DEFINITION AND CALCULATION OF EFFECTIVE AMBIPOLAR DIFFUSION COEFFICIENTS FOR A LAMINAR MULTICOMPONENT IONIZED BOUNDARY LAYER

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Effective diffusion coefficients substantially facilitate solution of detailed problems for multicomponent boundary layers with frozen-in reactions in the flow and heterogeneous reactions at the wall; they provide physically lucid correlation formulas and final equations for the convective heat flow to the undamaged solid as well as for the mass loss rate or effective erosion enthalpy if the walls are subject to thermochemical attack [1-5].

Here we extend the concept of effective diffusion coefficients to a partly ionized frozen-in multicomponent boundary layer with arbitrary reactions at the wall. We also derive the effective ambipolar diffusion coefficients, which allow one to relate the diffusion fluxes to the concentration gradients in the generalized form of Fick's law. These are represented in a form analogous to that for the effective diffusion coefficients in neutral gases, which substantially facilitates the elucidation of complicated diffusion processes in a multicomponent flow in the presence of charged components.

We examine in detail the important particular case of electrons and ions with charges n and n + 1; the above types of effective diffusion coefficient are calculated exactly in explicit form without reference to the boundary conditions. The formulas are new for the general case (n arbitrary).

We also calculate exactly the effective ambipolar Schmidt numbers for the outer boundary via the asymptotic form for the solutions to the boundary-layer equations.

The sufficient conditions are derived for identity in the profiles for the relative concentrations, diffusion fluxes, and effective ambipolar Schmidt numbers in a direction perpendicular to the boundary layer. The general analogy between mass-transfer coefficients is used to convert the calculation of the effective ambipolar coefficients at the wall to solution of a system of algebraic equations with and without influx through the wall. This system is solved approximately for typical mixtures produced at the surfaces of phenol-formaldehyde resins in ionized flows in the atmospheres of the earth and the other planets. Considerable use is made of the results from [3, 5].

1. If there are no external electromagnetic forces and if we neglect the magnetic field induced by charge separation, we get the following system of equations for a partly ionized frozen-in single-temperature asymptotically thin two-dimensional stationary-laminar boundary layer:

$$\rho\left(u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}\right)=-\frac{\partial p}{\partial x}+\frac{\partial}{\partial y}\left(\mu\frac{\partial u}{\partial y}\right),\quad 0=-\frac{\partial p}{\partial y}+qE$$

$$\frac{\partial}{\partial x}(\rho u r^{\nu})+\frac{\partial}{\partial y}(\rho v r^{\nu})=0,\quad \rho\left(u\frac{\partial c_i}{\partial x}+v\frac{\partial c_i}{\partial y}\right)+\frac{\partial J_i}{\partial y}=0$$

$$\rho c_p\left(u\frac{\partial T}{\partial x}+v\frac{\partial T}{\partial y}\right)=\frac{\partial}{\partial y}\left[\lambda\frac{\partial T}{\partial y}-R_A T\sum_{j=1}^{N}\sum_{k=1}^{N}\frac{x_j D_k}{m_k}a_{kj}\left(\frac{J_k}{\rho_k}-\frac{J_j}{\rho_j}\right)\right]$$

$$-\sum_{j=1}^{N}J_j c_{pj}\frac{\partial T}{\partial y}+u\frac{\partial p}{\partial x}+v\frac{\partial p}{\partial y}+\mu\left(\frac{\partial u}{\partial y}\right)^2+JE \tag{1.1}$$

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$$\rho \frac{\partial x_i}{\partial y} = \sum_{j=1}^{N} \frac{m^2}{m_i m_j} a_{ij} (c_i J_j - c_j J_i) + \frac{\rho x_i}{kT} \left(e_i - \frac{m_i q}{\rho N_0} \right) E$$
$$+ \frac{\partial \ln T}{\partial y} \sum_{j=1}^{N} \frac{m^2}{m_i m_j} a_{ij} (c_i D_j{}^T - c_j D_i{}^T) \quad (i = 1, \ldots, N)$$
$$\frac{\partial E}{\partial y} = 4\pi q, \quad q = \rho \frac{N_0}{m} \sum_{j=1}^{N} x_j e_j, \quad J = N_0 \sum_{j=1}^{N} \frac{e_j}{m_j} J_j + qv = j + qv$$
$$\sum_{j=1}^{N} J_j = 0, \quad \sum_{j=1}^{N} c_j = \sum_{j=1}^{N} x_j = 1, \quad p = \rho \frac{R_A T}{m}, \quad m = \sum_{j=1}^{N} x_j m_j$$
$$x_i = \frac{n_i}{n}, \quad n = \sum_{j=1}^{N} n_j, \quad \mathrm{v} = \sum_{j=1}^{N} c_j \mathrm{v}_j, \quad c_i = \frac{m_i}{m} x_i, \quad c_p = \sum_{j=1}^{N} c_j c_{pj} \tag{1.2}$$

Here x and y are linear coordinates respectively along the surface and normal to it, u and v are the projections of the mean-mass velocity vector v on these axes, $\nu = 0$ (flow along a plane) or $\nu = 1$ (flow over an axially symmetric body), r(x) is the radius of the cross section of a body of rotation, c_i is the mass concentration of component i, whose molar concentration is x_i, J_i is the projection of the mass diffusion flux for that component on the y axis, n_i is the number of moles of that component in unit volume, n is the total number of moles in unit volume, v_i is the statistical mean speed of component i, whose molecular weight is m_i and whose charge is e_i, m is the mean molecular weight of the mixture, q is the space charge, E is the projection of the electric vector on the y axis, J is the same for the current-density vector, and j is the same for the current vector, R_A is the universal gas constant, N_0 is Avogadro's number, k is Boltzmann's constant, N is the number of components in the mixture, whose pressure, density, and temperature are p, ρ, and T, while μ is the viscosity, λ is the thermal conductivity, c_p is the mean specific heat, and D_i^T is the thermal-diffusion coefficient for component i. The precise expressions for the resistance coefficients a_{ij} are dependent on the law of particle interaction, and they are as follows when neutral particles interact in accordance with the Lennard-Jones potential (first approximation) [6]:

$$\frac{1}{a_{ij}} = [D_{ij}]_1 = \frac{3}{16} \left(\frac{2kT\,(m_i + m_j)}{\pi m_i m_j} \right)^{1/2} \frac{kT}{p} \frac{1}{\sigma_{ij}^2 \Omega_{ij}^{(1,1)*}(\tau_{ij})}$$
$$\sigma_{ij} = (\sigma_i + \sigma_j)/2, \qquad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}, \qquad \tau_{ij} = kT/\varepsilon_{ij} \tag{1.3}$$

where σ_i and ε_i are the gas-kinetic interaction parameters and $\Omega_{ij}{}^{(1,1)*}(\tau_{ij})$ is a known function [6] that is only slightly dependent on its argument for $\tau_{ij} > 3$.

The first approximation is as follows [7] when charged particles interact via the inverse-square law:

$$\frac{1}{a_{ij}} = [D_{ij}]_1 = \frac{3}{8} \left(\frac{2kT\,(m_i + m_j)}{\pi m_i m_j} \right)^{1/2} \frac{kT}{p} \left(\frac{kT}{e_i e_j} \right)^2 \frac{1}{\ln \Lambda_{ij}} \tag{1.4}$$

Here D_{ij} is the binary diffusion coefficient, and $\ln \Lambda_{ij}$ is the Coulomb logarithm. We do not need more accurate resistance coefficients in what follows.

System (1.1) contains 2N+6 equations for the 2N+6 unknown functions of u, v, p. ρ, T, E, c_i, and J_i. To this we add the usual boundary conditions and the initial conditions with respect to the x coordinate, which will not be given here.

We convert (1.1) to dimensionless variables and give only Poisson's equation:

$$\varepsilon^2 \frac{\partial \mathscr{E}}{\partial \eta} = \sum_{j=1}^{N} x_j e_j, \qquad E = E^* \mathscr{E}, \qquad y = \delta\eta, \qquad \varepsilon \sim \frac{d}{\delta}$$

Here E^* is the characteristic electric-field strength, δ is the thickness of the boundary layer, and ε is a small parameter proportional to the ratio of d (the Debye length) to δ. If (1.1) in dimensionless form is solved as series in ε, we get for the first terms in those series a system of equations that differ from those of (1.1) only in that we must put

$$q = q_0 = 0, \qquad \frac{\partial p}{\partial y} = 0, \qquad \frac{dp}{dx} = -\rho_e U_e \frac{dU_e}{dx}$$

Here ρ_e is the density at the outer edge of the boundary layer, while U_e is the longitudinal velocity there. This system (the external solution) is true outside the thin charged layer (for $\eta \gg d$), which is the region of ambipolar diffusion, and the solution for the latter (internal solution) must be linked up with the external solution in the space-charge region (if the particle mean-free path is much less than the Debye length) [8, 9].

Consider the case where there is no current at the wall. The diffusion equations in (1.1) then imply that $J \equiv 0$ across the boundary layer. We also assume that the wall is fairly cold and that complete recombination of the charged particles occurs there. We can then neglect the small change in charged-particle concentration in the space-charge region in deriving the heat flux, friction, and mass-transfer coefficient at the wall, and we can solve the problem in the ambipolar region by equating to zero the charged-particle concentrations at the wall. The other boundary conditions are as usual [4, 10]. We must link up the two solutions correctly if we are to find the distributions of the electric field and charged-particle concentrations in the charged layer, which has to be done when there is a finite current.

Then Poisson's equation is replaced in (1.1) by the following equation in order to solve the problem in the ambipolar region:

$$\sum_{j=1}^{N} x_j e_j = 0 \tag{1.5}$$

which will serve as the condition for eliminating the field from the Stefan-Maxwell equations:

$$\frac{\partial x_i}{\partial y} = \sum_{j=1}^{N} \frac{m^2 a_{ij}}{\rho m_i m_j} (c_i J_j - c_j J_i) + \frac{e_i x_i}{kT} E + \frac{\partial \ln T}{\partial y} \sum_{j=1}^{N} \frac{m^2 a_{ij}}{\rho m_i m_j} (c_i D_j^T - c_j D_i^T) \qquad (i = 1, \ldots, N) \tag{1.6}$$

It is more convenient to use Eqs. (1.6) in describing convective processes, putting these in terms of the gradients in the mass concentrations:

$$-\rho \frac{\partial c_i}{\partial y} = J_i \sum_{j=1}^{N} x_j a_{ij} + c_i \sum_{j=1}^{N} A_{ij} J_j - \rho \nu_i c_i E \mp \rho_i \left(\Sigma_i^T - \sum_{k=1}^{N} c_k \Sigma_k^T \right) \frac{\partial \ln T}{\partial y} \qquad (i = 1, \ldots, N) \tag{1.7}$$

$$A_{ij} = \sum_{k=1}^{N} \left(\frac{m}{m_j} - \frac{m}{m_k} \right) c_k a_{jk} - \frac{m}{m_j} a_{ij}, \qquad \nu_i = \left(e_i - \sum_{j=1}^{N} e_j c_j \right) \frac{1}{kT}$$

$$\Sigma_i^T = \sum_{j=1}^{N} x_j a_{ij} \left(\frac{D_j^T}{\rho_j} - \frac{D_i^T}{\rho_i} \right) \qquad (i, j = 1, \ldots, N) \tag{1.8}$$

It is convenient to have equations for the mass diffusion fluxes in terms of the electric-field strength and the gradients in the mass concentrations. If we solve (1.7) for the fluxes, which are then substituted into the diffusion equations in (1.1), we get a system of equations in partial derivatives that cannot be solved for the first derivatives. The coefficients in this system take the form of complicated determinants and are dependent on $N(N-1)/2$ resistance coefficients (binary diffusion coefficients). The final system is difficult to solve even by computer methods [4, 5], so we introduce the effective diffusion coefficients for the multicomponent ionized boundary layer as proposed in [1, 3] for the case of a mixture of neutral gases.

2. The effective diffusion coefficients are $D_i{}^*$ and D_i for molar (numerical) and mass descriptions of the diffusion, which we define in accordance with (1.6) and (1.7) as

$$\frac{1}{D_i^*} = \sum_{j=1}^{N} x_j a_{ij} \left(1 - \frac{x_i J_i^*}{x_j J_i} \right), \qquad J_i^* = n_i (v_i - v^*), \qquad v^* = \sum_{j=1}^{N} x_j v_j \tag{2.1}$$

$$\frac{1}{D_i} = \sum_{j=1}^{N} x_j a_{ij} + c_i \sum_{j=1}^{N} A_{ij} \frac{J_j}{J_i} \ (i = 1, \ldots, N) \tag{2.2}$$

Then (1.6) and (1.7) become respectively as follows:

$$J_i^* = -n D_i^* \frac{\partial x_i}{\partial y} + \mu_i^* n_i E + n D_i^* \frac{\partial \ln T}{\partial y} \sum_{j=1}^{N} \frac{m^2 a_{ij}}{\rho m_i m_j} (c_i D_j^T - c_j D_i^T),$$

$$\mu_i^* = \frac{e_i}{kT} D_i^* \qquad (i = 1, \ldots, N) \tag{2.3}$$

$$J_i = -\rho D_i \frac{\partial c_i}{\partial y} + \mu_i \rho_i E + \rho_i D_i \left(\Sigma_i{}^T - \sum_{k=1}^{N} c_k \Sigma_k{}^T\right) \frac{\partial \ln T}{\partial y}$$

$$\mu_i = \left(e_i - \sum_{j=1}^{N} c_j e_j\right) \frac{D_i}{kT} \qquad (i = 1, \ldots, N) \tag{2.4}$$

We call $\mu_i{}^*$ the mobility of charged particles of type i, and Einstein's equation relates $\mu_i{}^*$ to $D_i{}^*$ (this equation has previously been used for an ion-electron-atom mixture). The relation of μ_i to D_i in (2.4) is an extension of Einstein's equation to the case of mass description of the diffusion.

The following are the conditions for quasineutrality and absence of conduction current in the ambipolar region in the zeroth approximation ($\varepsilon = 0$):

$$\sum_{j=1}^{N} e_j x_j = 0, \qquad \sum_{j=1}^{N} \frac{e_j}{m_j} J_j = 0 \tag{2.5}$$

which allow us to eliminate E from (2.4) and to put these equations in the form of generalized Fick's laws:

$$J_i = -\rho D_i{}^{(a)} \frac{\partial c_i}{\partial y} + \rho_i D_i{}^{(a)} \left[\Sigma_i{}^T - \sum_{k=1}^{N} c_k \Sigma_k{}^T - (e_i{}^* - \gamma) \sum_{k=1}^{N} x_k e_k \Sigma_k{}^T\right] \frac{\partial \ln T}{\partial y} \tag{2.6}$$

$$e_i{}^* = e_i \left(\sum_{k=1}^{N} x_k e_k{}^2\right)^{-1}, \qquad \gamma = \sum_{j=1}^{N} c_j e_j \left(\sum_{k=1}^{N} x_k e_k{}^2\right)^{-1} \qquad (i = 1, \ldots, N)$$

where the $D_i{}^{(a)}$ (effective ambipolar diffusion coefficients) by definition must be found from*

$$\frac{1}{D^{(a)}(\mathrm{E})} = \frac{1}{D(\mathrm{E})} - \frac{\nu(\mathrm{E})\, c(\mathrm{E})}{z} \sum_{k=1}^{N} \frac{z_k{}^* J_k}{D_k J(\mathrm{E})} \tag{2.7}$$

$$\frac{1}{D_i{}^{(a)}} = \frac{1}{D_i} + \frac{\nu_i c_i}{\nu(\mathrm{E})\, c(E)} \left[\frac{1}{D^{(a)}(\mathrm{E})} - \frac{1}{D(\mathrm{E})}\right] \frac{J(\mathrm{E})}{J_i} \qquad (i \neq \mathrm{E})$$

$$E = \frac{1}{\rho z} \sum_{k=1}^{N} \frac{z_k{}^*}{D_k} J_k, \qquad z_i{}^* = \frac{m(\mathrm{E})}{m_i} \frac{e_i}{e}, \qquad z = \sum_{k=1}^{N} c_k z_k{}^* \nu_k \tag{2.8}$$

We can put Eqs. (2.7) in the single form

$$\frac{1}{D_i{}^{(a)}} = \frac{1}{D_i} - \frac{\nu_i c_i}{z} \sum_{k=1}^{N} \frac{z_k{}^*}{D_k} \frac{J_k}{J_i} \qquad (i = 1, \ldots, N) \tag{2.9}$$

If we substitute from (2.2) for D_i into (2.9) and use the condition of quasineutrality, we get N equations for the $D_i{}^{(a)}$ in a form analogous to that for the effective diffusion coefficients in a neutral mixture:

$$\frac{1}{D_i{}^{(a)}} = \sum_{j=1}^{N} x_j a_{ij} + c_i \sum_{j=1}^{N} (A_{ij} + A_{ij}{}^{(e)}) \frac{J_j}{J_i} \tag{2.10}$$

$$A_{ij}{}^{(e)} = \frac{\nu_i m}{z} \sum_{k=1}^{N} c_k a_{kj} \left(\frac{z_k{}^*}{m_j} - \frac{z_j{}^*}{m_k}\right) = (e_i{}^* - \gamma) \sum_{k=1}^{N} \frac{m^2 c_k}{m_k m_j} a_{kj} (e_k - e_j)$$

$$-\frac{E}{kT} = \left[\sum_{j=1}^{N} \frac{J_j}{m_j n} \sum_{k=1}^{N} x_k a_{kj} (e_k - e_j) + \frac{\partial \ln T}{\partial y} \sum_{j=1}^{N} x_j e_j \Sigma_j{}^T\right] \left(\sum_{k=1}^{N} x_k e_k{}^2\right)^{-1}$$

Then (2.6) and (2.10) allow us to put Eq. (1.7) as

$$-\rho \frac{\partial c_i}{\partial y} = J_i \sum_{j=1}^{N} x_j a_{ij} + c_i \sum_{j=1}^{N} (A_{ij} + A_{ij}{}^{(e)}) J_j - \rho_i \left[\Sigma_i{}^T - \sum_{k=1}^{N} c_k \Sigma_k{}^T\right.$$

$$\left. - (e_i{}^* - \gamma) \sum_{k=1}^{N} x_k e_k \Sigma_k{}^T\right] \frac{\partial \ln T}{\partial y} \qquad (i = 1, \ldots, N) \tag{2.11}$$

The ambipolar coefficients can be defined also in the molar description of the diffusion by analogy with (2.6). In what follows we consider only the mass diffusion coefficients. The above various effective

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*If a chemical symbol has to be introduced as an index, it will be shown in parentheses, e.g., $D_E = D(E)$, $D_{EH_2} = D(E, H_2)$, etc.

coefficients are dependent on the ratios of the diffusion fluxes; in general, they can be derived only numerically for an N-component mixture. The $A_{ij}^{(e)}$ are zero only if there are no charged components; then (2.10) becomes (2.2). To (2.10) we must add three relationships homogeneous with respect to the fluxes:

$$\sum_{j\neq \mathrm{E}} \frac{J_j}{J(\mathrm{E})} = -1, \qquad \sum_{j\neq \mathrm{E}} z_j \frac{J_j}{J(\mathrm{E})} = 1, \qquad \sum_{j\neq \mathrm{E}} \frac{D^{(a)}(\mathrm{E})}{D_j^{(a)}} \frac{J_j}{J(\mathrm{E})} = -1 \tag{2.12}$$

The system of (2.10) and (2.12) serves to define the N coefficients $D_i^{(a)}$ and the N−1 ratios of the diffusion fluxes. Only N+2 out of the N+3 equations in (2.10) and (2.12) are independent [the second equation in (2.12) has been used in writing (2.10)]. System (2.10), (2.12) has a unique solution only if N = 3 for a plasma and N = 2 for a neutral mixture; in these particular cases the D_i and $D_i^{(a)}$ are calculated via the thermodynamic parameters before the problem is solved. The next section deals with the important particular case N = 3 for an ionized mixture.

3. An ionized gas mixture consists of the three components E, $I^{(n)}$, and $I^{(n+1)}$, which are produced via

$$\mathrm{I}^{(n)} + n\mathrm{E} \rightleftarrows \mathrm{I}^{(n+1)} + (n+1)\,\mathrm{E} \quad (n > 0); \qquad \mathrm{A} \rightleftarrows \mathrm{I} + \mathrm{E}\,(n = 0) \tag{3.1}$$

Here A represents atoms, I represents ions, E represents electrons, and n is the degree of ionization. The equilibrium constants show that usually

$$K_p^{(n)} \gg K_p^{(n+1)}, \qquad n = 0, 1, \ldots$$

so ionization occurs in steps as the temperature is raised. First n = 1 for nearly all the particles, then n = 2, and so on, so an ionized mixture from a given element virtually consists of only three components. Then from the statement made at the end of section 1 we find from (2.10), (2.12) successively the ratios of the diffusion fluxes and the various D:

$$J_n / J(\mathrm{E}) = -m_n / m(\mathrm{E}), \qquad J_{n+1} / J(\mathrm{E}) = m_{n+1} / m(\mathrm{E})$$

$$\frac{1}{D_n} = \left[1 + x(\mathrm{E})\left(\frac{m(\mathrm{E})}{m_{n+1}}\right) - 1\right] \frac{e^* a_{n,\,n+1}}{e^* + \overset{*}{e}_{n+1}} + \left[1 + x_{n+1}\left(\frac{m_{n+1}}{m(\mathrm{E})} - 1\right)\right] \frac{\overset{*}{e}_{n+1} a(n,\,\mathrm{E})}{e^* + \overset{*}{e}_{n+1}} + \left(\frac{m}{m(\mathrm{E})} + \frac{m}{m_{n+1}}\right) \frac{e_n^* c_n a(E,\,n+1)}{e^* + \overset{*}{e}_{n+1}} \tag{3.2}$$

$$\frac{1}{D_{n+1}} = \left[1 + x_n\left(\frac{m_n}{m(\mathrm{E})} - 1\right)\right] \frac{e_n^* a(n+1,\,\mathrm{E})}{e^* + e_n^*} + \left[1 + x(\mathrm{E})\left(\frac{m(\mathrm{E})}{m_n} - 1\right)\right] \times \frac{e^* a_{n,\,n+1}}{e^* + e_n^*} + \left(\frac{m}{m(\mathrm{E})} - \frac{m}{m_n}\right) \frac{\overset{*}{e}_{n+1} c_{n+1}}{e^* + e_n^*} a(\mathrm{E},\,n) \tag{3.3}$$

$$\frac{1}{D(\mathrm{E})} = \left[1 + x_n\left(\frac{m_n}{m_{n+1}} - 1\right)\right] \frac{e_n^* a(\mathrm{E},\,n+1)}{e_n^* - \overset{*}{e}_{n+1}} - \left[1 + x_{n+1}\left(\frac{m_{n+1}}{m_n} - 1\right)\right] \times \frac{\overset{*}{e}_{n+1} a(\mathrm{E},\,n)}{e_n^* - \overset{*}{e}_{n+1}} + \left(\frac{m_{n+1}}{m_n} - 1\right) \frac{m(\mathrm{E})}{m_{n+1}} \frac{e^* x(\mathrm{E})}{e_n^* - \overset{*}{e}_{n+1}} a_{n,\,n+1}$$

$$\begin{gathered} 1 / D_n^{(a)} = 1 / D_{n+1}^{(a)} = 1 / D^{(a)}(\mathrm{E}) = [\delta_1 a(\mathrm{E},\,n+1) + \delta_2 a(n,\,\mathrm{E}) + \delta_3 a_{n,\,n+1}]\,\delta^{-1} \\ e^* = e / m(\mathrm{E}), \qquad e_n^* = e_n / m_n, \qquad \overset{*}{e}_{n+1} = e_{n+1} / m_{n+1} \\ \delta_1 = n^2\,[(n+1) - (n+2)x(\mathrm{E})], \qquad \delta_2 = (n+1)^2\,[(n+1)x(\mathrm{E}) - n] \\ \delta_3 = x(\mathrm{E}), \qquad \delta = \delta_1 + \delta_2 + \delta_3 = (n+2)\,[(n+2)x(\mathrm{E}) - n] \end{gathered} \tag{3.4}$$

Equations (3.3) simplify considerably if we use

$$m(\mathrm{E}) / m_n \approx m(\mathrm{E}) / m_{n+1} \ll 1 \tag{3.5}$$

$$\begin{gathered} \frac{1}{D_n} = [1 - x(\mathrm{E})]\,a_{n,\,n+1} + (n+1)\left[x_{n+1} + \frac{m(\mathrm{E})}{m_{n+1}}\right] a(n,\,\mathrm{E}) + n x_n a(\mathrm{E},\,n+1) \\ \frac{1}{D_{n+1}} = [1 - x(\mathrm{E})]\,a_{n,\,n+1} + (n+1)\,x_{n+1} a(n,\,\mathrm{E}) + n\left[x_n + \frac{m(\mathrm{E})}{m_n}\right] a(\mathrm{E},\,n+1) \\ \frac{1}{D(\mathrm{E})} = \frac{m(\mathrm{E})}{m_n} x(\mathrm{E})\,a_{n,\,n+1} + (n+1)\,a(n,\,\mathrm{E}) - n a(n+1,\,\mathrm{E}) \qquad (3.6) \end{gathered} \tag{3.6}$$

We use (1.3) and (1.4) to simplify (3.4) and (3.6) further, which gives

$$a(n,\,\mathrm{E}) / a_{n,\,n+1} \approx a(n+1,\,\mathrm{E}) / a_{n,\,n+1} \approx [m(\mathrm{E}) / m_n]^{1/2} \ll 1 \tag{3.7}$$

Also, (3.7) gives from (3.4) and (3.6) that

$$1 / D_n = 1 / D_{n+1} = [1 - x(\mathrm{E})]\, a_{n,\, n+1}, \quad 1 / D(\mathrm{E}) = (n+1)\, a(n,\ \mathrm{E}) - na(n+1,\ \mathrm{E}) \tag{3.8}$$

$$1 / D_{n+1}^{(a)} = 1 / D_n^{(a)} = 1 / D^{(a)}(\mathrm{E}) = x(E)\{(n+1)\,[(n+2)\,x(\mathrm{E}) - n]\}^{-1} a_{n,\, n+1} \tag{3.9}$$

In writing (3.8) and (3.9) we use the obvious estimate

$$n / (n+1) \leqslant x(\mathrm{E}) \leqslant (n+1) / (n+2), \quad n \geqslant 0 \tag{3.10}$$

Then (3.4) for n = 0 gives

$$D^{(a)}(\mathrm{A}) = D^{(a)}(\mathrm{I}) = D^{(a)}(\mathrm{E}) = 2 / [a(\mathrm{E},\ \mathrm{A}) + a(\mathrm{I},\ \mathrm{A})] \tag{3.11}$$

From (3.9) with n = 0 we get the well-known result

$$D^{(a)}(\mathrm{A}) = D^{(a)}(\mathrm{I}) = D^{(a)}(\mathrm{E}) = 2D(\mathrm{A},\ \mathrm{I}) \tag{3.12}$$

It is readily shown that we have for the molar description that

$$D_n^{*(a)} = D_{n+1}^{*(a)} = D^{*(a)}(\mathrm{E}) \tag{3.13}$$

with the values given by (3.4).

Then a ternary mixture (ionized gas) in the mass and molar descriptions resembles a binary mixture of neutral gases in being described by a single diffusion coefficient, which is found from (3.4).

4. If the plasma contains four or more components, we can calculate the $D_i^{(a)}$ only after solving the entire detailed problem; but in some important particular cases one can establish some properties of the concentration distributions and $D_i^{(a)}$ that are not dependent on the boundary concentrations. Similar properties have been deduced [3] for mixtures of neutral gases.

We call components K and K' ones with similar or identical diffusion properties if we have

$$\begin{gathered} m(K) \approx m(K')\ (m(K) = m(K')), \\ a(K,\ i) \approx a(K',\ i)\ \ (a(K,\ i) = a(K',\ i)) \end{gathered} \tag{4.1}$$

The following theorem may be proved via (2.9) and (4.1) by analogy with [3].

Theorem 4.1. If in a gas mixture we can distinguish a group of neutral components with identical diffusion properties, then D_i and $D_i^{(a)}$ for the components that do not fall in the group will not depend explicitly on the diffusion fluxes for the components in this group.*

The theorem follows from (2.5) and (2.10).

Theorem 4.2. If a plasma has only one type of ions I, the various D_i will not depend on $a(\mathrm{I},\ \mathrm{E})$, the resistance coefficient between the electrons and ions.

As in [3], we convert (1.1) to the dimensionless parabolic variables $(\xi,\ \eta)$, whereupon the generalized Fick's laws, the condition for zero current, and the condition for quasineutrality take the forms

$$\begin{gathered} X_i = -\frac{l}{S_i^{(a)}} \frac{\partial c_i}{\partial \eta}, \quad \sum_{j=1}^{N} \frac{e_j}{m_j} X_j = 0, \quad \sum_{j=1}^{N} \frac{e_j}{m_j} c_j = 0, \quad S_i^{(a)} = \frac{\mu}{\rho D_i^{(a)}}, \\ S_i = \frac{\mu}{\rho D_i} \end{gathered} \tag{4.2}$$

Here X_i is a dimensionless diffusion flux [3]. In what follows we use the following numbering of the components: neutral species are represented by values from 1 to N_n, ions by $N_n + 1$ to $N - 1$, and electrons by N. The theorem follows from (2.2), (2.7), (2.10), and the diffusion equation of (1.1) (we neglect thermal diffusion).

Theorem 4.3. If all the ions in a plasma have identical diffusion properties [see (4.1)] and charges, and if at the wall we have

$$c_i = c_{iw} = 0 \qquad (i = N_n + 1, \ldots, N)$$

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*The assertion in theorem 2.1 of [3] should be corrected: "then the effective diffusion coefficients for all components that do not fall in this group will not ... ."

then the relative concentrations and fluxes for the ions are

$$z_i = c_i / c_{ie}, \qquad I_i = X_i / c_{ie} \qquad (i = N_n + 1, \ldots, N - 1) \tag{4.3}$$

while the effective Schmidt numbers S_i and effective ambipolar Schmidt numbers $S_i^{(a)}$ for the ions are respectively equal throughout the thickness of the boundary layer:

$$z_i \equiv z(\mathrm{I}), \quad I_i \equiv I(\mathrm{I}), \quad S_i \equiv S(\mathrm{I}), \quad S_i^{(a)} \equiv S^{(a)}(\mathrm{I}) \quad (i = N_n + 1, \ldots, N - 1) \tag{4.4}$$

Consequence 1. From (2.5) and (2.9) we have for the electrons

$$\begin{gathered} z(\mathrm{E}) = nz(\mathrm{I})\, m(\mathrm{E}) / m(\mathrm{I}), \quad I(\mathrm{E}) = nI(\mathrm{I})\, m(E) / m(\mathrm{I}) \\ S^{(a)}(\mathrm{E}) = S^{(a)}(\mathrm{I}) = [\nu(\mathrm{I}) S(\mathrm{E}) - \nu(\mathrm{E}) S(\mathrm{I})] / (n + 1) e \end{gathered} \tag{4.5}$$

where n is as above.

Consequence 2. We readily find from (2.2) and (2.9) that the $D_i^{(a)}$ and D_i for all components apart from the ions are not dependent on the a_{ij} (i, j = N_n + 1, ..., N) (resistance coefficients between the charged components).

5. Equations (1.2) and (2.5) allow us to eliminate the concentrations and fluxes of two components from (1.7); let these be the electrons (subscript N) and type N−1 of the ions. Then the concentrations of components 1 to N−2 can be represented as linear combinations of the dimensionless fluxes of these components. Let

$$l \frac{\partial c_i}{\partial \eta} = \sum_{j=1}^{N-2} g_{ij} X_j \qquad (i = 1, \ldots, N - 2) \tag{5.1}$$

Here the g_{ij} and l are functions only of the concentrations and temperature. The following system is implied by (1.1) and (5.1) when η is large [3]:

$$\frac{\partial X_i}{\partial \eta} = \frac{\varphi}{l} \sum_{j=1}^{N-2} g_{ij} X_j, \quad \varphi(\xi, \eta) \to a(\xi) + \eta \sim \eta, \quad i < N - 1 \tag{5.2}$$

The following is the asymptotic solution to (5.1) and (5.2) for η large:

$$X_i = \sum_{k=1}^{N-2} \gamma_{ki} \exp(-\lambda_k \eta^\circ), \quad c_i = c_{ie} + \frac{X_i}{\eta^\circ}, \quad d\eta^\circ = \varphi \frac{d\eta}{l} \quad (\eta^\circ,\ \eta \to \infty) \tag{5.3}$$

where γ_{ki} are constants to be determined and λ_k are the roots of the characteristic equation:

$$\det \| h_{ij} - \lambda \delta_{ij} \| = 0, \qquad h_{ij} = -g_{ji} \tag{5.4}$$

We assume that all the $\lambda_k > 0$ (the X_i must tend to zero for $\eta \to \infty$). It follows [3, 5] that

$$X_i = \gamma_{ii} \exp(-\lambda_i \eta^\circ), \qquad \lambda_i = \Big[\sum_{j=1}^{N} x_j S_{ij}\Big]_e \tag{5.5}$$

for components that, at infinity, vanish from the structure of the coefficients g_{ij}.

Comparison of (5.5) with the first equation in (4.2) gives us simple equations for the following quantities for all components that vanish at infinity:

$$S_{ie}^{(a)} = \lambda_i = \Big[\sum_{j=1}^{N} x_j S_{ij}\Big]_e \tag{5.6}$$

Then some of the roots of (5.4) are found,and so the order of the latter is reduced.

As an example we consider the burning of a thermosetting resin in a flow of ionized air. The following components are then released by the wall and are lost via the outer boundary [3]:

$$\mathrm{M}\,(\mathrm{CO}, \mathrm{CN}, \mathrm{HCN}, \mathrm{C_2}, \mathrm{C_3}, \mathrm{N_2}, \mathrm{NO}), \quad \mathrm{SiO}, \quad \mathrm{CO_2}, \quad \mathrm{H_2} \tag{5.7}$$

We assume that the outer boundary has ions I (O^+, N^+, NO^+), atoms A (O and N), and electrons E.

First from (5.6) we find the $S_e^{(a)}$ for the components of (5.7). The smallest is

$$S_e^{(a)}(\mathrm{H}_2) = \Big[\sum_{j=1}^{N} x_j S(\mathrm{H}_2, j)\Big]_e \tag{5.8}$$

These numbers are found from (5.4) for the components that do not vanish at infinity and are

$$S_e^{(a)}(\mathrm{I}) = S_e^{(a)}(\mathrm{A}) = S_e^{(a)}(\mathrm{E}) = S_e^{(a)}(\mathrm{H}_2) \tag{5.9}$$

Then these numbers are equal for the components that do not vanish at the outer edge and are equal to the value of (5.8) for the components that vanish at infinity.

The $S_e^{(a)}$ at the outer edge are found before the entire boundary-value problem is solved; their values facilitate elucidation of the diffusion in the boundary layer and provide a check on numerical calculations, the more so since it is difficult to compute these numbers at the outer edge because one has to divide the concentration gradient by the diffusion flux, and each of these tends exponentially to zero.

6. Consider the $D_i^{(a)}$ at the wall on the basis that there we have complete recombination of dissociation products and neutralization of ionization products in the incident flow.

These conditions are usually met for $T_w \lesssim 3000$°K and $p \geq 10^{-2}$ atm:

$$c_{iw} = 0 \quad (i = N_* + 1, \ldots, N_n, \ldots, N) \tag{6.1}$$

Here the neutral species that do not vanish at the wall are numbered 1 to N_*. The numbering of the other components has been described above.

First from (2.2) we readily find the D_i for all components that vanish at infinity (subscript w is omitted):

$$\frac{1}{D_i} = \sum_{j=1}^{N_*} x_j a_{ij} \quad (i = N_* + 1, \ldots, N) \tag{6.2}$$

As at the wall for $i > N_*$ we have

$$c_i / c(\mathrm{E}) = (\partial c_i / \partial \eta) / (\partial c(\mathrm{E}) / \partial \eta) = J_i D^{(a)}(\mathrm{E}) / (J(\mathrm{E}) D_i^{(a)}) \tag{6.3}$$

then (2.9) gives

$$D^{(a)}(\mathrm{E}) = D(\mathrm{E})\,[1 + (1 - D_i^{(a)} / D_i)\, e / e_i] \quad (i = N_n + 1, \ldots, N - 1) \tag{6.4}$$

From (6.2) and (6.4) we have

$$D^{(a)}(\mathrm{E}) / D(\mathrm{E}) \approx D_i^{(a)} / D(\mathrm{E}) \approx a(\mathrm{E}, i) / a_{ji} \approx 10^{-2}$$
$$(i = N_* + 1, \ldots, N - 1,\ j \leqslant N_*) \tag{6.5}$$

From (6.4) and (6.5) we find with less than 1% error for ions that

$$D_i^{(a)} = D_i \left(1 + \frac{e_i}{e}\right) \left(\sum_{j=1}^{N_*} x_j a_{ij}\right)^{-1} \quad (i = N_n + 1, \ldots, N - 1) \tag{6.6}$$

From (2.9), (6.4), and (6.5) we find for atoms that vanish at the wall that

$$D_i^{(a)} = D_i = \left(\sum_{j=1}^{N_*} x_j a_{ij}\right)^{-1} \quad (i = N_* + 1, \ldots, N_n) \tag{6.7}$$

The various D_i have thus been calculated for $i > N_*$. From (2.7), (6.2), and (6.5) we find for neutral species present in the body that

$$\frac{1}{D_k^{(a)}} = \frac{1}{D_k} + c_k \sum_{j=N_n+1}^{N-1} \frac{e_j}{e} \frac{1}{D_j^{(a)}} \frac{J_j}{J_k}, \qquad k \leqslant N_* \tag{6.8}$$

The $D_k^{(a)}$ for $k \leq N_*$ can be calculated only when we have found the ratios of the diffusion fluxes at the wall. To find approximately the $D_k^{(a)}$ for $k \leq N_*$ we use the general analogy between the mass-transfer coefficients that is derived from numerical and analytical solutions for particular cases of such boundary layers [1, 11] with reasonably small influx from the wall:

$$\left(\frac{J_i}{J_j}\right)_w = \left(\frac{D_i^{(a)}}{D_j^{(a)}}\right)_w^{\varkappa_{ij}} \frac{\Delta c_i}{\Delta c_j}, \quad \Delta c_k = c_{ke} - c_{kw} \tag{6.9}$$

where the $\varkappa_{ij}$ as functions of $(l/S_i^{(a)})_e$, $(l/S^{(a)}_j)_e$ and influx $\varphi(\xi, 0)$ have been found [5] and range from 0.1 to 2.

Note that the $(l/S_k^{(a)})_e$ are found before the problem is solved (see section 5). The $D_k^{(a)}$ calculated below are only slightly dependent on $\varkappa_{ij}$. We substitute (6.9) into (2.10) to get a system of nonlinear equations, which may be solved by the method of [3]. Among the components $k \le N_*$ there may be a group K with identical diffusion properties. We give the numbers 1 to N_{**} to components present at the wall that do not fall in group K. If a decomposing plastic is involved, group K contains components with molecular weights around 30 (O_2, N_2, CO, CN, HCN, etc.).

Let H_2, SiO_2, and CO_2 be components present at the wall that do not fall in group K. The following is the algebraic system for the $D_k^{(a)}$ with $k \le N_*$ (see above for those for $k > N_*$) with allowance for group K:

$$\begin{gathered}\frac{1}{D_k^{(a)}} = B_k + \sum_{j=1}^{N_{**}} B_{kj} c_{jw} \left[\frac{D_j^{(a)}}{D_k^{(a)}}\right]^{\varkappa_{jk}} - \sum_{j=1+N_*}^{N_n} B_{kj} c_{je} \left[\frac{D_j^{(a)}}{D_k^{(a)}}\right]^{\varkappa_{jk}} \\ - \sum_{j=N_n+1}^{N-1} c_{je} \left[B_{kj} + \left(\frac{m(\mathrm{E})}{m_j} B(k, \mathrm{E}) + \frac{1}{D_j^{(a)}}\right) \frac{e_j}{e}\right) \left[\frac{D_j^{(a)}}{D_k^{(a)}}\right]^{\varkappa_{jk}}\end{gathered} \tag{6.10}$$

$$\begin{gathered}B_k = a(k, K)\left(1 + \varepsilon^{(k)} + \varepsilon_k c_k \frac{m}{m(K)}\right), \quad B_{kj} = a(k, K)(b_{kj} + \varepsilon_{kj}) \frac{m}{m(K)} \\ \varepsilon^{(k)} = \sum_{j=1}^{N_{**}} x_j \left[\frac{a_{kj}}{a(k, K)} - 1\right], \quad b_{kj} = 1 - \frac{a(K, j)}{a(K, k)} + \left[\frac{a(K, j)}{a(K, k)} - \frac{a_{kj}}{a(K, k)}\right] \frac{m(K)}{m_j} \\ \varepsilon_j = \sum_{i=1}^{N_{**}} c_i \left[\left(\frac{m(K)}{m_j} - \frac{m(K)}{m_i}\right) \frac{a_{ij}}{a(K, j)} - \left(1 - \frac{m(K)}{m_i}\right) \frac{a(K, j)}{a(K, j)} + \left(1 - \frac{m(K)}{m_j}\right)\right] \\ \varepsilon_{kj} = \varepsilon_j \frac{a(K, j)}{a(K, k)}, \quad B(K, K) = 0, \quad k \leqslant N_*\end{gathered} \tag{6.11}$$

The system of (6.10)), (6.11) has been written for the case where the components present at the wall vanish at infinity, since this covers practically all cases of erosion of a plastic in a hot ionized gas flow. In fact, group K accounts for over 70% of the mass of the gas at the body when the incident flow is air or carbon dioxide, so

$$|\varepsilon^{(k)}|, \quad |\varepsilon_j| \ll 1, \quad |\varepsilon_{kj}| \approx 0.1 |b_{kj}|, \quad k \leqslant N_{**}, \quad j \neq E. \tag{6.12}$$

Then for such mixtures ($k \le N_{**}$) we get in the zeroth approximation from (6.10)-(6.12) that

$$\begin{gathered}\frac{1}{D_k^{(a)}} = a(k, K) - \sum_{j=1}^{N_n} c_{je} \overset{\circ}{B}_{kj} [a(j, K) D_k^{(a)}]^{-\varkappa_{jk}} - \sum_{j=1+N_n}^{N-1} c_{je} \chi_{jk} [a(j, K) D_k^{(a)}]^{-\varkappa_{jk}} \\ \chi_{jk} = [\overset{\circ}{B}_{kj} + a(j, K)(1 + e/e_j)^{-1}] (1 + e_j/e)^{\varkappa_{jk}}, \quad \overset{\circ}{B}_{kj} = a(k, K) b_{kj} \\ m/m(K) = 1, \quad a(i, \mathrm{E}) < 0.01 a_{ij} \quad (j \neq \mathrm{E}) \\ D_k^{(a)} = a^{-1}(k, K) \qquad (N_* < k \leqslant N_n), \quad D_k^{(a)} = (1 + e_k/e) a^{-1}(k, K) \quad (N_n < k < N)\end{gathered} \tag{6.13}$$

The solution to (6.13) with $\varkappa_{ij} = 1$ is

$$\begin{gathered}D_k^{(a)} = a^{-1}(k, K) + \sum_{j=1+N_*}^{N_n} c_{je} b_{kj} a^{-1}(j, K) + \sum_{j=1+N_n}^{N-1} c_{je} a^{-1}(j, K) \overset{\circ}{\chi}_{jk} \\ \overset{\circ}{\chi}_{jk} = (1 + e_j/e) b_{kj} + e_j a_{jk} / [e a(k, K)], \qquad k \leqslant N_{**}\end{gathered} \tag{6.14}$$

The solution to (6.13) for $\varkappa_{ij} \neq 1$ is obtained with less than 7% error for all components ($k = 1, \ldots, N_{**}$) apart from H_2 simply by substituting (6.14) into the right side of (6.13). Then (6.10) gives the solution for all $k \le N_*$. The method of [3] may be used to obtain the solution to (6.10) in the general case. A four-component mixture (atoms A, ions I, electrons E, and molecules M) gives us the following form (6.6), (6.7), and (6.14) on the assumption that the first three vanish at the wall and the molecules at infinity:

$$D^{(a)}(\mathrm{I}) = 2D(\mathrm{I}) = 2a^{-1}(\mathrm{I}, \mathrm{M}), \qquad D^{(a)}(\mathrm{A}) = D(\mathrm{A}) = a^{-1}(\mathrm{A}, \mathrm{M})$$
$$D^{(a)}(\mathrm{M}) = [1 - c_e(\mathrm{I})(1 - 2a(\mathrm{A}, \mathrm{M})/a(\mathrm{I}, \mathrm{M}))]\, a^{-1}(\mathrm{A}, \mathrm{M}) \tag{6.15}$$

Equation (6.15) gives 5-7% error for $[D^{(a)}(\mathrm{M})a(\mathrm{A}, \mathrm{M})]$ when reference is made to the exact numerical calculations of [5].

Numerical solutions [4, 5] show that the effective ambipolar Schmidt numbers are positive within the boundary layer and vary from the result of section 6 at the wall to the result of section 5 at the outer edge of the boundary layer.

LITERATURE CITED

1. G. A. Tirskii, "Determination of effective diffusion coefficients for a laminar multicomponent boundary layer," Dokl. AN SSSR, 155, No. 6, 1278-1281 (1964).
2. G. A. Tirskii, "Determination of heat fluxes near a critical point of dual curvature with a dissociating gas of arbitrary composition flowing around a body," Zh. Prikl. Mekh. Tekh. Fiz., No. 1 (1965).
3. G. A. Tirskii, "Calculation of effective diffusion coefficients in a laminar dissociating multicomponent boundary layer," Zh. Prikl. Mat. Mekh., 33, No. 1 (1969).
4. V. M. Ovsyannikov and G. A. Tirskii, "Erosion by a partly ionized air flow for an axially symmetric body of rotation having a complex chemical composition," Izv. AN SSSR, Mekh. Zhid. i Gaza, No. 5 (1968).
5. O. N. Suslov, "Calculation of the convective heat flux near the critical point for a partly ionized gas flowing around a body," Izv. AN SSSR, Mekh. Zhid. i Gaza, No. 4 (1969).
6. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (1954).
7. S. Chapman and T. G. Cowling, Mathematical Theory of Nonuniform Gases, Cambridge Univ. Press (1952).
8. P. M. Chung, Electrical characteristics of Couette and stagnation boundary-layer flows of weakly ionized gases," Phys. Fluids, 7, No. 1 (1964).
9. G. A. Lyubimov and V. N. Mikhailov, "Analysis of the perturbation region in a plasma near an electrode," Izv. AN SSSR, Mekh. Zhid. i Gaza, No. 3 (1968).
10. G. A. Tirskii, "Conditions at surfaces of large discontinuity in multicomponent mixtures," Zh. Prikl. Mat. i Mekh., 25, No. 2 (1961).
11. B. I. Reznikov and G. A. Tirskii, "A general analogy between the mass-transfer coefficients in a laminar multicomponent boundary layer with an arbitrary pressure gradient," Dokl. Akad. Nauk SSSR, 158, No. 4 (1964).