DESCRIPTION OF FLOWS OF MULTICOMPONENT IONIZED MIXTURES IN CHEMICAL EQUILIBRIUM WITHIN THE LIMITS OF THE NAVIER – STOKES AND PRANDTL EQUATIONS

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By eliminating the electrical field originating because of separation of the charged components, the Navier–Stokes equations for partially ionized multicomponent reacting gas mixtures without external electromagnetic fields are reduced to equations analogous to the equations for a chemically reacting mixture of neutral gases. Formulations of problems about flows in chemical equilibrium taking account of ionization, thermo- and barodiffusion reactions for arbitrary mixtures with different diffusion properties of the components are examined within the scope of the complete Navier–Stokes equations and the Prandtl equations of an asymptotically thin boundary layer around both impermeable and thermochemically destructible walls.

Equations for flows of ideal mixtures in chemical equilibrium have been formulated in [1]. Within the limits of boundary layer theory these equations have been presented in [2] for viscous, heat-conducting mixtures of electrically neutral components in chemical equilibrium in the presence of diffusion.

Equilibrium flows of ionized air in the boundary layer have been examined in many papers [3-5] in a simplified formulation for a binary diffusion model. In such a formulation the diffusion properties of all the ions and all the neutrals are, respectively, considered identical, which affords a possibility of describing the diffusion of all components by using a single effective ambipolar coefficient of diffusion. In this case (for nondestructible walls), the concentrations of the chemical elements in the stream will be constant, and, therefore, the component concentrations and the transport coefficients can be calculated in advance as functions of just the pressure and temperature.

A new logical description of the fundamental equations is presented herein for the case of equilibrium flows of ionized mixtures with different diffusion properties of the components. The reason for the difference, in principle, between the equations obtained and those found earlier in the literature is elucidated.

The presence of components with dissimilar binary diffusion coefficients (drag coefficients) in a moving gas mixture results in the elementary chemical composition (concentration of chemical elements) being variable in the stream. In this case, the equilibrium chemical composition (concentration of components) will depend not only on the pressure and temperature, but also on the concentration of the chemical elements as additional independent variables varying in the stream. The important deduction hence follows that in solving problems on the motion of chemical equilibrium mixtures with different diffusion properties of the components, the determination of the effective specific heat and the effective coefficient of heat conduction as functions of just the pressure and temperature turns out to be impossible. In the general case these quantities should be calculated in parallel with the solution of a specific problem and appropriate equations are presented for them herein. Boundary conditions on an impermeable and thermochemically destructible wall are formulated when the diffusion and thermal diffusion properties of the components are distinct.

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1. Let us write the closed system of Navier-Stokes equations for an arbitrary N-component chemically reacting gas mixture in the presence of ionization reactions, and in the absence of external electromagnetic fields and energy transfer by radiation under conditions of quasi-neutrality of the mixture.

1°. Continuity equation for the mixture as a whole

$$\frac{\partial\rho}{\partial t} + \operatorname{div}(\rho \mathbf{v}) = 0, \quad \rho\mathbf{v} = \sum_{k=1}^{N} \rho_k \mathbf{v}_k, \quad \rho = \sum_{k=1}^{N} \rho_k \tag{1.1}$$

where ρ_i is the mass density of the i-th component, $\mathbf{v}_i$ is the mean statistical velocity of the i-th component, ρ is the mixture density, $\mathbf{v}$ is the mean mass flow rate of the mixture, and t is the time.

2°. Diffusion equation for the components

$$\rho \frac{dc_i}{dt} + \operatorname{div} \mathbf{J}_i = \dot{w}_i, \quad c_i = \frac{\rho_i}{\rho}, \quad \mathbf{J}_i = \rho_i(\mathbf{v}_i - \mathbf{v}), \quad (i = 1, \ldots, N) \tag{1.2}$$

with their closing Stefan–Maxwell relationships written in terms of the molar concentrations [6, 7]

$$\nabla x_i = -\mathbf{J}_i' \sum_{k=1}^{N} x_k \Delta_{ik} + x_i \sum_{k=1}^{N} \Delta_{ik}^* \mathbf{J}_k' - K_{Ti} \nabla \ln T - K_{pi} \nabla \ln p \quad (i = 1, \ldots, N) \tag{1.3}$$

$$\begin{gathered}
\Delta_{ij}^* = \Delta_{ij} - e_i^* \sum_{k=1}^{N} x_k e_k - e_j^T, \quad \Delta_{ij} = \frac{a_{ij}}{n} \\
K_{Ti} = -x_i \Big(\Sigma_i^T - e_i^* \sum_{k=1}^{N} x_k e_k \Sigma_k^T\Big), K_{pi} = -x_i \Big(\frac{m_i}{m} - 1 - e_i^* \sum_{k=1}^{N} c_k e_k\Big) \\
\mathbf{J}_i' = \frac{1}{m_i} \mathbf{J}_i, \quad e_i^* = e_i \Big(\sum_{k=1}^{N} x_k e_k^2\Big)^{-1}, \quad x_i = \frac{n_i}{n}, \quad n = \sum_{k=1}^{N} n_k \\
\Sigma_i^T = \sum_{k=1}^{N} x_k a_{ik} \Big(\frac{D_k^T}{\rho_k} - \frac{D_i^T}{\rho_i}\Big), \quad \sum_{i=1}^{N} K_{Ti} = \sum_{i=1}^{N} K_{pi} = 0 \\
\sum_{k=1}^{N} D_k^T = 0, \quad \sum_{k=1}^{N} x_k \Sigma_k^T = 0
\end{gathered} \tag{1.4}$$

or their equivalent relationships written in terms of the mass concentrations [6, 7]

$$\nabla c_i = -\mathbf{J}_i \frac{1}{m} \sum_{k=1}^{N} x_k \Delta_{ik} + c_i \sum_{k=1}^{N} \Delta_{ik}^{(c)} \mathbf{J}_k' - K_{Ti}^{(c)} \nabla \ln T - K_{pi}^{(c)} \nabla \ln p \quad (i = 1, \ldots, N) \tag{1.5}$$

$$\begin{gathered}
\Delta_{ij}^{(c)} = \Delta_{ij} - \sum_{k=1}^{N} x_k \Delta_{kj} \Big(\frac{m_k}{m} - \frac{m_j}{m}\Big) - e_i^{**} \sum_{k=1}^{N} x_k \Delta_{kj} (e_k - e_j) \\
K_{Ti}^{(c)} = -c_i \Big(\Sigma_i^T - \sum_{k=1}^{N} c_k \Sigma_k^T - e_i^{**} \sum_{k=1}^{N} x_k e_k \Sigma_k^T\Big) \\
K_{pi}^{(c)} = -c_i \Big(\frac{m_i}{m} - \sum_{k=1}^{N} \frac{m_k c_k}{m} - e_i^{**} \sum_{k=1}^{N} c_k e_k\Big), \quad \frac{1}{m} = \sum_{k=1}^{N} \frac{c_k}{m_k} \\
e_i^{**} = e_i^* - \sum_{k=1}^{N} c_k e_k \Big(\sum_{k=1}^{N} x_k e_k^2\Big)^{-1}, \quad \sum_{k=1}^{N} c_k e_k^{**} = 0
\end{gathered} \tag{1.6}$$

Here c_i, x_i, m_i, e_i, n_i, $\mathbf{J}_i$, w_i are, respectively, the mass concentration, the molar concentration, the molecular weight, the charge, the number of moles per unit volume, the mass diffusion flux vector, and the velocity of mass origination because of the chemical reactions per unit volume of the i-th component per unit time; p, T, m, and n are, respectively, the pressure, temperature, mean molecular weight, and number of moles per unit volume; D_i^T is the coefficient of thermal diffusion of the i-th component; a_{ij} are the drag coefficients which turn out to equal the reciprocals of the binary diffusion coefficients [7, 8] under the assumption that the multicomponent coefficients of diffusion can be replaced by a first approximation in

Chapman–Enskog theory,† i.e., by D_{ij}^{-1} (1), K_{Ti} and $K_{Ti}^{(c)}$ are the generalized thermal diffusion ratios, respectively, for the molar and mass description of diffusion, K_{pi} and $K_{pi}^{(c)}$ are the generalized barodiffusion ratios, respectively, for the molar and mass description of diffusion.

For the case of a binary mixture of neutral gases we obtain

$$\Delta_{ij} = \Delta, \quad D_i^T = -D_j^T, \quad e_i = e_j = 0, \quad \Sigma_i^T = -\frac{K_T}{x_i}$$
$$K_T = K_{Ti} = \frac{m^2}{m_i m_j} \frac{D_i^T}{\rho D_{ij}^T}, \quad K_{Ti}^{(c)} = \frac{m_i m_j}{m^2} K_T$$
$$K_p = K_{pi} = x_i - c_i = x_i x_j \frac{m_j - m_i}{m}, \quad K_{pi}^{(c)} = \frac{m_i m_j}{m^2} K_p$$

where K_T and K_p are, respectively, the ordinarily defined coefficients of thermo- and barodiffusion [8].

The relationships (1.3) and (1.5) have been obtained from their initial expressions [8] by elimination of the electric field originating because of separation of the charged components, by using the quasi-neutrality condition [6, 7].

It should be noted that (1.3), (1.5) are valid only when neglecting viscous momentum transport in the gas [9]. However, it can be shown that for Reynolds numbers much greater than unity the influence of viscous momentum transport on the diffusion streams can be neglected.

3°. Momentum equation for the mixture as a whole

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla p + \operatorname{div} \tau \qquad (\tau_{ij} = 2\mu e_{ij})$$
$$\tau_{ii} = \left(\zeta - \frac{2}{3}\mu\right) \operatorname{div} \mathbf{v} + 2\mu e_{ii}, \qquad e_{ii} = \frac{\partial v_i}{\partial x_i} \tag{1.7}$$
$$e_{ij} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right) \qquad (i, j = 1, 2, 3)$$

Here τ_{ij} are the components of the viscous stress tensor, e_{ij} are components of the strain rate tensor, μ is the dynamic coefficient of mixture viscosity, and ζ is the second coefficient of viscosity. The relation between the components of the tensors τ and e is presented under the assumption that the presence of chemical reactions in the stream does not affect the stress tensor.

4°. Equation of heat influx for the mixture as a whole

$$\rho \frac{dh}{dt} = \frac{dp}{dt} - \operatorname{div} \mathbf{J}_q + \Phi, \quad h = \sum_{k=1}^{N} c_k h_k, \quad \mathbf{J}_q = \mathbf{q} + \sum_{k=1}^{N} h_k \mathbf{J}_k$$
$$\mathbf{q} = -\lambda \nabla T + R_A T \sum_{i=1}^{N} \sum_{k=1}^{N} \frac{x_i D_k^T}{m_k} a_{ki} \left(\frac{\mathbf{J}_k}{\rho_k} - \frac{\mathbf{J}_j}{\rho_j}\right) = -\lambda \nabla T - R_A T \sum_{k=1}^{N} \mathbf{J}_k' \Sigma_k^T \tag{1.8}$$
$$\lambda = \lambda' - R_A \sum_{i=1}^{N} \sum_{k=1}^{N} \frac{x_i D_k^T}{m_k} a_{ik} \left(\frac{D_k^T}{\rho_k} - \frac{D_i^T}{\rho_i}\right) = \lambda' + R_A \sum_{k=1}^{N} \frac{D_k^T}{m_k} \Sigma_k^T$$

$$\Phi = \operatorname{div}(\tau \cdot \mathbf{v}) - \mathbf{v} \operatorname{div} \tau = (\zeta - {}^2/_3\,\mu)(\operatorname{div} \mathbf{v})^2 + 2\mu\,[e_{11}^2 + e_{22}^2 + e_{33}^2 + 2(e_{12}^2 + e_{13}^2 + e_{23}^2)] \tag{1.9}$$

where h_i is the specific enthalpy of the i-th component, h is the specific enthalpy of the mixture, J_q is the total heat flux, q is the reduced heat flux, Φ is a dissipative function, R_A is the absolute gas constant, γ is the ordinary coefficient of mixture heat conductivity, and the coefficient λ' is calculated in the kinetic theory of gases in terms of coefficients of expansions in Sonin polynomials [8].

In writing (1.8) it is assumed that the medium is a mixture of perfect gases. If (1.7), multiplied first by v is then added to (1.8), we obtain the energy equation for the mixture as a whole

$$\rho \frac{d}{dt}\left(h + \frac{\mathbf{v}^2}{2}\right) = \frac{\partial p}{\partial t} - \operatorname{div}(\mathbf{J}_q + \tau \mathbf{v}) \tag{1.10}$$

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†See the remarks at the end of this paper for more details.

5°. The equation of state for the mixture considered as a mixture of perfect gases

$$p = \rho R_A T / m \tag{1.11}$$

closes the system for the 2N + 6 desired functions

$$v_1, v_2, v_3, p, T, \rho, c_1, \ldots, c_N, \mathbf{J}_1, \ldots, \mathbf{J}_N$$

Let us note some trivial algebraic integrals of this system. From the definitions of the concentrations and diffusion flows, the relationships

$$\sum_{k=1}^{N} c_k = 1 \quad \left(\sum_{k=1}^{N} x_k = 1\right), \qquad \sum_{k=1}^{N} \mathbf{J}_k = 0 \tag{1.12}$$

are always satisfied.

The condition of quasi-neutrality of the mixture and the absence of an electric current yield two integrals of the fundamental equations of motion

$$\sum_{k=1}^{N} e_k c_k' = 0 \quad \left(c_i' = \frac{c_i}{m_i}\right), \qquad \sum_{k=1}^{N} e_k \mathbf{J}_k' = 0 \tag{1.13}$$

Taking account of (1.12) and the condition of conservation of the total mass of the mixture in the presence of chemical reactions

$$w_1^{\cdot} + \ldots + w_N^{\cdot} = 0 \tag{1.14}$$

we obtain that N − 1 equations will be independent in the system (1.2). Taking account of (1.12), we find that, exactly as (1.5), there will be N − 1 independent relationships (1.3). Hence, one of the components can always be eliminated in specific computations of the concentration and diffusion flow. Conditions (1.13) can be used to eliminate another component, say the electronic one, from the considerations.

Let us transform (1.2) and (1.8) by explicitly introducing the heat of reaction in the latter. In the flow around a streamlined body let there be N components as a result of all possible homogeneous and heterogeneous reactions. Let the number of independent (basis) components, for which the chemical elements and the electronic component can be chosen in particular, be N_e. Then, because of the independent reactions, all the remaining components (the reaction products) A_i ($i = 1, \ldots, N_r$, $N_r = N - N_e$) can be expressed in terms of the basis components A_j ($j = N_r + 1, \ldots, N$), in particular, as follows:

$$A_i = \sum_{j=1+N_r}^{N} \nu_{ij} A_j \qquad (i = 1, \ldots, N_r) \tag{1.15}$$

Here A_i, A_j are the chemical symbols of the components, and ν_{ij} are stoichiometric coefficients.

If each diffusion equation (1.2) of the components is multiplied, respectively, by the constant $\nu_{ij} m_j / m_i$ ($i = 1, \ldots, N$) and all the equations thus obtained are added, then, taking account of conservation of the elements in the chemical reactions

$$\sum_{k=1}^{N} \nu_{kj} \frac{m_j}{m_k} w_k^{\cdot} = 0 \qquad (j = 1 + N_r, \ldots, N)$$

we obtain the diffusion equations of the elements

$$\rho \frac{dc_j^*}{dt} + \operatorname{div} \mathbf{J}_j^* = 0 \qquad (j = N_r + 1, \ldots, N) \tag{1.16}$$

$$c_j^* = c_j + \sum_{k=1}^{N_r} \nu_{kj} \frac{m_j}{m_k} c_k, \qquad \mathbf{J}_j^* = \mathbf{J}_j + \sum_{k=1}^{N_r} \nu_{kj} \frac{m_j}{m_k} \mathbf{J}_k \tag{1.17}$$

where c_j^*, $\mathbf{J}_j^*$ ($j = N_r + 1, \ldots, N$) are, respectively, the concentration and mass diffusion flow of the j-th element.

An additional system of equations relating c_j^* and $\mathbf{J}_j^*$ ($j = N_r + 1, \ldots, N$) is obtained from (1.5) by using (1.17)

$$\nabla c_j^* = -\mathbf{J}_j^* m^{-1} \sum_{k=1}^{N} x_k \Delta_{jk} + \sum_{k=1}^{N_r} d_{jk} \mathbf{J}_k' + \sum_{l=N_r+1}^{N} b_{jl} \mathbf{J}_l^{*\prime} - K_{Tj}^{*(c)} \nabla \ln T - K_{pj}^{*(c)} \nabla \ln p \tag{1.18}$$

where

$$d_{jk} = c_j \Delta_{jk}^{*(c)} + \sum_{i=1}^{N_r} \nu_{ij} \frac{m_j}{m_i} c_i \Delta_{ik}^{*(c)} + \frac{\nu_{kj} m_j}{m} \sum_{i=1}^{N} x_i (\Delta_{ji} - \Delta_{ki})$$

$$b_{jl} = c_j \Delta_{jl}^{(c)} + \sum_{i=1}^{N_r} \nu_{ij} \frac{m_j}{m_i} c_i \Delta_{il}^{(c)}, \quad \Delta_{jk}^{*(c)} = \Delta_{jk}^{(c)} - \sum_{l=N_r+1}^{N} \Delta_{jl}^{(c)} \nu_{kl}$$

$$K_{Tj}^{*(c)} = K_{Tj}^{(c)} + \sum_{i=1}^{N_r} \nu_{ij} \frac{m_j}{m_i} K_{Ti}^{(c)}, \quad K_{pj}^{*(c)} = K_{pj}^{(c)} + \sum_{i=1}^{N_r} \nu_{ij} \frac{m_j}{m_i} K_{pi}^{(c)}$$

Taking account of the mass conservation condition in the reactions (1.15) we obtain from (1.17)

$$\sum_{j=1+N_r}^{N} c_j^* = 1, \qquad \sum_{j=1+N_r}^{N} \mathbf{J}_j^* = 0 \tag{1.19}$$

Moreover, let us note that conditions (1.13) for an electron element yield two more final relationships†

$$c^*(E) = 0, \qquad \mathbf{J}^*(\mathrm{E}) = 0 \tag{1.20}$$

Taking account of (1.19) and (1.20), we then have that just $N_e - 2$ equations should remain from the $N_e = N - N_r$ equations (1.16). The two equations omitted are replaced by the algebraic integrals (1.19) and (1.20).

Equations (1.16), (1.19), and (1.20) always hold independently of whether there are reactions or not, whether they proceed at a finite or infinite (chemical equilibrium) rate. Hence, in the general case the system (1.2) can be modified as follows: Let us just retain N_r independent equations corresponding to the formation of products in the reactions (1.15), and let us replace the rest of the diffusion equations by $N - N_r - 2$ homogeneous equations ($N - N_r - 1$ in the case of a mixture of electrically neutral components) of diffusion of the elements (1.16) and the algebraic relations (1.19), (1.20).

Let us transform the energy conservation equation by explicitly extracting the terms containing the heat of chemical reaction. In conformity with the first law of thermodynamics, the heat of reaction Q_i ($i = 1, \ldots, N_r$) needed to form unit mass of a product A_i in the reactions (1.15) for constant p and T is determined in terms of the enthalpy of the components by means of

$$h_i = \sum_{j=1+N_r}^{N} \nu_{ij} \frac{m_j}{m_i} h_i - Q_i(T) \qquad (i = 1, \ldots, N_r) \tag{1.21}$$

$$\frac{dh_i}{dT} = c_{pi} \qquad (i = 1, \ldots, N) \tag{1.22}$$

where c_{pi} ($i = 1, \ldots, N$) is the specific heat of the i-th component at constant pressure. Then the total heat flux $\mathbf{J}_q$ can be represented, taking account of (1.9), (1.17), and (1.21), in the following physically graphic form:

$$\mathbf{J}_q = -\lambda \nabla T - \sum_{k=1}^{N_r} Q_k' \mathbf{J}_k + \sum_{j=N_r+1}^{N} h_j' \mathbf{J}_j^* \tag{1.23}$$

$$Q_i' = Q_i + R_A T \sigma_i^T m_i^{-1}, \quad \sigma_i^T = \Sigma_i^T - \sum_{j=1+N_r}^{N} \nu_{ij} \Sigma_j^T$$

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† When it is needed to introduce the symbol of the chemical element as a subscript, it will be enclosed in parentheses. For example, for electrons $c_E^* = c^*(\mathrm{E})$.

$$h_j' = h_j - R_A T m_j^{-1} \Sigma_j^T \quad (i = 1, \ldots, N_r,\ j = N_r + 1, \ldots, N) \tag{1.24}$$

If the "effective" heats of reaction Q_i' ($i = 1, \ldots, N_r$) and the "effective" specific enthalpies of the basis components h_j' ($j = N_r + 1, \ldots, N$) are introduced, then the formula for the total heat flux will agree, outwardly, with the expression for the total heat flux in the absence of a diffusion heat effect. In conformity with (1.21), (1.22), the differential of the mixture enthalpy will be

$$dh = c_p dT - \sum_{k=1}^{N_r} Q_k dc_k + \sum_{j=1+N_r}^{N} h_j dc_j^* = d\left(\sum_{j=1+N_r}^{N} c_j^* h_j - \sum_{k=1}^{N_r} c_k Q_k\right) \tag{1.25}$$

The second sum in (1.25) in the first expression corresponds to the change in enthalpy in a thermodynamically open system [10]. Taking account of (1.25), (1.16), and (1.23), the heat influx equation (1.8) will be

$$\rho\left(c_p \frac{dT}{dt} - \sum_{k=1}^{N_r} Q_k \frac{dc_k}{dt}\right) = \frac{dp}{dt} + \operatorname{div}\left(\lambda \nabla T + \sum_{k=1}^{N_r} Q_k' \mathbf{J}_k + R_A T \sum_{j=1+N_r}^{N} \mathbf{J}_j^{*\prime} \Sigma_j^T\right) + \Phi - \sum_{j=1+N_r}^{N} \nabla h_j \mathbf{J}_j^* \tag{1.26}$$

The influence of the heat of reaction on the temperature profile is easily estimated in such a form of writing the heat influx equation. The energy equation (1.10) becomes

$$\rho \frac{d}{dt}\left(h + \frac{\mathbf{v}^2}{2}\right) = \frac{\partial p}{\partial t} + \operatorname{div}\left(\lambda \nabla T + \sum_{k=1}^{N_r} Q_k' \mathbf{J}_k - \sum_{j=1+N_r}^{N} h_j' \mathbf{J}_j^* + \tau \mathbf{v}\right) \tag{1.27}$$

Writing the energy equation thus is inconvenient because the enthalpies of components, which are determined from (1.22) for given specific heats of the components to the accuracy of arbitrary additive constants, enter therein. Let us note that these constants do not enter into (1.26). To eliminate the additive constants from (1.27), let us introduce the new desired function

$$H = \sum_{j=1+N_r}^{N} c_{j\infty}^* h_j - \sum_{k=1}^{N_r} c_k Q_k + \frac{\mathbf{v}^2}{2} \tag{1.28}$$

where $c_{j\infty}^*$ are given concentrations of elements in the free stream. The sense of the function H is that the difference $H - H_\infty$ equals the heat needed to heat unit mass of the free stream to the temperature of the point under consideration without taking account of physicochemical transformations, plus the heat of reaction of the formations of all the possible products with concentrations c_i ($i = 1, \ldots, N_r$) for the pressure, temperature, and elementary chemical composition at this point, plus the difference in kinetic energy densities at the point under consideration and in the free stream. Taking account of (1.28) and (1.16), Eq. (1.27) can be transformed into a new form containing just derivatives of the specific enthalpy

$$\begin{gathered}\rho \frac{dH}{dt} + D_{eff} = \frac{\partial p}{\partial t} + \operatorname{div}\left[\lambda \nabla T + \sum_{k=1}^{N_r} Q_k' \mathbf{J}_k + R_A T \sum_{j=1+N_r}^{N} \Sigma_j^T \mathbf{J}_j^{*\prime} + \tau \mathbf{v}\right] \\ D_{eff} = \sum_{j=1+N_r}^{N} \left\{\rho \frac{d}{dt}\left[(c_j^* - c_{j\infty}^*) h_j\right] + \operatorname{div}(h_j \mathbf{J}_j^*)\right\} \equiv \sum_{j=1+N_r}^{N} \left\{(c_j^* - c_{j\infty}^*)\rho \frac{dh_j}{dt} + \nabla h_j \mathbf{J}_j^*\right\}\end{gathered} \tag{1.29}$$

The function D_{eff} is connected with the effect of "diffusing specific heats" of the chemical elements.† The electron element does not enter into the expression for D_{eff} by virtue of (1.20). For identical specific heats of the elements, or when the mixture consists of one chemical element, $D_{eff} \equiv 0$. The assumption about equality (nearness) of the specific heats of elements is much weaker than the assumption about the equality of the specific heats of all the components‡

If ∇H is introduced on the right in (1.29) instead of ∇T, then by using (1.25) and (1.28) we obtain

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† The last component on the right in (1.26) is connected with this same effect.

‡ It is possible to select $N_e = N - N_r$ components with the nearest specific heats as the elements.

$$\rho \frac{dH}{dt} + D_{eff} = \frac{\partial p}{\partial t} + \operatorname{div} \left\{ \frac{\lambda}{c_p} \left[\nabla H + \frac{\sigma}{\mu} \boldsymbol{\tau} \mathbf{v} - \nabla \left(\frac{\mathbf{v}^2}{2} \right) \right. \right.$$

$$\left. \left. - \sum_{j=1+N_r}^{N} (c_{j\infty}^{*} - c_j{}^{*}) \nabla h_j \right] + \sum_{k=1}^{N_r} \left(Q_k{}' \mathbf{J}_k + \frac{\lambda}{c_p} Q_k \nabla c_k \right) + R_A T \sum_{j=1+N_r}^{N} \mathbf{J}_j{}^{*\prime} \Sigma_j{}^{T} \right\} \qquad (1.30)$$

This last mode of writing the energy equation is quite convenient for the solution of hydrodynamic problems since the function H depends so much more weakly on the heat of reaction, the work of the pressure forces, and the dissipation of the mechanical energy than on the temperature and, hence, changes more weakly in the stream.

2. The boundary conditions at infinity for the equations formulated above will consist in assigning v_∞, ρ_∞, T_∞, and $c_{1\infty}, \ldots, c_{N\infty}$. The boundary conditions on the impermeable and indestructible wall with possible heterogeneous reactions in the coordinate system coupled to the body will be

$$(v_n)_w = (v_\tau)_w = 0, \qquad T = T_w \qquad (2.1)$$

$$(J_{in})_w = r_i^{\cdot} \quad (i = 1, \ldots, N_r), \qquad (J_{jn}^{*})_w = 0 \quad (j = N_r + 1, \ldots, N) \qquad (2.2)$$

where v_n and v_τ are, respectively, the components of the velocity vector normal and tangential to the body, $r_i^{\cdot}$ $(i = 1, \ldots, N_r)$ is the surface velocity of the formations of the i-th components due to heterogeneous reactions. The determination of the function $r_i^{\cdot}$ in each specific case is a fundamental problem.

In the absence of heterogeneous reactions $(r_i^{\cdot} = 0,\ i = 1, \ldots, N_r)$ the conditions (2.2) reduce,when taking account of (1.17), to

$$(J_{in})_w = 0 \quad (i = 1, \ldots, N) \qquad (2.3)$$

Conditions (2.2) or (2.3) substantially impose a relation on the derivatives of the concentration with respect to the normal. Conditions (2.1) and (2.2) or (2.1) and (2.3) are sufficient to find a unique solution. After solving the problem the stress on the wall and the total heat flux to the wall can be calculated by the usual formulas from the expressions

$$-(J_{qn})_w = \left(\lambda \frac{\partial T}{\partial n} + \sum_{k=1}^{N_r} Q_k{}' J_{kn} \right)_w = \left[\frac{\lambda}{c_p{}^{*}} \frac{\partial H}{\partial n} + \sum_{k=1}^{N_r} \left(Q_k{}' J_{kn} + \frac{\lambda}{c_p{}^{*}} Q_k \frac{\partial c_k}{\partial n} \right) \right]_w \qquad (2.4)$$

where

$$c_p{}^{*} = c_p + \sum_{j=N_r+1}^{N} (c_{j\infty}^{*} - c_j{}^{*}) c_{pj}$$

Let us consider the case when the material of the body surface enters into a physicochemical interaction with the free stream gases, i.e., it can be thermochemically destroyed without the formation of a liquid film. In this case, under the assumption of quasi-stationarity of the destruction, the boundary conditions will be [6, 11]

$$(v_\tau)_w = 0, \quad (\rho v)_w (c_{iw} - c_i^{(1)}) + J_{inw} = r_i^{\cdot} \quad (i = 1, \ldots, N_r)$$

$$(\rho v)_w (c_j{}^{*} - c_j^{*\,(1)}) + J_{jnw}^{*} = 0 \quad (j = N_r + 1, \ldots, N)$$

$$\left(\lambda \frac{\partial T}{\partial n} + \sum_{k=1}^{N_r} Q_k{}' J_k \right)_w = (\rho v)_w \Delta \qquad (2.5)$$

or

$$\left[\frac{\lambda}{c_p{}^{*}} \frac{\partial H}{\partial n} + \sum_{k=1}^{N_r} \left(Q_k{}' J_{kn} + \frac{\lambda}{c_p{}^{*}} Q_k \frac{\partial c_k}{\partial n} \right) \right]_w = (\rho v)_w \Delta$$

where

$$\Delta = \left[h^{(1)} - h_{-\infty}^{(1)} + \Delta_\Phi - \sum_{k=1}^{N_r} Q_k{}' (c_k - c_k^{(1)}) + R_A T \sum_{j=N_r+1}^{N} (c_j{}^{*} - c_j^{*\,(1)}) m_j{}^{-1} \Sigma_j{}^{T} \right]_w$$

$$= \left[h^{(1)} - h^{(1)}_{-\infty} + \Delta_{\Phi} - \sum_{k=1}^{N_r} Q_k' (c_k - c_k^{(1)}) + R_A T \sum_{k=1}^{N} m_k^{-1} \Sigma_k^{T} (c_k - c_k^{(1)})\right]_w \qquad (2.6)$$

Here $h_w^{(1)} - h_{-\infty}^{(1)}$ is the heat needed to heat unit mass of the body material from the initial temperature to the temperature on the body surface (the temperature of the destruction front is T_w) taking account of all possible physicochemical transformations of the body material prior to the formation of the compounds $c_1^{(1)}, \ldots, c_N^{(1)}$ [$c_i^{(1)}$ (i = 1, . . . , N) are concentrations of components upon approaching the destruction front from the body], Δ_Φ is the heat of the phase transition; the last two sums in Δ yield the heat of heterogeneous reactions taking account of the diffusion thermoeffect.

Conditions (2.5) are not sufficient to determine a unique solution of the problem. Hence, in thermochemical destruction problems it is necessary to add still another condition which should result from the concrete destruction mechanism, in addition to the conservation laws, temperature continuity condition, and adhesion condition. For example, in the case of pure evaporation this can be either the condition of equilibrium evaporation, or the condition of evaporation at a finite rate. In the case of destruction of heat shield materials of complex chemical composition, the missing condition can be taken from experiment in the form of the kinetic curve connecting the mass rate of destruction $(\rho v)_w$ to the surface temperature [12].

After the problem has been solved in such a formulation, the surface temperature T_w and the mass rate of entrainment $(\rho v)_w$ are found.

3. If no other assumptions are made about the nature of the chemical reactions and the properties of the transport coefficients, then any further simplification of the fundamental system of equations (Sec. 1) and the boundary conditions (Sec. 2) is impossible.

However, if all the chemical reactions in the stream, including the ionization reaction, are equilibrium reactions, the fundamental system of equations of motion and the boundary conditions can be simplified substantially.

Under chemical equilibrium the N_r independent equations of diffusion of the components (1.2) are replaced by equilibrium conditions (Goldberg–Waage conditions for chemical reactions and Saha conditions for ionization reactions), which in conformity with the writing of the reaction (1.15) will be

$$\prod_{j=N_r+1}^{N} \frac{x_j^{\nu_{ij}}}{x_i} = \frac{K_{pi}(T)}{p^{\nu_i}}, \quad \nu_i = \sum_{j=N_r+1}^{N} \nu_{ij} - 1 \quad (i = 1, \ldots, N_r) \qquad (3.1)$$

where the functions $K_{pi}(T)$, called the equilibrium constants, are given. The relationship (3.1) can be examined as algebraic integrals replacing the N_r independent diffusion equations. If a linear system of equations

$$c_j + \sum_{k=1}^{N_r} \nu_{kj} \frac{m_j}{m_k} c_k = c_j^* \quad (j = N_r + 1, \ldots, N - 1)$$
$$c(\mathrm{E}) + \sum_{k=1}^{N_r} \nu(k, \mathrm{E}) \frac{m(\mathrm{E})}{m_k} c_k = c^*(\mathrm{E}) = 0 \qquad (3.2)$$

is added to the system (3.1), then compositions can be found, i.e., $c_1, \ldots, c_N$ or $x_1, \ldots, x_N$ as a function of p, T, and c_j^* ($j = N_r + 1, \ldots, N$). Therefore, an analysis of the equilibrium composition of a mixture at each point of a stream in chemical equilibrium is no different than its analysis for a closed system. However, for a motion taking account of diffusion, the quantities c_j^* ($j = N_r + 1, \ldots, N$) will vary together with p and T since the system (1.17), (1.16) does not admit the integrals†

$$c_j^* = \mathrm{const} \quad (j = N_r + 1, \ldots, N)$$

for different coefficients of diffusion of the components (for $N_e > 2$).

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† The integrals $c_j^* = c_{j\infty}^* = \mathrm{const}$ ($j = N_r + 1, \ldots, N$) will hold for identical diffusion coefficients and in the absence of a supply of new chemical elements in the stream.

Hence, the equilibrium chemical composition of a mixture with different diffusion properties of the components cannot possibly be defined in advance as a function of just p and T even in the absence of the supply of additional chemical elements in the stream, from the wall, say. The equilibrium composition in such a stream will be determined by the pressure, temperature, and concentrations of the chemical elements c_j* ($j = N_r + 1, \ldots, N$) as new independent variables varying in the stream.

In the general case the analysis of the equilibrium composition in the presence of diffusion must be performed in parallel with the solution of the fundamental system of differential equations. Let us use the system (1.16), (3.1), and (3.2) to simplify writing the heat influx and energy equations. Let us express the derivatives of the concentrations of the reaction products in (1.26), (1.30) in terms of the derivatives of p, T and c_j* ($j = N_r + 1, \ldots, N$), and the diffusion fluxes of these products in terms of gradients of p, T, and the diffusion fluxes of the elements J_j* ($j = N_r + 1, \ldots, N$).

Let us go over to mass concentrations c_i ($i = 1, \ldots, N$) in the system (3.1), and let us take the logarithmic differential of each equation; furthermore, let us replace dc_j ($j = N_r + 1, \ldots, N$) by dc_j* ($j = N_r + 1, \ldots, N$) and $dc_{k'}$ ($k = 1, \ldots, N_r$) by using (1.17), we then obtain the following system of joint algebraic equations to determine $dc_{k'}$:

$$\sum_{k=1}^{N_r} B_{ik} dc_k' = -\frac{m_i Q_i}{R_A m T} d \ln T + \frac{\nu_i}{m} d \ln p + \sum_{j=N_r+1}^{N} \left(\frac{\nu_{ij}}{x_j} - \nu_i \right) dc_j*', \quad c_i' = \frac{c_i}{m_i} (i = 1, \ldots, N_r) \tag{3.3}$$

where

$$B_{ik} = B_{ki} = \sum_{i=N_r+1}^{N} \frac{\nu_{ij} \nu_{kj}}{x_j} - \nu_i \nu_k + \frac{\delta_{ik}}{x_j} \quad (i, k = 1, \ldots, N_r) \tag{3.4}$$

The Van't Hoff isochor equations have hence been used

$$\frac{d \ln K_{pi}}{dT} = \frac{m_i Q_i}{R_A T^2} \quad (i = 1, \ldots, N_r)$$

The solution of the linear system (3.3) is written down at once. Let us just present here the sum needed later

$$\sum_{k=1}^{N_r} Q_k dc_k = \sum_{k=1}^{N_r} m_k Q_k dc_k' = -c_{pr} dT + B(\nu, mQ) dp + \sum_{i=N_r+1}^{N} B_j(\nu_j*, mQ) dc_j* \tag{3.5}$$

$$c_{pr} = -\frac{M^{(1)}}{R_A m T^2}, \quad B(\nu, m, Q) = -\frac{M^{(2)}}{mp}, \quad B_n(\nu_n*, mQ) = -\frac{M^{(3)}}{m_n} \tag{3.6}$$

$$\nu_{ij}* = -\nu_i + \nu_{ij} / x_j \quad (j = 1 + N_r, \ldots, N)$$

Here $M^{(s)}$ denotes the ratio between the determinants in (3.6)

$$M^{(s)} = \frac{\mathrm{Det} \| \Psi_{kl}^{(s)} \|}{\mathrm{Det} \| B_{ij} \|} \begin{pmatrix} k, l = 0, \ldots, N_r & \\ i, j = 1, \ldots, N_r; & s = 1, 2, 3. \end{pmatrix} \tag{3.7}$$

$$\Psi_{00}^{(s)} = 0, \quad \Psi_{kl}^{(s)} = B_{kl} \quad (kl \neq 0; \ s = 1, 2, 3)$$

$$\Psi_{0l}^{(1)} = \Psi_{l0}^{(1)} = m_l Q_l \quad (l = 1, \ldots, N_r) \tag{3.8}$$

$$\Psi_{0l}^{(2)} = \Psi_{0l}^{(3)} = m_l Q_l, \quad \Psi_{l0}^{(2)} = \nu_l, \quad \Psi_{l0}^{(3)} = \overset{*}{\nu}_{ln} \quad (l = 1, \ldots, N_r)$$

The differentials of the concentrations of the remaining components are found from the expressions

$$dc_j = dc_j* + \sum_{k=1}^{N_r} \nu_{kj} \frac{m_j}{m_k} dc_k \quad (j = N_r + 1, \ldots N) \tag{3.9}$$

Let us turn to the calculation of the diffusion streams. Let us take the logarithmic gradient of the equilibrium conditions (3.1) and let us substitute ∇x_i ($i = 1, \ldots, N$) from the relationships (1.3) therein, but first expressing the diffusion streams of the basis components J_j ($j = N_r + 1, \ldots, N$) in terms of J_j* ($j = N_r + 1, \ldots, N$) and J_j ($1, \ldots, N_r$).

Then taking account of the conservation of mass and charge in the reactions (1.15)

$$e_i = -\sum_{j=N_r+1}^{N} \nu_{ij} e_j, \quad m_i = -\sum_{j=N_r+1}^{N} \nu_{ij} m_j \quad (i = 1, \ldots N_r)$$

we obtain a system of linear equations for the fluxes

$$\mathbf{J}_i \ (i = 1, \ldots, N_r)$$

$$\sum_{k=1}^{N_r} A_{ik} \mathbf{J}_k{}' = \frac{m_i Q_i'}{R_A T} \nabla \ln T + \sum_{j=N_r+1}^{N} E_{ij} \mathbf{J}_j{}^{*\prime} \tag{3.10}$$

where

$$A_{ik} = A_{ki} = \sum_{j=N_r+1}^{N} \sum_{l=N_r+1}^{N} \frac{\nu_{ij} \Delta_{il}}{x_j} (\nu_{kj} x_l - \nu_{kl} x_j) + \sum_{j=N_r+1}^{N} \sum_{l=1}^{N_r} \nu_{ij} \nu_{kl} \frac{x_l \Delta_{jl}}{x_j}$$
$$+ \sum_{j=N_r+1}^{N} (\nu_{ij} \Delta_{kj} + \nu_{kj} \Delta_{ij}) - \Delta_{ik} = \frac{1}{2} \sum_{j=N_r+1}^{N} \sum_{l=N_r+1}^{N} \Delta_{jl} \frac{(\nu_{kj} x_l - \nu_{kl} x_j)(\nu_{ij} x_l - \nu_{il} x_j)}{x_j x_l}$$
$$+ \sum_{j=N_r+1}^{N} \sum_{l=1}^{N_r} \nu_{ij} \nu_{kj} \frac{x_l}{x_j} \Delta_{jl} + \sum_{j=N_r+1}^{N} (\nu_{kj} \Delta_{ij} + \nu_{ij} \Delta_{kj}) - \Delta_{ik} \, (i, k = 1, \ldots, N_r \cdot i \neq k) \tag{3.11}$$

$$A_{ii} = \sum_{k=1}^{N} \frac{x_k \Delta_{ik}}{x_i} + \frac{1}{2} \sum_{j=N_r+1}^{N} \sum_{l=N_r+1}^{N} \Delta_{jl} \frac{(\nu_{ij} x_l - \nu_{il} x_j)^2}{x_j x_l}$$
$$+ \sum_{j=N_r+1}^{N} \sum_{l=1}^{N_r} \nu_{ij}{}^2 \frac{x_l \Delta_{jl}}{x_j} + 2 \sum_{j=N_r+1}^{N} \nu_{ij} \Delta_{ij} - \Delta_{ii} = \frac{1}{2} \sum_{j=N_r+1}^{N} \sum_{l=N_r+1}^{N} \Delta_{jl}$$
$$\times \frac{(\nu_{ij} x_l - \nu_{il} x_j)^2}{x_j x_l} + \sum_{j=N_r+1}^{N} \sum_{l=1,\ l \neq i}^{N_r} \nu_{ij}{}^2 \frac{x_l \Delta_{jl}}{x_j} + \sum_{j=N_r+1}^{N} \Delta_{ij} \frac{(x_j + \nu_{ij} x_i)^2}{x_i x_j} + \sum_{k=1,\ k \neq i}^{N_r} \frac{x_k \Delta_{ik}}{x_i} \quad (i = 1, \ldots, N_r) \tag{3.12}$$

$$E_{ij} = \Delta_{ij} + \sum_{k=1}^{N} \frac{x_k \nu_{ij} \Delta_{ik}}{x_j} - \sum_{l=1+N_r}^{N} \nu_{il} \Delta_{jl}$$
$$(i = 1, \ldots, N_r; \ j = N_r + 1, \ldots, N) \tag{3.13}$$

It is interesting to note that, as follows from the system (3.10), the expressions for the diffusion fluxes of the reaction products J_i $(i = 1, \ldots, N_r)$ do not contain the pressure gradient explicitly for a flow in chemical equilibrium taking account of barodiffusion. If the barodiffusion effect is neglected, then a member proportional to ∇p will appear on the right in (3.10).

Again we shall not write down the solution of the system (3.10), but we present the expression for the sum at once

$$\sum_{k=1}^{N_r} Q_k' \mathbf{J}_k = \sum_{k=1}^{N_r} m_k Q_k' \mathbf{J}_k' = -\lambda_r \nabla T + \sum_{j=N_r+1}^{N} A_j (E_j, mQ') \, \mathbf{J}_j{}^{*\prime} \tag{3.14}$$

$$\lambda_r = -\frac{K^{(1)}}{R_A T^2}, \quad A_n (E_n, mQ') = -K^{(2)} \tag{3.15}$$

Here $K^{(s)}$ denotes the ratio between the determinants in the relationships (3.15) as well as later [relationships (3.23)]

$$K^{(s)} = \frac{\mathrm{Det} \| \pi_{kl}^{(s)} \|}{\mathrm{Det} \| A_{ij} \|} \quad \begin{pmatrix} k, l = 0, \ldots, N_r \\ i, j = 1, \ldots, N_r; \ s = 1, \ldots, 4 \end{pmatrix}$$
$$\pi_{00}^{(s)} = 0, \ \pi_{kl}^{(s)} = A_{kl} \quad (kl \neq 0, \ s = 1, \ldots, 4)$$
$$\pi_{0l}^{(2)} = \pi_{0l}^{(1)} = \pi_{l0}^{(1)} = m_l Q_l', \ \pi_{l0}^{(2)} = E_{ln} \quad (l = 1, \ldots, N_r) \tag{3.16}$$

Taking account of (3.5), (3.14), and (1.16), the heat influx equation (1.26) can be represented for flows in chemical equilibrium in the following final form:

$$\rho c_p^{eff} \frac{dT}{dt} = [1 + \rho B(\mathrm{v}, mQ)] \frac{dp}{dt} + \operatorname{div} \Big\{ \lambda_{eff} \nabla T + \sum_{t=N_r+1}^{N} [A_j(E_j, mQ') + R_A T \Sigma_j{}^T] \mathbf{J}_j{}^{*\prime} \Big\} - \sum_{j=N_r+1}^{N} [\nabla h_j \mathbf{J}_j{}^* + B_j(\mathrm{v}_j{}^*, mQ) \operatorname{div} \mathbf{J}_j{}^*] + \Phi \tag{3.17}$$

$$c_p^{eff} = c_p + c_{pr}, \quad \lambda_{eff} = \lambda + \lambda_r \tag{3.18}$$

Here c_p^{eff} is the effective specific heat, λ_{eff} is the effective heat conduction coefficient. The energy equation (1.29), taking account of (3.14) will become

$$\rho \frac{dH}{dt} + D_{eff} = \frac{\partial p}{\partial t} + \operatorname{div} \Big\{ \lambda_{eff} \nabla T + \sum_{j=N_r+1}^{N} [A_j(E_j, mQ') + R_A T \Sigma_j{}^T] \mathbf{J}_j{}^{*\prime} + \tau \mathrm{v} \Big\} \tag{3.19}$$

or by introducing ∇H in the right side in place of ∇T in conformity with the equation

$$\nabla H = c_p \nabla T - \sum_{k=1}^{N_r} Q_k \nabla c_k + \nabla \left(\frac{\mathbf{v}^2}{2} \right) + \sum_{j=N_r+1}^{N} (\overset{*}{c}_{j\infty} - c_j{}^*) \nabla h$$

$$= c_p^{eff} \nabla T - B(\mathrm{v}, mQ) \nabla p - \sum_{j=N_r+1}^{N} B_j(\mathrm{v}_j{}^*, mQ) \nabla c_j{}^* + \nabla \left(\frac{\mathbf{v}^2}{2} \right) + \sum_{j=N_r+1}^{N} (\overset{*}{c}_{j\infty} - c_j) \nabla h_j \tag{3.20}$$

we finally obtain

$$\rho \frac{dH}{dt} + D_{eff} = \frac{\partial p}{\partial t} + \operatorname{div} \Big\{ \frac{\mu}{\sigma_{eff}} \Big[\nabla H + \frac{\sigma_{eff}}{\mu} \tau \mathrm{v} - \nabla \left(\frac{\mathbf{v}^2}{2} \right) \Big] + B(\mathrm{v}, mQ) \nabla p + \sum_{j=N_r+1}^{N} (c_j{}^* - \overset{*}{c}_{j\infty}) \nabla h_j + \sum_{j=N_r+1}^{N} [A_j(E_j, mQ') + R_A T \Sigma_j{}^T] \frac{\sigma_{eff}}{\mu} \mathbf{J}_j{}^{*\prime} + \sum_{j=N_r+1}^{N} B_j(\mathrm{v}_j{}^*, mQ) \nabla c_j{}^* \Big\}, \quad \sigma_{eff} = \frac{\mu c_p^{eff}}{\lambda_{eff}} \tag{3.21}$$

where σ_{eff} is the effective Prandtl number constructed in the ordinary manner from the effective specific heat and the effective heat conduction coefficient. The relation between $\nabla c_j{}^*$ and $J_j{}^*$ ($j = N_r + 1, \ldots, N$) needed to close the system of equations is obtained from the relationships (1.18) if the diffusion fluxes J_i($i = 1, \ldots, N_r$) determined from the system (3.10) are eliminated therein

$$\nabla c_j{}^* = - \mathbf{J}_j{}^* m^{-1} \sum_{k=1}^{N} x_k \Delta_{jk} + A_j(d_j, mQ') \nabla T + \sum_{l=N_r+1}^{N} [b_{jl} + A_{jl}(d_j, E_l)] \mathbf{J}_l{}^{*\prime} - K_{Tj}^{*(c)} \nabla \ln T - K_{pj}^{*(c)} \nabla \ln p. \tag{3.22}$$

$$A_{mn}(d_m, E_n) = - K^{(3)}, \quad A_m(d_m, mQ') = - K^{(4)} / R_A T^2 \quad (m = N_r + 1, \ldots, N)$$
$$\pi_{0l}^{(3)} = \pi_{0l}^{(4)} = d_{ml}, \quad \pi_{l0}^{(3)} = E_{ln}, \quad \pi_{l0}^{(4)} = m_l Q_l{}' \quad (l = 1, \ldots, N_r) \tag{3.23}$$

Therefore, in the case of a flow in chemical equilibrium of a multicomponent gas mixture with different diffusion properties of the components in the presence of ionization, we arrive at a fundamental system of $N + 2N_e + 6$ equations (1.1), (1.7), (1.11), (1.16), (3.1), (3.22), (3.2), and (3.21) or (3.17) for N concentrations, N_e diffusion fluxes of the elements, N_e concentrations of the elements, the density, three components of the velocity, pressure, the function H, or the temperature. The diffusion fluxes of the components are eliminated from the direct solution of the problem. They can be calculated from the system (1.17) or (3.40) after the problem has been solved.

After the problem has been solved, the mass sources can also be found from the diffusion equations of the components because of the equilibrium reactions $\dot{w}_i$ ($i = 1, \ldots, N_r$).

The system of boundary layer equations can be obtained by the usual method from the closed system of Navier-Stokes equations presented above for high Reynolds number. Let us present just the energy equation for the plane case from this system:

$$\rho \frac{dH}{dt} + D_{eff} = \frac{\partial p}{\partial t} + \frac{\partial}{\partial y} \Big\{ \frac{\mu}{\sigma_{eff}} \Big[\frac{\partial H}{\partial y} + (\sigma_{eff} - 1) \frac{\partial}{\partial y} \left(\frac{u^2}{2} \right) + \sum_{j=N_r+1}^{N} (c_j{}^* - \overset{*}{c}_{j\infty}) \frac{\partial h_j}{\partial y} \Big]$$

$$+\sum_{j=N_r+1}^{N}[A_j(E_j,\ mQ')+R_A T\Sigma_j{}^T]J_{jy}^{*\prime}+\frac{\mu}{\sigma_{eff}}\sum_{j=N_r+1}^{N}B_j(\nu_j{}^*,\ mQ)\frac{\partial c_j{}^*}{\partial y}\Big\}$$

$$D_{eff}=\sum_{j=N_r+1}^{N}\left\{\rho\frac{d}{dt}[(c_j{}^*-c_{je}^*)h_j]+\frac{\partial}{\partial y}(h_jJ_{jy}^*)\right\}=\sum_{j=N_r+1}^{N}\left[(c_j{}^*-c_{je}^*)\rho\frac{dh_j}{dy}+\frac{\partial h_j}{\partial y}J_{jy}^*\right] \tag{3.24}$$

where y is the coordinate axis directed along the normal to the body surface, $J_{jy}{}^{*\prime} = (J'_j{}^* \cdot y^\circ)$. The subscript e denotes quantities on the outer boundary of the boundary layer. All the vectors in relationships (3.22) should be replaced by their projections on the y axis and the term with barodiffusion should be discarded if $K_{pj}^{*(c)} \sim 1$.

4. The boundary conditions for chemical equilibrium flows with equilibrium conditions on the impermeable wall remain in the form (2.1) and (2.2) with the exception of the conditions

$$(J_{in})_w = r_i \cdot \quad (i=1,\ldots,N_r)$$

which should be replaced by the equilibrium conditions (3.1).

After the problem has been solved with such boundary conditions, the friction stress is found by the ordinary formula, and the heat flux to the wall will be determined from the expression

$$-(J_{qn})_w=\left(\lambda_{eff}\frac{\partial T}{\partial n}\right)_w=\left\{\frac{\lambda_{eff}}{c_p^{*eff}}\left[\frac{\partial H}{\partial n}+B(\nu,mQ)\frac{\partial p}{\partial n}+\sum_{j=N_r+1}^{N}B_j(\nu_j{}^*,mQ)\frac{\partial c_j{}^*}{\partial n}\right]\right\}_w \qquad c_p^{*eff}=c_p{}^*+c_{pr} \tag{4.1}$$

From the relationship (3.22) we obtain on the wall

$$\frac{\partial c_j{}^*}{\partial n}=\left[A_j(d_j,mQ')-\frac{K_{Tj}^{*(c)}}{T}\right]\frac{\partial T}{\partial n}-\frac{K_{Pj}^{*(c)}}{P}\frac{\partial p}{\partial n} \tag{4.2}$$

Then the expression (4.1) can be given the following form:

$$(-J_{qn})_w=\left\{\frac{\lambda_{eff}}{(c_p^{**})_{eff}}\left[\frac{\partial H}{\partial n}+(B(\nu,mQ)-\frac{1}{p}\sum_{j=N_r+1}^{N}B_j(\nu_j^*,mQ)K_{pj}^{*(c)})\frac{\partial p}{\partial n}\right]\right\}_w \tag{4.3}$$

where

$$(c_p{}^{**})_{eff}=c_p^{*eff}-\sum_{j=N_r+1}^{N}B_j(\nu_j{}^*,mQ)\left[A_j(d_j,mQ')-\frac{K_{Tj}^{*(c)}}{T}\right] \tag{4.4}$$

It is important to note that for different diffusion coefficients of the components, the concentration gradients of the elements along the normal to the surface are not zero thereon and are proportional to the temperature gradient [see (4.2)] despite the fact that the diffusion fluxes of the elements on the wall equal zero [see (2.2)]. For identical diffusion coefficients, all the quantities are (see Sec. 5)

$$A_j(d_j,mQ)=0 \quad (j=N_r+1,\ldots,N)$$

In the boundary layer approximation we will have

$$-(J_q)_w=\left(\frac{\lambda_{eff}}{(c_p^{**})_{eff}}\frac{\partial H}{\partial n}\right)_w \tag{4.5}$$

In the case of a thermochemically destructible wall in the presence of chemical equilibrium, the conservation equations of the reaction products on the wall should be replaced by the relationships (3.1). The energy balance equation becomes

$$\left(\lambda_{eff}\frac{\partial T}{\partial n}\right)_w=(\rho v)_w\Delta \tag{4.6}$$

or, taking account of (3.20), (3.22),

$$\left[\frac{\lambda_{eff}}{(c_p^{**})_{eff}}\right]_w\left[\frac{\partial H}{\partial n}+B(\nu,mQ)\frac{\partial p}{\partial n}-\sum_{j=N_r+1}^{N}J_{jy}^{*\prime}\left\{\frac{m_j}{m}B_j(\nu,mQ)\right.\right.$$

$$- \sum_{l=N_r+1}^{N} B_l(\nu^*, mQ)\,[b_{lj} + A_{lj}(d_l, E_j)]\Big\}\Big]_w = (\rho v)_w \Delta$$

or

$$\left[\frac{\lambda_{eff}}{(c_p^{**})_{eff}}\right]_w \left[\frac{\partial H}{\partial n} + B(\nu, mQ)\frac{\partial p}{\partial n}\right]_w = (\rho v)_w \Delta - \left[\frac{\lambda_{eff}}{(c_p^{**})_{eff}}\right]_w \sum_{j=N_r+1}^{N}$$
$$\times \frac{c_{jw}^* - c_j^{*(1)}}{m_j}\left\{\frac{m_j}{m} B_j(\nu, mQ) - \sum_{l=N_r+1}^{N} B_l(\nu^*, mQ)\,[b_{lj} + A_{lj}(d_l, E_j)]\right\}_w \tag{4.7}$$

In the boundary layer approximation, the term with the derivative with respect to the pressure should be omitted in (4.7).

5. Let us consider as an example a ternary mixture consisting of atoms (A), ions (I), and electrons (E) in which one equilibrium ionization reaction occurs

$$\mathrm{I} = \mathrm{A} - \mathrm{E}$$

For this case, we find from the appropriate formulas of the preceding sections [x = x(I)]

$$c^*(\mathrm{E}) = 0, \quad c^*(A) = 1, \quad J^*(\mathrm{E}) = J^*(\mathrm{A}) = 0$$
$$x(\mathrm{A}) = 1 - 2x, \quad x(\mathrm{E}) = x(\mathrm{I}) = x, \quad c(\mathrm{A}) = (1 - 2x)(1 - x)^{-1}$$
$$e(\mathrm{I}) = e, \ e(\mathrm{E}) = -e, \ e(\mathrm{A}) = 0, \ m = m(\mathrm{A})(1 - x)$$
$$e^{**}(\mathrm{E}) = -\frac{1}{2e}\left(\frac{1}{x} + \frac{m(\mathrm{I}) - m(\mathrm{E})}{m}\right), \quad e^{**}(\mathrm{I}) = \frac{1}{2e}\left(\frac{1}{x} + \frac{m(\mathrm{E}) - m(\mathrm{I})}{m}\right)$$
$$e^{**}(\mathrm{A}) = \frac{m(\mathrm{E}) - m(\mathrm{I})}{2me}, \quad K_p^{(c)}(\mathrm{A}) = -\frac{1}{2}\frac{x(1 - 2x)}{(1 - x)^3}$$
$$K_p^{(c)}(\mathrm{I}) = \frac{m(\mathrm{I})\,x(1 - 2x)}{2m(\mathrm{A})(1 - x)^3}, \quad K_p^{(c)}(E) = \frac{m(\mathrm{E})\,x(1 - 2x)}{m(\mathrm{A})(1 - x)^3}$$
$$K_p^{*(c)}(A) = K_p^{*(c)}(\mathrm{E}) = 0, \quad K_T^{(c)}(\mathrm{A}) = \frac{x}{2(1 - x)^2}(\Sigma^T(\mathrm{I}) + \Sigma^T(\mathrm{E}))$$
$$K_T^{(c)}(\mathrm{I}) = -\frac{c(\mathrm{I})}{2(1 - 2x)}(\Sigma^T(\mathrm{I}) + \Sigma^T(\mathrm{E})) + \frac{c(\mathrm{I})}{c(\mathrm{A})}K_T^{(c)}(\mathrm{A})$$
$$K_T^{(c)}(\mathrm{E}) = -\frac{c(E)}{2(1 - 2x)}(\Sigma^T(\mathrm{I}) + \Sigma^T(\mathrm{A})) + \frac{c(\mathrm{E})}{c(\mathrm{A})}K_T^{(c)}(\mathrm{A})$$
$$K_T^{*(c}(A) = K_T^{*(c)}(\mathrm{E}) = 0, \quad \Delta^{(c)}(\mathrm{A}, \mathrm{A}) = \Delta(\mathrm{A}, \mathrm{A}) = \frac{x(\Delta(\mathrm{I}, \mathrm{A}) + \Delta(\mathrm{E}, \mathrm{A}))}{2(1 - x)}$$
$$\Delta^{(c)}(\mathrm{E}, \mathrm{E}) = \Delta(\mathrm{E}, \mathrm{E}) + \Delta(\mathrm{I}, \mathrm{E}) + \frac{(1 - 2x)^2\,\Delta(\mathrm{A}, \mathrm{E})}{2x(1 - x)}$$
$$\Delta^{(c)}(\mathrm{I}, \mathrm{I}) = \Delta(\mathrm{I}, \mathrm{I}) + \Delta(\mathrm{E}, \mathrm{I}) + \frac{(1 - 2x)^2\,\Delta(\mathrm{A}, \mathrm{I})}{2x(1 - x)}$$
$$\Delta^{(c)}(\mathrm{A}, \mathrm{I}) = \frac{\Delta(\mathrm{A}, \mathrm{I})}{2(1 - x)}, \quad \Delta^{(c)}(\mathrm{A}, \mathrm{E}) = \frac{\Delta(\mathrm{A}, \mathrm{E})}{2(1 - x)}, \quad \Delta^{(c)}(\mathrm{I}, \mathrm{A}) = \frac{\Delta(\mathrm{I}, \mathrm{A}) + \Delta(\mathrm{E}, \mathrm{A})}{2(1 - x)}$$
$$\Delta^{(c)}(\mathrm{I}, \mathrm{E}) = \frac{\Delta(\mathrm{A}, \mathrm{E})}{2x(x - 1)}, \quad \Delta^{(c)}(\mathrm{E}, \mathrm{I}) = \frac{\Delta(\mathrm{A}, \mathrm{I})}{2x(x - 1)}$$
$$\Delta^{(c)}(\mathrm{E}, \mathrm{A}) = \frac{\Delta(\mathrm{E}, \mathrm{A}) + \Delta(\mathrm{I}, \mathrm{A})}{2(1 - x)}, \quad \Delta^{*(c)}(\mathrm{A}, \mathrm{I}) = \Delta^{(c)}(\mathrm{A}, \mathrm{I}) - \Delta^{(c)}(\mathrm{A}, \mathrm{A}) + \Delta^{(c)}(\mathrm{A}, \mathrm{E})$$
$$\Delta^{*(c)}(\mathrm{I}, \mathrm{I}) = \Delta^{(c)}(\mathrm{I}, \mathrm{I}) - \Delta^{(c)}(\mathrm{I}, \mathrm{A}) + \Delta^{(c)}(\mathrm{I}, \mathrm{E}), \quad \Delta^{*(c)}(\mathrm{E}, \mathrm{I}) =$$
$$= \Delta^{(c)}(\mathrm{E}, \mathrm{I}) - \Delta^{(c)}(\mathrm{E}, \mathrm{A}) + \Delta^{(c)}(\mathrm{E}, \mathrm{E}), \quad d(\mathrm{A}, \mathrm{I}) = d(\mathrm{E}, \mathrm{I}) = 0$$
$$b(\mathrm{A}, \mathrm{A}) = \frac{(1 - 2x)\,\Delta(\mathrm{A}, \mathrm{A}) + x(\Delta(\mathrm{I}, \mathrm{A}) + \Delta(\mathrm{E}, \mathrm{A}))}{1 - x}, \quad b(\mathrm{E}, \mathrm{A}) = b(\mathrm{A}, \mathrm{E}) = 0$$
$$b(\mathrm{E}, \mathrm{E}) = \frac{m(E)}{m}[x(\Delta(\mathrm{E}, \mathrm{E}) + \Delta(\mathrm{I}, \mathrm{E})) + (1 - 2x)\,\Delta(\mathrm{A}, \mathrm{E})]$$
$$B(\mathrm{I}, \mathrm{I}) = \frac{2(1 - x)^2}{x(1 - 2x)}, \quad c_{pr} = \frac{x(1 - 2x)\,[m(\mathrm{I})\,Q]^2}{(1 - x)^3\,2m(\mathrm{A})\,R_{\mathrm{A}}\,T^2}$$
$$Q = Q(\mathrm{I}), \quad B(\nu, mQ) = \frac{x(2x - 1)\,m(\mathrm{I})\,Q}{(1 - x)^3\,2pm(\mathrm{A})}$$

$$B(\mathrm{A}, \nu^*(\mathrm{A}), mQ) = \frac{xm(\mathrm{I})\,Q}{(1 - x)\,m(\mathrm{A})}, \quad B(\mathrm{E}, \nu^*(\mathrm{E}), mQ) = \frac{x(2x - 1)\,m(\mathrm{I})\,Q}{2(1 - x)\,m(\mathrm{E})}$$
$$A(\mathrm{I}, \mathrm{I}) = \frac{(1 - x)^2(\Delta(\mathrm{A}, \mathrm{E}) + \Delta(\mathrm{I}, \mathrm{A}))}{x(1 - 2x)}, \quad A_{jl} = 0 \ (j, \ l = \mathrm{A}, \mathrm{E})$$
$$E(\mathrm{I}, \mathrm{A}) = \frac{1 - x}{1 - 2x}[\Delta(\mathrm{A}, \mathrm{I}) + \Delta(\mathrm{A}, \mathrm{E})], \quad E(\mathrm{I}, \mathrm{E}) = \frac{(x - 1)\,\Delta(\mathrm{E}, \mathrm{A})}{x}$$

$$A(\mathrm{A},\ E(\mathrm{A}),\ mQ') = \frac{xm(\mathrm{I})\,Q'}{1-x},\ A(\mathrm{E},\ E(\mathrm{E}),\ mQ') = \frac{(2x-1)\,\Delta(\mathrm{E},\ \mathrm{A})\,m(\mathrm{I})\,Q'}{(1-x)\,[\Delta(\mathrm{A},\ \mathrm{E}) + \Delta(\mathrm{I},\mathrm{A})]}$$

$$Q' = Q'(\mathrm{I}),\ A(\mathrm{A},\ d(\mathrm{A}),\ mQ') = A(\mathrm{E},\ d(\mathrm{E}),\ mQ') = 0$$

$$\lambda_r = \frac{x(1-2x)\,[m(\mathrm{I})\,Q']^2}{(1-x)^2\,R_A T^2\,[\Delta(\mathrm{A},\ \mathrm{E}) + \Delta(\mathrm{I},\ \mathrm{A})]}$$

As is seen, the diffusion properties in such a mixture can be described by one effective ambipolar diffusion coefficient (see [7] also)

$$D^{(a)}(\mathrm{A}) = D^{(a)}(\mathrm{I}) = D^{(a)}(\mathrm{E}) = D^{(a)} = \frac{2}{n\,(\Delta(\mathrm{A},\ \mathrm{E}) + \Delta(\mathrm{A},\ \mathrm{I}))} = \frac{2D(\mathrm{A},\ \mathrm{E})\,D(\mathrm{A},\ \mathrm{I})}{D(\mathrm{A},\ \mathrm{I}) + D(\mathrm{A},\ \mathrm{E})} \approx 2D(\mathrm{A},\ \mathrm{I})$$

The Prandtl number σ_r constructed by means of C_{pr} and λ_r will be

$$\sigma_r = \frac{\mu c_{pr}}{\lambda_r} = \left(\frac{Q}{Q'}\right)^2 S^{(a)} \approx S^{(a)},\ S^{(a)} = \frac{\mu}{\rho D^{(a)}},\ L^{(a)} = \frac{\sigma_r}{S^{(a)}}$$

Therefore, the Lewis–Semenov number $L^{(a)}$ is close to one for a maximum development of the ionization reaction.

The considered case is unique when the diffusion properties of all the components are described by one diffusion coefficient [7]. For ionized mixtures consisting of four and more components (if $N_e > 2$), the concentrations of the elements will not be constants in the streams, but will be the desired functions.

Remarks

1. It is known that for mixtures of ionized gases it is sometimes necessary to use higher approximations in calculating the transport coefficients by the Chapman–Enskog theory [13].[†]

Multicomponent diffusion coefficients in a second approximation can differ from their values in a first approximation by up to 20%, and this second approximation is completely satisfactory to describe diffusion for an arbitrary degree of ionization [13]. The thermodiffusion coefficients must be calculated in a fourth approximation. For approximations higher than the first the drag coefficients a_{ij} can already not be replaced by $D_{ij}^{-1}(1)$ but should be calculated by those known, but in a complex manner in terms of the multicomponent diffusion coefficients D_{ij} [8]. In this case the coefficients will already not possess the property $a_{ij} = a_{ji}$ (i, j = 1, . . . , N) although the structural form of (1.3), (1.5) remain unchanged.[‡] In this case the discussion presented above can be repeated, but it is hence impossible to use the symmetry condition for the coefficients a_{ij}. The final results become more complex. However, because of some uncertainty in the collision cross sections (for example, the ion–atomic interaction), and the comparatively good accuracy of the first approximation, for simplicity it is possible to put $a_{ij} = D_{ij}^{-3}(1)$ in certain cases.[††] It is certainly interesting to estimate the influence of this assumption on the boundary layer characteristics. Such an estimate will be connected with a great deal of computational effort even for the simplest problems of boundary layer theory. Taking account of higher approximations for the heat conduction coefficient does not alter the structural formula for the total heat flux J_q, but changes the coefficient in the term connected with the diffusion thermoeffect. However, since this effect is small even for ionized mixtures [13], taking account of the higher approximations is reflected only directly in the heat conduction coefficient itself, which must sometimes be calculated up to the fourth approximation inclusive for ionized mixtures.

The second approximation for the viscosity coefficient is completely satisfactory to describe the viscosity for mixtures of ionized gases [13].

2. Formulation of the problem of a chemical equilibrium flow of multicomponent ionized air taking account of different coefficients of diffusion of the components has been considered within the limits of the boundary layer equations in recently published papers [14, 15]. A term proportional to the intensity of the electrical field originating because of separation of the charged components (electrons and ions) has hence

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[†] That is, to take account of a larger number of terms in the series expansions in Sonin polynomials for the perturbed part of the distribution function.

[‡] The proof of the invariance of the structure of (1.3) and (1.5) can be obtained by using methods of irreversible thermodynamics also if the influence of viscous momentum transfer, small for sufficiently high Reynolds number, is neglected.

[††] The first approximation for D_{ij} is completely satisfactory for mixtures of neutral components.

been omitted in the initial Stefan–Maxwell relations (transport equations). Hence, the transport equations in these papers do not agree with (1.3) herein. Not taking account of this field results in the free (not ambipolar) diffusion of electrons to the cold wall and to the accumulation of significant space charges in the stream, i.e., to spoilage of the quasi-neutrality condition.

In calculating the heat and diffusion fluxes the authors do not remark that an equilibrium composition in the boundary layer will depend not only on p and T but also on the concentration of the chemical elements as new independent variables varying in the stream. Hence, the formulas for c_p^{eff} and λ_{eff} used in [14, 15] are different.

The energy equation used by the authors of [14, 15] in the cases they examined does not agree with (3.24) since the phenomenon of diffusion of the chemical elements was not taken into account in [14, 15].

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