conditions $c_i(0, \eta) = c_{i0}(\eta)$ $(i = 1, \ldots, N)$, and with the functions $\varphi(\xi, \eta)$ and $l(\xi, \eta)$ given, constitute a mixed problem for a system of $2(N-1)$ independent nonlinear equations. In general, solution of this problem is a prerequisite for calculating the generalized Schmidt numbers from the formulas

$$S_i = \frac{\mu}{\rho D_i} = -\frac{l}{X_i} \frac{\partial c_i}{\partial \eta} = \sum_{j=1}^{N} x_j S_{ij} + c_i \sum_{j=1}^{N} A_{ij} \frac{X_j}{X_i} \qquad (i = 1, \ldots, N) \tag{3.9}$$

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*) The conditions $c_i(\xi, \infty) =$ const hold for all blown-in components. They also hold for the dissociation products of the oncoming stream, provided that the flow is frozen at the outer edge of the boundary layer. They also hold with a high degree of accuracy when the flow is in equilibrium, since in this case concentrations of the dissociation products vary little with distance from the critical point along the body [11].

Theorem 3.1. If the mixture contains group M of components with equal diffusion properties (see (2.1)) whose concentrations are all equal to zero at infinity (or at the wall), then all the generalized Schmidt numbers relative to the concentration $z(\mathrm{M})$ and all relative diffusion fluxes $I(\mathrm{M})$, where

$$z(\mathrm{M}) = \frac{c(\mathrm{M})}{c_w(\mathrm{M})} \quad \text{or} \quad z(\mathrm{M}) = \frac{c(\mathrm{M})}{c_e(\mathrm{M})}, \quad I(\mathrm{M}) = \frac{X(\mathrm{M})}{c_w(\mathrm{M})} \quad \text{or} \quad I(\mathrm{M}) = \frac{X(\mathrm{M})}{c_e(\mathrm{M})}$$

are identically equal to each other for all these components over the whole thickness of the frozen boundary layer provided that the boundary values of the concentrations are kept constant.

Proof. If groups of components with equal diffusion properties exist, then by (2.2), Eqs. (3.6) and (3.8) and the corresponding boundary conditions for these components can be written as

$$-l\frac{\partial z(\mathrm{M})}{\partial\eta} = I(\mathrm{M})\sum_{j=1}^{N} x_j S(\mathrm{M}, j) + z(\mathrm{M})\sum_{j=1}^{N'}[A(\mathrm{M}, j) - A(\mathrm{M}, \mathrm{M})]X_j \qquad (3.10)$$

$$-l\frac{\partial I(\mathrm{M})}{\partial\eta} = \varphi I(\mathrm{M})\sum_{j=1}^{N} x_j S(\mathrm{M}, j) + \varphi z(\mathrm{M}) \times$$

$$\times \sum_{j=1}^{N'}[A(\mathrm{M}, j) - A(\mathrm{M}, \mathrm{M})]X_j + 2\xi l\frac{\partial f}{\partial\eta}\left[\frac{\partial z(\mathrm{M})}{\partial\xi} + \frac{z(\mathrm{M})}{c_w(\mathrm{M})}\frac{dc_w(\mathrm{M})}{d\xi}\right] \qquad (3.11)$$

$$z_{\mathrm{M}}(\xi, 0) = 1, \quad z_{\mathrm{M}}(\xi, \propto) = 0, \; z_{\mathrm{M}}(0, \eta) = z_0(\mathrm{M}) \qquad (3.12)$$

Formulation of problem (3.10) - (3.12) implies that for a frozen boundary layer and $dc_w(\mathrm{M})/d\xi = 0$ the equations for the relative concentrations and fluxes and the boundary conditions are identical for all components of the group M . Then from the assumption of the uniqueness of the uniqueness of the solution implies directly that

$$z_\alpha \equiv z_\beta, \quad I_\alpha \equiv I_\beta, \quad S_\alpha \equiv S_\beta\left(S_\alpha = -\frac{l}{I_\alpha}\frac{dz_\alpha}{d\eta}\right), \quad (\alpha, \beta = 1, \ldots, N_M) \qquad (3.13)$$

Q.E.D.

Corollary. If all components not belonging to the group M form another group A of components with equal diffusive properties and vanish (let us say) at the wall, then all the relative concentrations $z(\mathrm{A}) = c(\mathrm{A})/c_e(\mathrm{A})$ and all relative diffusive fluxes $I(\mathrm{A}) = X(\mathrm{A})/c_e(\mathrm{A})\,(\mathrm{A} = 1, \ldots, N')$ for these components are identically equal to each other for the frozen boundary layer and $c_e(\mathrm{A})$ – const; the generalized Schmidt numbers are equal to the binary Schmidt numbers

$$S(\mathrm{A}) = S(\mathrm{A}, \mathrm{M}) \; (A = 1, \ldots, N_{\mathrm{A}}) \qquad (3.14)$$

The first two assertions can be proved as above; the numbers $S(\mathrm{A})$ can be determined from system (3.10) written out for the group of components A

$$-l\frac{\partial z(\mathrm{A})}{\partial\eta} = I(\mathrm{A})\left[S(\mathrm{A}, \mathrm{M}) + (S(\mathrm{A}, \mathrm{A}) - S(\mathrm{A}, \mathrm{M}))\sum_{\mathrm{A}=1}^{N_{\mathrm{A}}} x(\mathrm{A})\right] +$$

$$+ z(\mathrm{A}) \frac{m}{m(\mathrm{A})} [S(\mathrm{A}, \mathrm{M}) - S(\mathrm{A}, \mathrm{A})] \sum_{\mathrm{A}=1}^{N_\mathrm{A}} X(\mathrm{A}) (\mathrm{A} = 1, \ldots, N_\mathrm{A}), \quad N_\mathrm{A} = N - N_\mathrm{M} \qquad (3.15)$$

Recalling (3.13), we can write

$$\sum_{\mathrm{A}=1}^{N_\mathrm{A}} X(\mathrm{A}) = I_\mathrm{A} \sum_{\mathrm{A}=1}^{N_\mathrm{A}} c_e(\mathrm{A}), \qquad z(\mathrm{A}) \frac{m}{m(\mathrm{A})} \sum_{\mathrm{A}=1}^{N_\mathrm{A}} X_\mathrm{A} = I(\mathrm{A}) \sum_{\mathrm{A}=1}^{N_\mathrm{A}} x(\mathrm{A}) \qquad (3.16)$$

This together with (3.15) implies statement (3.14),

$$S(\mathrm{A}) = -\frac{l}{I(A)} \frac{\partial z(A)}{\partial \eta} = S(\mathrm{A}, \mathrm{M}) \qquad (\mathrm{A} = 1, \ldots, N_\mathrm{A}) \qquad (3.17)$$

Theorem 3.2. If the whole mixture can be separated into two groups of components A and M, each group possessing equal diffusion properties within itself, then the necessary and sufficient condition for the diffusion of such a mixture to be describable in terms of a single binary diffusion coefficient $D(\mathrm{A}, \mathrm{M})$ is that these components diffuse into each other, and that the boundary values of the concentrations be constant.

To prove this we make use of equations (3.11), which in the case of just two groups of components can be written as

$$-l \frac{\partial c(\mathrm{M})}{\partial \eta} = X(\mathrm{M}) \left[S(\mathrm{A}, M) + (S(\mathrm{M}, \mathrm{M}) - S(\mathrm{A}, \mathrm{M})) \sum_{\mathrm{M}=1}^{N_m} x(\mathrm{M}) \right] +$$

$$+ c(\mathrm{M}) \frac{m}{m(\mathrm{M})} [S(\mathrm{A}, \mathrm{M}) - S(\mathrm{M}, \mathrm{M})] \sum_{\mathrm{M}=1}^{N_\mathrm{M}} X(M) \qquad (3.18)$$

From this it follows at once that if all components belonging to the group M satisfy the boundary conditions $c_e(\mathrm{M}) = 0$ $(\mathrm{M} = 1, \ldots, N_\mathrm{M})$ (boundary conditions $c_w(\mathrm{M}) = 0$ $(\mathrm{M} = 1, \ldots, N_\mathrm{M})$ need not be included here, since they are already satisfied by all the components of A), then

$$c(\mathrm{M}) \frac{m}{m(M)} \sum_{\mathrm{M}=1}^{N_\mathrm{M}} X(\mathrm{M}) = c(\mathrm{M}) \frac{m}{m(\mathrm{M})} I(\mathrm{M}) \sum_{\mathrm{M}=1}^{N_\mathrm{M}} c_w(\mathrm{M}) = c_w(\mathrm{M}) I(\mathrm{M}) \sum_{\mathrm{M}=1}^{N_\mathrm{M}} x(\mathrm{M}) \qquad (3.19)$$

which on substitution into (3.18) yields

$$S(\mathrm{M}) = -\frac{l}{I(\mathrm{M})} \frac{\partial z(\mathrm{M})}{\partial \eta} = S(\mathrm{A}, \mathrm{M}) \qquad (3.20)$$

Similarly, for the components of the Group A we have

$$D(\mathrm{A}) \equiv D(\mathrm{M}) = D(\mathrm{A}, \mathrm{M}) \qquad (3.21)$$

If even one of the components of the group M fails to satisfy the condition $c_e(\mathrm{M}) = 0$ (this can happen in the case of the component N_2 in a dissociated air stream), then, denoting this component symbolically by N_2, we obtain from (3.18)

$$S_{\mathrm{N}_2} = -\frac{l}{X(\mathrm{N}_2)} \frac{\partial c(\mathrm{N}_2)}{\partial \eta} = S(\mathrm{A}, \mathrm{M}) +$$
$$+ \frac{m}{m(\mathrm{M})} [S(\mathrm{M}, \mathrm{M}) - S(\mathrm{A}, \mathrm{M})] (1 - c_w(\mathrm{N}_2)) (x(M) - c(\mathrm{N}_2) \frac{I(\mathrm{M})}{X(\mathrm{N}_2)}. \qquad (3.22)$$

From this we see that $S(\mathrm{N}_2) \neq S(\mathrm{A}, \mathrm{M})$. When $C_e(\mathrm{N}_2) \neq 0$ we infer from (3.22) that the condition (3.21) is necessary for interdiffuion.

Corollary. If n ($n \leqslant N-2$) or $N-1$ or N components in such a two-group mixture become zero neither at the wall nor at the outer edge of the boundary layer, then in general we have, $n+2$ (or $N-1$ and N, respecitvely) distinct effective diffusion coefficients. At the same time we have only three distinct binary diffusion coefficients, namely D (A, A), D (A, M), and D (M, M). This is due to the fact that the effective diffusion coefficients for such components depend on the values of the ratio c_{iw}/c_{ie}. This general case does not occur in the theory of heat transfer and mass ablation either in air or in planetary atmospheric streams, nor does it arise in the majority of combustion product streams.

Indeed, in determining the heat flux from a dissociating gas of arbitrary chemical composition we find that the diffusion fluxes of the initial components of the incident flow at the wall can be expressed, by virtue of the law of conservation of the chemical elements, in terms of the diffusion fluxes of the dissociation products [4], so that the latter only require knowledge of the number S_i But all these components satisfy the boundary conditions $c_{iw} = 0$, i.e. S_i can be computed for them (see Sects. 4–6). If these components are similar atoms, then (3.21) will hold for them. In determining the rate of ablation of disintegrating plastics we find that in air the two conditions $c_w(\mathrm{N}_2) \neq 0$ and $c_e(\mathrm{N}_2) \neq 0$ can be simultaneously satisfied for N_2 only. However, since a single component can always be omitted from considerations, the need to calculate $S(\mathrm{N}_2)$ is thus obviated.

4. The authors of [1,11] assumed that the corresponding Schmidt numbers S_i are positive within the boundary layer in order to establish a general analogy between the mass transfer coefficients both for selfsimilar and for nonselfsimilar solutions of equations of a multicomponent boundary layer in the case where only heterogeneous reactions of the type

$$\left(\frac{J_i}{J_j}\right)_w = \frac{\Delta c_i}{\Delta c_j} \left(\frac{D_i}{D_j}\right)_w^{\varkappa} = \frac{\Delta c_i}{\Delta c_j} \left(\frac{S_j}{S_i}\right)_w^{\varkappa}, \quad \Delta c_i = c_{ie} - c_{iw} \quad (i = 1, \ldots, N) \qquad (4.1)$$

occur. Here exponent $\varkappa$ varies from e.g. 0.5 to 2 (moderate blow-in intensities) when the temperature factors are not too small ($T_w/T_e > 0.1$) ; its value depends on the temperature factor, the blow-in intensity, the values of the generalized Schmidt numbers at the wall, the pressure gradient along the surface of the solid, and the concentration gradients at the edge of the boundary layer. It is remarkable, however, that the effective diffusion coefficients at the wall obtained below by means of (4.1), are practically independent of $\varkappa$ ($0.5 \lesssim \varkappa \lesssim 2$).

Let us first compute D_{iw} for weak blow-in. We find that $\varphi(\xi, 0) = 0.2$ to 0.6, when $\varkappa \approx 1$. On the other hand, when $\varkappa = 1$, then the solution for D_{iw} can be obtained very simply and without any restrictions due to the diffusive properties of the components in the mixture. Inserting (4.1) with $\varkappa = 1$ into (1.6), we obtain the following linear algebraic system of equations defining $S_{iw}^{-1} \sim D_{iw}$:

$$\sum_{j=1}^{N} \frac{a_{ij}}{S_{jw}} = 1 \qquad (i = 1, \ldots, N) \tag{4.2}$$

where

$$a_{ii} = \sum_{j \neq i}^{N} (x_i c_j - x_j c_i + x_j) S_{ij} \qquad\qquad a_{ij} = \left[\sum_{k=1}^{N} (x_j c_k - x_k c_j) S_{kj} - x_j S_{ij}\right] \frac{\Delta c_j}{\Delta c_i} \frac{c_i}{c_j}$$

It should be kept in mind that the coefficients a_{ij} $(i, j = 1, \ldots, N)$ should be computed under the conditions at the wall. The solution of (4.2) is

$$\frac{1}{S_{iw}} = \left(\frac{\rho D_i}{\mu}\right)_w = \frac{1}{\operatorname{Det} \| a_{kl} \|} \sum_{j=1}^{N} A_{ji}^{*} \qquad (i = 1, \ldots, N) \tag{4.3}$$

where A_{ji}^{*} is the algebraic complement of the element a_{ji} of the determinant $\operatorname{Det} \| a_{kl} \|$. From (4.3) it follows that if $\Delta c_i \to 0$ for some component, then the corresponding S_{iw} may become $\pm \infty$. We have, however, excluded this case (see Sect. 3). It follows therefore that the expressions for a_{ij} are finite for the remaining components, and additional considerations indicate that all S_{iw} will also be finite (see below). If the given mixture contains a group of components with similar (equal) diffusion properties (see Sect. 2), then, for these components S_{iw} can be written at once (using (2.2) and (4.1) with $\varkappa = 1$) as

$$S_w^{-1}(\mathrm{M}) = \left[1 + \sum_{j=1}^{N'} (A(\mathrm{M}, \mathrm{M}) - A(\mathrm{M}, j)) \frac{\Delta c_j}{\Delta c(\mathrm{M})} \frac{c(\mathrm{M})}{S_j}\right] \left(\sum_{j=1}^{N} x_j S_{ij}\right)^{-1} \tag{4.4}$$

where S_{iw} $(i = 1, \ldots, N')$ for the remaining components must be obtained from the following system of lower order $N' = N - N_{\mathrm{M}}$

$$\frac{1}{S_i} \left(\sum_{j=1}^{N} x_j S_{ij}\right)_w + \sum_{j=1}^{N'} (A_{ij} - A(i, \mathrm{M})) \frac{\Delta c_j}{\Delta c_i} \frac{c_i}{c_j} = 1 \qquad (i = 1, \ldots, N') \tag{4.5}$$

In particular, if all these components satisfy the boundary conditions $c_{iw} = 0$ $(i = 1, \ldots, N')$, then (4.5) immediately yields

$$S_{iw} = \sum_{\mathrm{M}=1}^{N_{\mathrm{M}}} x(\mathrm{M}) S(i, \mathrm{M}) \qquad (i = 1, \ldots, N') \tag{4.6}$$

Inserting (4.6) into (4.4) we obtain the remaining generalized Schmidt numbers $S(\mathrm{M})$ $(\mathrm{M} = 1, \ldots, N_{\mathrm{M}})$.

In conclusion we note that the following assertion can be proved readily: if the mixture can be divided into several groups of components with equal diffusive properties within each group and if the components of each group satisfy similar boundary conditions, i.e. if $c_w(\mathrm{M}) / \Delta c(\mathrm{M}) = 0$ or -1, then the effective diffusion coefficients at the wall are equal within each group. Using the results of Sect. 3, we can extend this theorem to the whole of the boundary-layer region (*)

$$(0 \leqslant \xi < \infty, \quad 0 < \eta < \infty).$$

5. When $\varkappa$ lies in the range $(0.5 \lesssim \varkappa \lesssim 2)$, the coefficients D_{iw} in the generalized analogy (4.1) should be obtained from the transcendental equations, whose solution is, in the general case, awkward. Nevertheless, in the case of mixtures appearing in the boundary layer of a thermoplastic burning in an air or CO_2 stream, a group of components with similar diffusive properties exists, e.g. N_2, CO, HCN, C_2H_2, which, together with O, N and C atoms, consitutes the main bulk of the gas in the boundary layer [2]. Numerous other components such as H, Mg, Si, H_2, H_2O, SiO, SiO_2, MgO, CO_2, SiC, SiC_2, Si_2C, SiN, CH, CH_2, CH_3, CH_4, as well as other hydrocarbons and radicals, constitute a minor part of the mixture (less than 20 to 25%). This remarkable property of such mixtures enables us to obtain an approximate (analytic) expression for the generalized Schmidt numbers at the wall for arbitrary $\varkappa$ and an arbitrary number of components in the mixture.

Let us therefore consider mixtures satisfying the following conditions:

1. A group of components (index M) with similar (equal) diffusion properties exists, and constitutes the main bulk of the gas at the wall. All the components of this group, with the possible exception of one, satisfy the boundary conditions

$$c_M(\xi, \infty) = c_e(M) = 0 \qquad (M = 1, \ldots, N_M) \tag{5.1}$$

2. Let us also assume, for the sake of completeness, that there is a second group of components (index A) with similar (equal) diffusion properties whose components (e.g. O, N) satisfy the boundary conditions

$$c_A(\xi, 0) = c_w(A) = 0 \qquad (A = 1, \ldots, N_A) \tag{5.2}$$

3. The remaining components, which are present in small amounts, satisfy the boundary conditions

$$c_i(\xi, \infty) = c_{ie} = 0 \qquad (i \neq A, M) \tag{5.3}$$

Then, taking into account (4.1) and the conditions (5.1) - (5.3), we find from (2.2) that at the wall (the subscript w is omitted)

$$\frac{1}{D(A)} = B(A) \equiv \sum_{j=1}^{N} \frac{x_j}{D(A, j)} = \frac{1 + \varepsilon^{(A)}}{D(A, M)} \tag{5.4}$$

$$\frac{1}{D_i} = B_i + \sum_{j \neq A, M, i} B_{ij} c_j \left(\frac{D_j}{D_i}\right)^{\varkappa} - B(i, A)\, c_e^*(A) \left(\frac{D(A)}{D(M)}\right)^{\varkappa} \qquad (i \neq A) \tag{5.5}$$

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*) Non-selfsimilar flows require an additional condition, i.e. that the concentration gradients at the borders of the boundary layer be equal. All combustion products satisfy this condition.

where

$$B_i = \frac{1}{D(i, M)}\left(1 + \varepsilon^{(i)} + \frac{m}{m(M)} \varepsilon_i c_i,\right) \quad B_{ij} = \frac{m}{m(M)} \frac{1}{D(i, M)} (b_{ij} + \varepsilon_{ij})$$

$$\varepsilon^{(A)} = \sum_{k \neq A, M} \left(\frac{(D(AM)}{D(Ak)} - 1\right) x_k, \qquad \varepsilon^{(i)} = \sum_{k \neq A, M, i} \left(\frac{D(i, M)}{D(i, k)} - 1\right) x_k$$

$$b_{ij} = 1 - \frac{D(i, M)}{D(j, M)} + \frac{m(M)}{m_j}\left(\frac{D(i, M)}{D(j, M)} - \frac{D(i, M)}{D(i, j)}\right) \tag{5.6}$$

$$\varepsilon_{ij} = \sum_{k \neq A, M}\left[\left(\frac{m(M)}{m_j} - \frac{m(M)}{m_k}\right)\frac{D(i, M)}{D(k, j)} - \left(1 - \frac{m(M)}{m_k}\right)\frac{D(i, M)}{D(k, M)} - \right.$$

$$\left. - \left(\frac{m(M)}{m_j} - 1\right)\frac{D(i, M)}{D(M, j)}\right] c_k \equiv \frac{D(i, M)}{D(j, M)} \varepsilon_j, \qquad c_e^*(A) = \sum_{A=1}^{N_A} c_e(A)$$

From (5.4) it follows that the effective coefficients at the wall for the components belonging to Group **A** can be obtained explicitly and independently of the remaining coefficients. Similarly, if the concentrations of any of the components belonging to the Group M (e.g. O_2 or NO) are equal to zero at the wall, then (2.2) immediately yields the following expression for these components:

$$D(NO) = D(O_2) = D(M, M)(1 + \varepsilon^M)^{-1}$$

These components need not satisfy boundary conditions (5.1). For mixtures appearing in the boundary layer at the surface of the thermoplastics disintegrating in air or CO_2, we have $|\varepsilon^{(A)}|$, $|\varepsilon^{(M)}|$, $|\varepsilon^{(i)}|$, $|\varepsilon_j| \ll 1$ and, as a rule, $|\varepsilon_j| \leqslant 0.05 - 0.10\,|b_{ij}|$. Thus the solution of the following system (the subscript w is omitted):

$$\frac{1}{D_i^{(0)}} \doteq \frac{1}{D(i, M)} - \left(\frac{1}{D(i, M)} + \frac{1}{D(A, M)}\right) - \frac{2}{D(i, A)}\left(\frac{D(A, M)}{D_i^{(0)}}\right)^{\varkappa} c_e^*(A) \quad (i \neq A) \tag{5.7}$$

can serve as the zeroth approximation of the coefficients D_{iw} for the mixtures considered, since in the zeroth approximation we have

$$m / m(M) = 1, \qquad D^{(0)}(A) = D(A, M), \qquad \frac{m}{m(A)} = 2$$

With $\varkappa = 1$ the solution of (5.7) is

$$D_i^{(0)} = D(i, M)\left[1 + \left(1 + \frac{D(A, M)}{D(i, M)} - 2\frac{D(A, M)}{D(i, A)} c_e^*(A)\right]\right. \quad (i \neq A) \tag{5.8}$$

The solution of (5.7) with $\varkappa \neq 1$ was obtained for certain components by numerical methods; the results appear in Table 1 (values in parentheses). The table shows that the effective diffusion coefficients are weakly dependent on $\varkappa$ for all components except H_2, i.e. that the D_{iw} depend chiefly on the diffusion properties of the components when the concentration $c_e^*(A)$ of the Group A of components at the outer edge of the boundary layer is given.

Table 1

	$\frac{D(\mathrm{M},\,\mathrm{M})}{D^{(0)}(\mathrm{M})}$			$\frac{D(\mathrm{SiO_2},\,\mathrm{M})}{D^{(0)}(\mathrm{SiO_2})}$		$\frac{D(\mathrm{H_2},\,\mathrm{M})}{D^{(0)}(\mathrm{H_2})}$	
$c_e^*(\mathrm{A})$	0	0.5	1	0.5	1	0.5	1
$\varkappa = 0.6$	1 (1)	0.843 (0.838)	0.712 (0.712)	0.909 (0.908)	0.814 (0.815)	0.548 (0.597)	0.215 (0.384)
$\varkappa = 1$	1 (1)	0.829 (0.829)	0.712 (0.712)	0.881 (0.881)	0.789 (0.789)	0.729 (0.729)	0.573 (0.573)
$\varkappa = 1.5$	1 (1)	0.819 (0.819)	0.712 (0.712)	0.834 (0.845)	0.719 (0.743)	0.854 (0.826)	0.799 (0.718)
$\varkappa = 2$	1 (1)	0.803 (0.807)	0.712 (0.712)	0.769 (0.805)	0.628 (0.703)	0.924 (0.886)	0.906 (0.770)

Consequently, a satisfactory solution of (5.7) can be obtained for any $\varkappa$ in the range $(0.5 \leqslant \varkappa \leqslant 2)$ if the solution of (5.8) is substituted into the right side of (5.7). This yields the following approximate solution:

$$\frac{D(i,\,\mathrm{M})}{D_i^{(0)}} = 1 - \frac{\left(1 + \frac{D(i,\,\mathrm{M})}{D(\mathrm{A},\,\mathrm{M})} - 2\,\frac{D(i,\,\mathrm{M})}{D(i,\,\mathrm{A})}\right)\left(\frac{D(\mathrm{A},\,\mathrm{M})}{D(i,\,\mathrm{M})}\right)^{\varkappa} c_e^*(\mathrm{A})}{\left[1 + \left(1 + \frac{D(\mathrm{A},\,\mathrm{M})}{D(i,\,\mathrm{M})} - 2\,\frac{D(\mathrm{A},\,\mathrm{M})}{D(i,\,\mathrm{A})}\right) c_e^*(\mathrm{A})\right]^{\varkappa}} \quad (i \neq \mathrm{A}) \qquad (5.9)$$

A comparison of approximate solution (5.9) with the exact one (values in parentheses) is given in Table 1. We see that the basic effective diffusion coefficients $D_w(\mathrm{M})$ are obtainable from (5.9) with an error smaller than 0.5%, while $D(\mathrm{H_2})$ is obtainable from (5.9) with the same accuracy only for $\varkappa = 1$. For this reason, the values of $D(\mathrm{H_2})$ should be taken from the Table if $\varkappa$ differs markedly from unity. Let us now insert the zeroth approximation (5.9) into the terms under this summation sign in (5.5) (this sum contains the small factors $B_{ij}c_j$). Neglecting the squares of small order terms $\varepsilon(\mathrm{M},\, j)\, c_j$, $\varepsilon_{ij} c_j$ $(j \neq \mathrm{A},\, \mathrm{M})$ we obtain

$$\frac{D(i,\,M)}{D_i} = 1 + \varepsilon^{(i)} + \sum{}' - \frac{m}{m(\mathrm{M})}\,[b(i,\,\mathrm{A}) + \varepsilon(i,\,\mathrm{A})]\left(\frac{D(\mathrm{A})}{D_i}\right)^{\varkappa} c_e^*(\mathrm{A}) \quad (i \neq \mathrm{A}) \qquad (5.10)$$

where

$$\sum{}' = \sum_{j \neq \mathrm{A},\,\mathrm{M},\,i} \frac{m}{m(\mathrm{M})}\, b_{ij} \left(\frac{D_j}{D_i^{(0)}}\right)^{\varkappa} c_j$$

The solution of this system for $\varkappa \neq 1$ can be obtained as before

$$\frac{D(i,\,\mathrm{M})}{D_i} = 1 + \varepsilon^{(i)} + \sum{}' - \frac{m}{m(\mathrm{M})}\,[b(i,\,\mathrm{A}) + \varepsilon(i,\,\mathrm{A})]\left(\frac{D(\mathrm{A})}{D(i,\,\mathrm{M})}\right)^{\varkappa}\left((1 + \varepsilon^{(i)} + \sum{}'\right)^{\varkappa} \times$$
$$\times \left[1 + \frac{m}{m(\mathrm{M})}\,(b(i,\,\mathrm{A}) + \varepsilon(i,\,\mathrm{A}))\,\frac{D(\mathrm{A})}{D(i,\,\mathrm{M})}\, c_e^*(\mathrm{A})\right]^{-\varkappa} \qquad (5.11)$$

When $\varkappa \neq 1$, the solution given by (5.11) entails an error of less then 5% for all components except for the low-molecular-weight H_2. When $\varkappa$ differs appreciably from unity, the effective diffusion coefficient for H_2 should be obtained using the following transcendental equation:

$$\frac{D(H_2M)}{D(H_2)} = 1 + e^{(H_2)} + \sum_{j \neq A, M, i}^{N} \frac{m}{m(M)} b(H_2, j) \left(\frac{D_j^{(0)}}{D^{(0)}(H_2)} \right)^{\varkappa} c_j - $$
$$- \frac{m}{m(M)} (b(H_2A) + e(H_2, A)) \left(\frac{D(A)}{D(H_2)} \right)^{\varkappa} c_e^*(A) \qquad (5.12)$$

Analysing the solution of (5.11) we find that the presence of any component not belonging to Group M will not affect significantly the effective diffusion coefficients if and only if either the diffusion properties of this component are similar to the diffusion properties of Group M (e.g. $D(i, M) / D(i, SiO), D(i, M) / D(i, CO_2) \approx 1.2$), or the concentration of this component is low (e.g. $c(H_2) < 0.01 \div 0.02$).

We find that these conditions are almost always fulfilled in the case of a high-temperature boundary layer at the surface of a disintegrating plastic. An appreciable influence on the value of D_{iw} is exerted by the diffusive counterflow of atoms towards the wall. This dependence is expressed in (5.11) in terms of the degree of dissociation of the outer flow $c_e^*(A) = c_e(0) + c_e(N)$. It follows that to within an error of $\pm 5\%$ (provided that $c_w(M_1) + c_w(M_2) + \ldots c_w(M_{N_M}) \gtrsim 0.7$) we can obtain the effective diffusion coefficients at the wall using the formulas (5.9) where we take N_2 as our M

We note that the error present in (5.9) depends on the accuracy with which the binary diffusion coefficients (gas kinetic potential parameters of molecular interaction) are known.

6. Let us turn our attention to the behavior of the generalized Schmidt numbers (effective diffusion coefficients) at the outer edge of the boundary layer. As $\eta \to \infty$ the last term in (3.8) tens to zero faster than the penultimate term (see below). Therefore the behavior of the solution for large η (i.e. $\varphi(\xi, \eta) \to a(\xi) + \eta \sim \eta$) as $\eta \to \infty$) should be studied with the help of the following system of equations

$$-l \frac{\partial X_i}{\partial \eta} = \varphi X_i \sum_{j=1}^{N} x_j S_{ij} + \varphi c_i \sum_{j=1}^{N} A_{ij} X_j, \qquad \frac{\partial X_i}{\partial \eta} - \varphi \frac{\partial c_i}{\partial \eta} = 0 \quad (i = 1, \ldots, N) \qquad (6.1)$$

For large η the asymptotic solution of (6.1) is

$$X_i = \gamma_i e^{-\lambda \eta^*}, \quad c_i = c_{ie} + \frac{\gamma_i}{\eta^*} e^{-\lambda \eta^*} \qquad (i = 1, \ldots, N) \qquad (6.2)$$

$$d\eta^* = \frac{\varphi d\eta}{l} \; (\eta^* \to \infty \quad \text{as} \quad \eta \to \infty) \qquad (6.3)$$

where γ_i is an unknown constant and the parameter $\lambda > 0$. The latter follows from the physical condition, since all the fluxes X_i should tend to zero as $\eta \to \infty$, or from a more detailed investigation of the characteristic equation for λ obtained by substituting the solution (6.2) into the first system of (6.1).

For all components vanishing at infinity, e.g. for all combustion products in an air stream, $c_{ie} = 0$. Then, by (6.2) we obtain from (3.9) the following expression for the generalized Schmidt numbers:

$$S_{i\infty} = \lambda = \lambda_i = \left(\sum_{j=1}^{N} x_j S_{ij} \right)_\infty \qquad (c_{ie} = 0) \tag{6.4}$$

Let us denote the smallest of the generalized Schmidt numbers given by (6.4), by $S_\infty(H_2)$. As a rule, this will be the Schmidt number associated with the components of smallest molecular weight. By (6.4), provided that only atoms and molecules are present at the outer edge, it is equal to

$$S_\infty(H_2) = S_\infty(A, H_2) \left[1 + \frac{1 - c_e^*(A)}{1 + c_e^*(A)} \left(\frac{S(H_2, M)}{S(H_2 A)} - 1 \right)_\infty \right] \tag{6.5}$$

Then the atomic and molecular fluxes, together with the $X(H_2)$ flux, will be the only remaining ones for the components vanishing at infinity in the system (6.1) as $\eta \to \infty$. In order to simplify the argument to follow, we limit ourselves to the practically important case where a Group A of atoms exists at infinity, their concentration at the wall being zero, and where there are O_2 and N_2 molecules which have equal diffusion properties and whose concentrations at the wall can assume arbitrary values (the case of an arbitrary composition with $\eta \to \infty$, is discussed below). Then the system (6.1) becomes

$$-\frac{\partial X_i}{\partial \eta^*} = X_i \left[x_e^*(A) S(i, A) + (1 - x_e^*(A)) S(i, M) \right] + {}$$

$$+ c_{ie} \sum_{j = A, O_2, N_2} (A_{ij} - A(i, H_2)) X_j \tag{6.6}$$

$$x_e^*(A) = \sum_{A=1}^{N_A} x_e(A) \quad (i = A, O_2, N_2) \tag{6.7}$$

as $\eta^* \to \infty$.

If the solution of (6.6) is sought in the form (6.2), then the parameter λ is given by a third-degree characteristic equation (the derivation is omitted) whose roots are

$$\lambda_1 = S_\infty(A, H_2) \left[1 + \frac{1 - c_e^*(A)}{1 + c_e^*(A)} \left(\frac{S(M, H_2)}{S(A, H_2)} - 1 \right) \right]_\infty, \quad \lambda_2 = S_\infty(A, M)$$

$$\lambda_3 = S_\infty(A, M) \left[1 + \frac{1 - c_e^*(A)}{1 + c_e^*(A)} \left(\frac{S(M, M)}{S(A, M)} - 1 \right) \right]_\infty \tag{6.8}$$

It is easily seen that $\lambda_1 < \lambda_2 < \lambda_3$, so that only the term contining the smallest λ will remain in the general solution for the fluxes as $\eta^* \to \infty$. Then, by (6.4), the Schmidt numbers at infinity for all components not vanishing at infinity, i.e. for $S(A)$, $S(O_2)$, $S(N_2)$, are equal to λ_1, i.e. to the effective Schmidt number of the lightest component diffusing from the wall and vanishing at the exterior border of the boundary layer (see formula 6.5)).

Generalizing this result, we obtain the following theorem.

Theorem 6.1. If N_∞ components exist at the outer edge of the boundary layer and there is a light component (e.g. H_2) at the wall, such that its binary diffusion coefficients exceed all the remaining coefficients in value, i.e. $D(\mathrm{H}_2, i) > D_{ij}$ $(i, j = 1, \ldots, N_{\infty})$ and if this light component vanishes at infinity, then all generalized Schmidt numbers (coefficients D_i) for these components are equal and given by (6.4) as $\eta \to \infty$.

Corollary. If the lightest component is among the components not vanishing at infinity, then the effective diffusion coefficients for these components at infinity are equal to the smallest root of a characteristic equation which can be obtained from (6.1) if its solution is sought in the form of (6.2).

Comparing (5.8) or (5.9) with (6.4), we find that the generalized Schmidt numbers at the wall and at infinity are almost equal, except in the case of $S(\mathrm{H}_2)$. Additional numerical solutions given in [11] show that $S_i / S(i, \mathrm{A})$ have practically no extremum within the boundary layer, i.e. that the generalized Schmidt numbers vary as the binary Schmidt numbers for the given boundary values of the concentrations. In the case of atoms, the Schmidt numbers vary from $S^{(0)}{}_{iw} \approx S(\mathrm{A}, \mathrm{M})$ to the values given by (6.5).

Finally, using the properties of the system (6.1) and (6.2) we can easily prove the statement that if the concentration of any component is zero at the wall or at the outer edge of the boundary layer, then the corresponding generalized Schmidt number is positive within the boundary layer, provided that the blow-in intensity is sufficiently small.

We conclude that for real mixtures appearing in the process of combustion of thermoplastics in a dissociated air stream it is sufficient to introduce the following five distinct effective diffusion coefficients: $D(\mathrm{M})(\mathrm{M} = \mathrm{CO}, \mathrm{CN}, \mathrm{HCN}, \mathrm{C}_2, \mathrm{C}_3)$, $D(\mathrm{O}_2) = D(\mathrm{NO})$, $D(\mathrm{SiO}) \approx D(\mathrm{CO}_2)$, $D(\mathrm{H}_2)$, in the frozen boundary layer. Expressions for these coefficients can be obtained from the general formulas given above.

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