DIFFUSION IN MULTICOMPONENT GASEOUS MIXTURES IN A MODEL OF LOCAL THERMODYNAMIC EQUILIBRIUM

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Diffusion of chemical elements into an ionized multicomponent gaseous mixture is considered in a model of local thermodynamic equilibrium. A linear dependence of the mass flows of chemical elements and the heat flow on the temperature gradient, mass fractions of the chemical elements, and the electric field is obtained. An example is given of a calculation of the effective diffusion coefficients for a hydrogen–helium mixture.

The solution of hydrodynamic problems for a multicomponent gas or plasma, given chemical reactions ocurring at finite rates, constitutes a complex problem. Therefore most of them are considered in limiting cases ("frozen" or locally balanced flows). In the first case, numerical integration of the system of hydrodynamic equations is complicated because of the large number of diffusion equations for the separate components.

In the second case (within the limits of local thermodynamic equilibrium) the kinetic component equations are purely formal and methods for their solutions are lacking, though a phenomenological description of the medium is nevertheless possible [1, 2]. It is worthwhile to pass from component diffusion equations to diffusion equations for the chemical elements, i.e., the number of variables is substantially decreased in most cases.

In this work, effective diffusion and thermal-conductivity coefficients relating the mass flows of chemical elements and the heat flow to the temperature gradient and gradients of the mass fractions of chemical elements and the electric field are introduced.

Suppose we have a mixture of N components, chemical reactions occurring between them. Let us consider for each component a kinematic equation with elastic- and inelastic-collision integrals in the right side. We assume that the cross section of inelastic processes is less than the cross section of the elastic processes; the elastic-collision integral for charged and neutral particles is Boltzmann (we also include the charge-exchange reaction in the Boltzmann collision integral). The equilibrium function for particle distribution is Maxwellian, since the cross sections of inelastic processes are small and the Chapman–Enskog method can be used to solve the kinematic equation, i.e., the inelastic-collision integral is not taken into account in the kinematic equation. The presence of the latter is indicated in the hydrodynamic equations, in particular, a chemical term appears in the diffusion equation. We may decide at the hydrodynamic level whether flow is "frozen" or locally balanced relative to diffusion as a function of the parameter.

$$\varepsilon = \frac{\tau}{\tau_x} = \frac{L^2}{D\tau_x}.$$

Here τ and τ_x are the characteristic diffusion chemical reaction rates, L is the characteristic hydrodynamic length, and D is the diffusion coefficient. When $\varepsilon \gg 1$ flow is frozen, while when $\varepsilon \ll 1$, it is locally balanced.

We will consider a system that is in mechanical equilibrium, at each point of which

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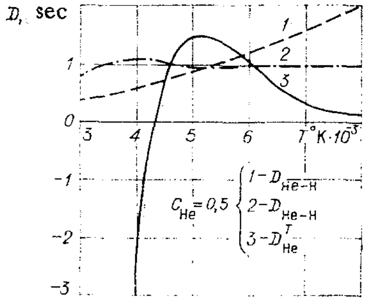

Fig. 1

chemical equilibrium holds at the local temperature. In this case, multicomponent diffusion reduces to diffusion of the chemical elements. Let us define the mass flow and mass fraction of a chemical element,

$$\mathbf{I}_a = \sum_{i=1}^{N} u_{ia} \frac{m_a}{m_i} \mathbf{I}_i; \quad c_a = \sum_{i=1}^{N} \frac{m_a}{m_i} c_i u_{\;a}. \tag{1}$$

Here u_{ia} is the number of nuclei of element a in component i, m_i and m_a are the masses of component i and atom a, c_i is the mass fraction of component i, and I_i is the mass flow of component i.

We will proceed on the basis of an equation for I_i previously [3] obtained in order to obtain the effective diffusion and thermal-conductivity coefficients, in this case neglecting thermal diffusion,

$$\mathbf{I}_i = \frac{n^2}{\rho} m_i \sum_{j=1}^{N} m_j D_{ij} \mathbf{d}_j; \tag{2}$$

$$\mathbf{d}_j = \nabla x_j = \frac{\rho_j}{p} \left(\mathbf{F}_j - \sum_{k=1}^{N} \frac{\rho_k}{\rho} \mathbf{F}_k \right), \tag{3}$$

where $x_j = n_j / n$ are the relative concentrations, F_j are the forces acting on component j, p is pressure, ρ and n are the total density and concentrations, and ρ_j and n_j are the density and concentration of component j. We assume that the gaseous mixture is ideal, so that the chemical equilibrium equation for each component of the mixture can be written in the form

$$x_i = \prod_t x_t^{u_{ti}} K_i(T, p), \tag{4}$$

where $K_i(T, p)$ is the equilibrium constant and $\{x_t\}$ is the set of relative concentrations of the basis components. We find ∇x_j in Eq. (3) by using Eq. (4),

$$\nabla x_j = \sum_t \left(\frac{\partial x_j}{\partial x_t} \right)_{p,T} \nabla x_t + \left(\frac{\partial x_j}{\partial t} \right)_{p,\{x_t\}} \nabla T. \tag{5}$$

The coefficients for ∇x_t and ∇T can be analytically determined. In addition, we will use the dependence of x_j on the mass fractions of chemical elements, temperature, and pressure,

$$x_t = x_t \left(c_1 \ldots c_{N_a - 1},\ p,\ T \right),$$

where N_a is the number of chemical elements forming the mixture. Then ∇x_t is a function of Δc_a and ΔT.

$$\nabla x_t = \sum_{a=1}^{N_a - 1} \left(\frac{\partial x_t}{\partial c_a} \right)_{c_b \neq c_a, p, T} \nabla c_a + \left(\frac{\partial x_t}{\partial T} \right)_{\{c_a\}, p} \Delta T. \tag{6}$$

The coefficient for the gradients in Eq. (6) can be calculated both numerically on a computer and analytically. Substituting Eq. (6) in (5), Eq. (5) in (2), and Eq. (2) in (1) and grouping terms with identical gradients, we obtain the desired diffusion coefficients:

$$D_{ab} = \sum_{i,j=1}^{N} u_{ia} \frac{n}{\rho} m_j D_{ij} x_j \sum_{t=1}^{N_a + 1} \frac{u_{jt}}{x_t} \left(\frac{\partial x_t}{\partial c_b} \right)_{c_a \neq c_b, p, T};$$

$$D_a^T = T \sum_{i,j=1}^{N} u_{ia} \frac{n}{\rho} m_j D_{ij} x_j \left[\frac{1}{x_j} \left(\frac{\partial x_j}{\partial T} \right)_{p,\{x_t\}} + \sum_{t=1}^{N_a+1} \frac{u_{jt}}{x_t} \left(\frac{\partial x_t}{\partial T} \right)_{p,\{c_a\}} \right];$$

$$D_a^E = \sum_{i,j=1}^{N} u_{ia} m_j \frac{n_i}{\rho} D_{ij} z_j.$$

The mass flow of a chemical element here is represented in the form

$$\mathbf{I}_a = n m_a \left(\sum_{b=1}^{N_a-1} D_{ab} \nabla c_b + D_a^T \nabla \ln T + D_a^E \frac{e\mathbf{E}}{kT} \right). \qquad (7)$$

To obtain the effective thermal-conductivity coefficients we proceed, as in [4], on the basis of an equation for a heat flow,

$$\mathbf{I}_q = -\lambda \nabla T + \sum_{i=1}^{N} h_i \frac{\mathbf{I}_i}{m_i},$$

where λ is the thermal conductivity in the "frozen' mixture of gases and h_i is the enthalpy for one particle of type i. Following transformations similar to those used in obtaining Eq. (7), we find the effective coefficients of thermal conductivity,

$$\lambda_1 = T\lambda - T \sum_{i,j=1}^{N} h_i \frac{n^2}{\rho} m_j D_{ij} x_j \left[\frac{1}{x_j} \left(\frac{\partial x_j}{\partial T} \right)_{p,\{x_t\}} + \sum_{t=1}^{N_a+1} \frac{u_{jt}}{x_t} \left(\frac{\partial x_t}{\partial T} \right)_{p,\{c_a\}} \right];$$

$$\lambda_a = -\sum_{i,j=1}^{N} h_j \frac{n^2}{\rho} m_j D_{ij} x_j \sum_{t=1}^{N_a+1} \frac{u_{jt}}{x_t} \left(\frac{\partial x_t}{\partial c_a} \right)_{c_b \neq c_a, p, T};$$

$$\lambda_E = -\sum_{i,j=1}^{N} h_i \frac{n}{\rho} m_j D_{ij} n_j z_j.$$

Then the heat flow is written in the form

$$\mathbf{I}_q = -\lambda_1 \nabla \ln T - \sum_{a=1}^{N_a-1} \lambda_a \nabla c_a - \lambda_E \frac{e\mathbf{E}}{kT}. \qquad (8)$$

We have omitted in Eqs. (7) and (8) a term on the order of $\sim \sum_{k=1}^{N} (\rho_k/\rho) \mathbf{F}_k$.

Unlike previous works [4], no artificial constraints are imposed on the mass flows in finding the heat flow (8). The coefficients of thermal conductivity defined above do not coincide with the corresponding equations in a completely ionized plasma obtained in [5], since the calculation of multicomponent diffusion coefficients D_{ij} is carried out taking into account a finite number of Sonin polynomials.

Let us present as an example results from a numerical calculation of the effective diffusion coefficients in a hydrogen–helium mixture for parameters characteristic for the entry of a space vehicle into the atmosphere of Jupiter.

A mixture was considered at a pressure of 10 atm and temperatures between 3000°K and 8000°K and it was assumed that a single hydrogen dissociation reaction occurs. Taking into account the rate of the chemical reactions [6], we obtain $\varepsilon \gg 1$, i.e., the mixtrue is chemically balanced relative to diffusion and consists of the components H_2, H, and He. The degree of ionization is insignificant (at 8000°K, approximately 10^{-4}). The thermodynamic composition was calculated using a previous technique [7]. Figure 1 depicts the effective D_{He-H}, D_{He}^T, and binary D_{He-H} diffusion coefficients.

In this case $D_{He-H} > 0$, and D_{He}^T changes sign, but are on the same order of magnitude. It is possible that the sign of D_{He-H} remains constant only by accident, since it does not follow from the positive entropy derivation. We will show this by writing an equation for entropy generation suitable for investigating diffusion [1],

$$\sigma = -\frac{1}{T}\sum_{k=1}^{N} \mathbf{I}_k \nabla_T \mu_k,$$

where μ_k is the chemical potential of the k-th component. By the Curie law,

$$\mathbf{I}_k = -\sum_{j=1}^{N} \alpha_{kj} \nabla_T \mu_k .$$

The coefficients α_{kj} are symmetric and related to D_{ij} [3]. Since

$$\mu_k = \mu_k(\{x_t\}, p, T);\ x_t = x_t(c_1 \ldots c_{N_a - 1}, p, T),$$

for constant p and T in a model of local thermodynamic equilibrium, we obtain, as was done above, entropy generation for the case of a two-element mixture,

$$\sigma = \frac{1}{T}\sum_{k,j,t,l} \alpha_{kj} \left(\frac{\partial \mu_j}{\partial x_t}\right)_{p,T} \left(\frac{\partial x_t}{\partial c_a}\right)_{p,T} \left(\frac{\partial \mu_k}{\partial x_l}\right)_{p,T} \left(\frac{\partial x_l}{\partial c_a}\right)_{p,T} (\Delta c_a)^2, \tag{9}$$

which must be positive. The equation for the mass flow of element *a* has the form [under the same assumptions as in Eq. (9)]

$$\mathbf{I}_a = \sum_{k,j,t} \frac{u_{ka} m_a}{m_k} \alpha_{kj} \left(\frac{\partial \mu_j}{\partial x_t}\right)_{p,T} \left(\frac{\partial x_t}{\partial c_a}\right)_{p,T} \nabla c_a . \tag{10}$$

We cannot definitely conclude regarding the sign of the effective diffusion coefficients by comparing Eqs. (9) and (10). In the same sense, there is no definite sign to the effective coefficients of thermal conductivity.

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