EFFECT OF CHEMICAL REACTIONS ON THERMAL CONDUCTIVITY AND DIFFUSION FLUXES IN PLASMA

A. A. Luchina

UDC 533.932

On the basis of rigorous kinetic theory, we consider the question of the effect of chemical reactions on thermal conductivity and diffusion fluxes in plasma of arbitrary composition with no magnetic fields under conditions of local chemical equilibrium.

When there is a temperature gradient, the heat and mass fluxes arising in plasma depend to a considerable extent on the chemical reactions taking place under the existing conditions. The composition of the plasma and the nature of the chemical reactions are determined by the thermodynamic parameters and external fields.

Over a wide range of temperatures and pressures, plasma is a multicomponent mixture consisting of molecules and atoms, positively and negatively charged ions (with single or multiple charges), and electrons. Chemical reactions of various kinds may take place in such plasma: dissociation reactions, reactions of electron and ion formation (positive and negative ions, atomic, molecular, or complex ions, with one, two, or more elementary charges), and also various kinds of recombination reactions. As a result of chemical reactions, additional fluxes of mass and energy are created in the gas mixture. The resulting effect depends on all the chemical reactions taking place under the existing conditions in the plasma.

The literature contains some estimates for the contribution of chemical reactions to the thermal conductivity of plasma in certain special cases [1-5]. In [1-4] the calculations are carried out on the basis of elementary kinetic theory for plasma consisting of a single chemical element. In [5] rigorous kinetic theory is used for considering a plasma without external fields, which consists of atoms of different chemical elements, singly charged ions, and electrons, characterized by reactions of a single type: $A \rightleftarrows A^+ + e^-$.

The case of a multicomponent mixture of nonionized gases has been investigated in [6].

The question of thermal conductivity and mass transfer in multicomponent plasma of arbitrary composition in which chemical reactions of various kinds (dissociations, ionizations of all degrees, and corresponding recombinations) are taking place is a matter of some practical interest.

In the present paper we make use of rigorous kinetic theory to calculate the component of thermal conductivity λ_r resulting from chemical reactions of various kinds in a multicomponent plasma of arbitrary composition under stationary conditions. We also calculate diffusion fluxes and gradients of kilogram-mole fractions of plasma components, taking account of the chemical reactions. The calculations are carrried out under the following assumptions:

1) magnetic fields may be disregarded;
2) the gradients of the pressure p are zero;
3) there is local chemical equilibrium;
4) thermal diffusion may be disregarded because it is an infinitesimal of higher order than ordinary diffusion;
5) deviations from thermodynamic equilibrium are slight (this justifies the use of the Chapman–Enskog method for solving the kinetic equations).

S. Ordzhonikidze Institute of Aviation, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 29, No. 4, pp. 706-715, October, 1975. Original article submitted May 29, 1974.

In Sec. 1 we give the calculations for λ_r and the vectors of the kilogram-mole fluxes W_a of the components ($a = 1, 2, \ldots, \nu$).

In Sec. 2 we calculate the gradients of the kilogram-mole fractions of the components x_a ($a = 1, 2, \ldots, \nu$). In Sec. 3 we consider the stationary case with no external fields.

1. For given values of the thermodynamic parameters in a plasma of known chemical composition there are a specific number μ of independent reactions ($\mu < \nu$): the equation for any of these reactions cannot be obtained as a linear combination of the equations of the other reactions. The equations for all the independent reactions can be written in the form of the following system:

$$X^i = \sum_{k=\mu+1}^{\nu} n_{ik} X^k \quad (i = 1, 2, \ldots, \mu). \tag{1}$$

The left sides of Eqs. (1) are the symbols of the components taking part in one reaction, while the right sides contain the symbols for those taking part in two or more reactions. It is therefore convenient to refer to the components with indices k($k = \mu + 1, \mu + 2, \ldots, \nu$) as independent components, and to those with indices i($i = 1, 2, \ldots, \mu$) as dependent components or reaction products. In particular, the chemical elements and the electron component may be regarded as independent components. Inert gases should also be considered independent components (i.e., included in the group of k-components), for which $n_{ik} = 0$ for all values of i. For reactions numbered i in which some k-component does not participate, we write $n_{ik} = 0$.

For example, for air at high temperatures the most important chemical reactions are the following [7, 8]:

$$1)\ N_2 \rightleftarrows 2N;\ 2)\ O_2 \rightleftarrows 2O;\ 3)\ N \rightleftarrows N^+ + e^-;$$
$$4)\ O \rightleftarrows O^+ + e^-;\ 5)\ NO \rightleftarrows N + O;\ 6)\ NO \rightleftarrows NO^+ + e^-;$$
$$7)\ N_2 + O_2 \rightleftarrows 2NO.$$

However, in calculating the transfer coefficients for air in the relevant region of thermodynamic parameters, we cannot use the above system of equations for the chemical reactions. The independent equations of the chemical reactions under consideration must be written in the following form:

$$1)\ N_2 \rightleftarrows 2N;\quad 2)\ O_2 \rightleftarrows 2O;\quad 3)\ N^+ \rightleftarrows N - e^-;$$
$$4)\ O^+ \rightleftarrows O - e^-;\quad 5)\ NO \rightleftarrows N + O;\quad 6)\ NO^+ \rightleftarrows N + O - e^-.$$

This is because the Butler–Brokaw formula [6] can be extended to the case of a multicomponent mixture in which there are simultaneous reactions of dissociation and ionization provided that the equations of the chemical reactions are written in the form of the system (1).

To calculate the components of the thermal conductivity λ_r, we make use of the heat balance of a chemically reacting mixture of gases [9]. The heat-flux component q_r due to the chemical reactions is given by the following expression:

$$\mathbf{q}_r = \sum_{a=1}^{\nu} H_a \mathbf{W}_a. \tag{2}$$

The vector W_a is related to the diffusion velocity V_a of component a by the known formula

$$\mathbf{W}_a = \frac{x_a p}{RT} \mathbf{V}_a \quad (a = 1, 2, \ldots, \nu). \tag{3}$$

Taking account of the condition of equilibrium of the kilogram-mole fluxes [5-7],

$$\mathbf{W}_k = -\sum_{i=1}^{\mu} n_{ik}\mathbf{W}_i \quad (k = \mu+1,\ \mu+2,\ \ldots,\ \nu), \tag{4}$$

we transform the right side of relation (2) in such a way that it will contain the heats of chemical reaction in explicit form: then the vector $\mathbf{q}_r$ can be expressed by using only the kilogram-mole vectors of the fluxes $\mathbf{W}_i$ of the dependent components:

$$\mathbf{q}_r = -\sum_{i=1}^{\mu} \mathbf{W}_i \Delta H_i, \tag{5}$$

where

$$\Delta H_i = \sum_{k=\mu+1}^{\nu} n_{ik} H_k - H_i \quad (i = 1,\ 2,\ \ldots,\ \mu). \tag{6}$$

As will be shown later, under the conditions of the problem considered here the diffusion velocities $\mathbf{V}_i$ and the flux vectors $\mathbf{W}_i$ are proportional to the gradient of the temperature T, and therefore the relation (2) can be reduced to the form

$$\mathbf{q}_r = -\lambda_r \operatorname{grad} T. \tag{7}$$

The coefficient of proportionality λ_r between the vector quantities $\mathbf{q}_r$ and grad T represents the component of the thermal conductivity due to the chemical reactions.

The expressions for the vectors $\mathbf{W}_i$ can be obtained by using the equations for the chemical equilibrium of the reactions:

$$\prod_{k=\mu+1}^{\nu} \frac{x_k^{n_{ik}}}{x_i} = \frac{K_{pi}(T)}{p^{\nu_i}}, \quad \nu_i = \sum_{k=\mu+1}^{\nu} n_{ik} - 1 \quad (i = 1,\ 2,\ \ldots,\ \mu) \tag{8}$$

and the Van't Hoff isochor equations:

$$\frac{d \ln K_{pi}}{dT} = \frac{\Delta H_i}{RT^2} \quad (i = 1,\ 2,\ \ldots,\ \mu), \tag{9}$$

where K_{pi} is the so-called equilibrium constant, which depends on temperature. Performing some simple transformations and eliminating the quantities $K_{pi}(T)$ from these equations, on condition that grad p = 0, we have

$$\sum_{l=\mu+1}^{\nu} \frac{n_{jl}}{x_l} \operatorname{grad} x_l - \frac{1}{x_j} \operatorname{grad} x_j = \frac{\Delta H_j}{RT^2} \operatorname{grad} T \tag{10}$$

$$(j = 1,\ 2,\ \ldots,\ \mu).$$

When we have no thermal diffusion and no pressure gradients, in the first approximation of the Chapman–Enskog method the gradients of the kilogram-mole fractions of the components are connected with the flux vectors of the kilogram-mole components and the forces acting on the components by the well-known relation [9]

$$\sum_{\substack{b=1 \\ (b \neq a)}}^{\nu} \frac{RT}{p\mathcal{D}_{ab}} (x_a \mathbf{W}_b - x_b \mathbf{W}_a) = \operatorname{grad} x_a - \frac{n_a m_a}{p\rho} \left(\frac{\rho}{m_a} \mathbf{F}_a - \sum_{b=1}^{\nu} n_b \mathbf{F}_b \right) \quad (a = 1,\ 2,\ \ldots,\ \nu). \tag{11}$$

When there are no magnetic fields or other external influences on the neutral components,

$$\mathbf{F}_a = Z_a e \mathbf{E} \quad (a = 1,\ 2,\ \ldots,\ \nu) \tag{12}$$

(for an electron Z = –1, for a neutral particle Z = 0), and

$$\sum_{\substack{b=1 \\ (b \neq a)}}^{\nu} \frac{RT}{p\mathcal{D}_{ab}} (x_a \mathbf{W}_b - x_b \mathbf{W}_a) = \operatorname{grad} x_a - \frac{n x_a}{p} Z_a e \mathbf{E} + \frac{n x_a m_a}{p\rho} \left(\sum_{b=1}^{\nu} n_b Z_b e \right) \mathbf{E} \tag{13}$$

$$(a = 1,\ 2,\ \ldots,\ \nu).$$

For a quasineutral plasma the last term of formula (13) vanishes, and the formula can be written as

$$\sum_{\substack{b=1 \\ (b \neq a)}}^{\nu} \frac{RT}{p\mathcal{D}_{ab}} (x_a \mathbf{W}_b - x_b \mathbf{W}_a) = \operatorname{grad} x_a - \frac{n x_a}{p} Z_a e \mathbf{E} \tag{14}$$

$$(a = 1,\ 2,\ \ldots,\ \nu).$$

From this we obtain the following expressions for the gradients of the kilogram-mole fractions of the components:

$$\operatorname{grad} x_a = \sum_{\substack{i=1 \\ (i \neq a)}}^{\mu} \frac{RT}{p\mathcal{D}_{ia}} (x_a \mathbf{W}_i - x_i \mathbf{W}_a) + \sum_{\substack{k=\mu+1 \\ (k \neq a)}}^{\nu} \frac{RT}{p\mathcal{D}_{ka}} (x_a \mathbf{W}_k - x_k \mathbf{W}_a) + \frac{n x_a Z_a e}{p} \mathbf{E} \quad (a = 1,\ 2,\ \ldots,\ \nu). \tag{15}$$

The right sides of the relations (15) differ from the expressions obtained by Butler and Brokaw [6] for the gradients of the concentrations of the components of chemically reacting neutral gaseous mixtures in that they include terms involving the electric field E.

The value of E in the plasma is nonzero not only when there are external electric fields, but also when there are no such external fields. Thus, the specific nature of the problem concerning the effect of chemical reactions on heat and mass transfer in an ionized gas (unlike the proglem solved by Butler and Brokaw for nonionized gas mixtures) lies in the fact that the system we are considering is subject to the forces $\mathbf{F}_a$.

Substituting the expressions (15) found above for the gradients of the concentrations of the components into relation (10), we transform it to obtain

$$\frac{\Delta H_j}{RT^2} \operatorname{grad} T = \sum_{i=1}^{\mu} A_{ij} \mathbf{W}_i + \left(\sum_{l=\mu+1}^{\nu} \frac{n_{jl} n Z_l e}{p} \right) \mathbf{E} - \frac{n Z_j e}{p} \mathbf{E}, \tag{16}$$

where

$$A_{ij} = A_{ji} = \sum_{l=\mu+1}^{\nu} \sum_{\substack{k=\mu+1 \\ (k \neq l)}}^{\nu} \frac{RT}{p\mathcal{D}_{lk}} \left(\frac{x_k}{x_l} n_{jl} n_{il} - n_{jl} n_{ik} \right) + \sum_{l=\mu+1}^{\nu} \sum_{p=1}^{\mu} \frac{RT}{p\mathcal{D}_{pl}} \frac{x_p}{x_l} n_{jl} n_{il} + \sum_{l=\mu+1}^{\nu} \frac{RT}{p} \left(\frac{n_{jl}}{\mathcal{D}_{il}} + \frac{n_{il}}{\mathcal{D}_{jl}} \right) - \frac{RT}{p\mathcal{D}_{ij}} \tag{17}$$

$$(i,\ j = 1,\ 2,\ \ldots,\ \mu; \quad i \neq j),$$

$$A_{jj} = \sum_{l=\mu+1}^{\nu} \sum_{k=\mu+1}^{\nu} \frac{RT}{p\mathcal{D}_{lk}} \left(\frac{x_k}{x_l} n_{jl}^2 - n_{jl} n_{jk} \right) + \sum_{l=\mu+1}^{\nu} \sum_{p=1}^{\mu} n_{jl}^2 \frac{RT}{p\mathcal{D}_{pl}} \cdot \frac{x_p}{x_l} + 2 \sum_{l=\mu+1}^{\nu} \frac{RT}{p\mathcal{D}_{jl}} n_{jl} + \sum_{\substack{b=1 \\ (b \neq j)}}^{\nu} \frac{RT}{p\mathcal{D}_{jb}} \cdot \frac{x_b}{x_j} \tag{18}$$

$$(j = 1,\ 2,\ \ldots,\ \mu).$$

By the law of conservation of charge, the last two terms on the right in the system (16) compensate each other, and the solution of the system can be written in the form

$$\mathbf{W}_i = \frac{1}{RT^2}\,\frac{\begin{vmatrix} A_{11}A_{12}\ldots A_{1,i-1}\Delta H_1 A_{1,i+1}\ldots A_{1\mu} \\ A_{21}A_{22}\ldots A_{2,i-1}\Delta H_2 A_{2,i+1}\ldots A_{2\mu} \\ \ldots\ldots\ldots\ldots\ldots \\ A_{\mu 1}A_{\mu 2}\ldots A_{\mu,i-1}\Delta H_\mu A_{\mu,i+1}\ldots A_{\mu\mu} \end{vmatrix}}{\begin{vmatrix} A_{11}A_{12}\ldots A_{1\mu} \\ A_{21}A_{22}\ldots A_{2\mu} \\ \ldots\ldots \\ A_{\mu 1}A_{\mu 2}\ldots A_{\mu\mu} \end{vmatrix}}\,\mathrm{grad}\,T. \tag{19}$$

From this it can be seen that the vectors of the kilogram-mole fluxes W_i are proportional to grad T. Substituting the values found for W_i into relation (5), we obtain an expression for the components of the thermal conductivity λ_r:

$$\lambda_r = -\frac{1}{RT^2}\cdot\frac{\begin{vmatrix} A_{11}A_{12}\ldots A_{1\mu}\Delta H_1 \\ \ldots\ldots \\ A_{\mu 1}A_{\mu 2}\ldots A_{\mu\mu}\Delta H_\mu \\ \Delta H_1\Delta H_2\ldots\Delta H_\mu\ 0 \end{vmatrix}}{\begin{vmatrix} A_{11}\ldots A_{1\mu} \\ \ldots \\ A_{\mu 1}\ldots A_{\mu\mu} \end{vmatrix}}. \tag{20}$$

Formula (20), giving the value of the components of the thermal conductivity λ_r resulting from the chemical reactions in a plasma of arbitrary composition, is a generalization of the formula obtained by Brokaw and Butler [6] for nonionized gases. In obtaining the values of the A_{ij}, we take account of the dissociation and ionization reactions [formulas (17) and (18)].

The diffusion fluxes of the dependent components can be calculated directly by means of formulas (19). The diffusion fluxes of the independent components can be found by using relations (4):

$$\mathbf{W}_k = \frac{1}{RT^2}\,\frac{\begin{vmatrix} A_{11}\ldots A_{1\mu}\Delta H_1 \\ \ldots\ldots \\ A_{\mu 1}\ldots A_{\mu\mu}\Delta H_\mu \\ n_{1k}\ldots n_{\mu k}\ 0 \end{vmatrix}}{\begin{vmatrix} A_{11}\ldots A_{1\mu} \\ \ldots \\ A_{\mu 1}\ldots A_{\mu\mu} \end{vmatrix}}\,\mathrm{grad}\,T. \tag{21}$$

It should be noted that relations (20), (19), and (21), giving the components of the thermal conductivity λ_r and the diffusion fluxes in the plasma, are valid both when there is an external electric field and when there is no such field. The dependence of the quantities considered above on the intensity of the electric field E is contained in the formulas in implicit form, since an electric field in the plasma affects its composition and the nature of the chemical reactions.

The expressions obtained in the case of a multicomponent quasineutral plasma for the components of thermal conductivity λ_r [formula (20)] and the vectors of the kilogram-mole fluxes of the components W_i and W_k [formulas (19) and (21)] resulting from chemical reactions of various kinds can be used for calculating the thermal conductivity and the diffusion fluxes in an ionized gas in the case when the quasineutrality condition is not satisfied. To show this, we note that the derivation of the above-mentioned relations is based on the system of equations (16), which holds with sufficient accuracy even when the quasineutrality condition is not satisfied. In this case the last term of formula (13) cannot be omitted, and as a result the right sides of Eqs. (16) must be supplemented by the expressions

$$-\frac{n}{p\rho}\sum_{a=1}^{\nu} n_a Z_a e\left(\sum_{l=\mu+1}^{\nu} n_{jl} m_l - m_j\right)\mathrm{E} \quad (j=1,\ 2,\ \ldots,\ \mu).$$

However, by the law of conservation of mass, in any j-th reaction the term in parentheses in these expressions can be set equal to zero. The error resulting from this does not exceed $10^{-3}\%$ and arises from the fact that in the energy (mass) balance equation the thermal effect of the reaction has not been taken into account.

2. Diffusion fluxes caused by chemical reactions in a nonuniformly heated plasma cause gradients of concentration of the components which are linear functions of the temperature gradient. The gradients of the concentrations of charged components are also affected by electric fields existing in the plasma; the concentration gradients will also be linear functions of the electric field intensity.

Using formula (4) to eliminate from relations (15) the kilogram-mole vectors of the fluxes of the independent components W_k ($k = \mu + 1,\ \mu + 2,\ \ldots,\ \nu$) and substituting into them the expressions (19) for the kilogram-mole vectors of the fluxes of the dependent components W_i ($i = 1,\ 2,\ \ldots,\ \mu$), we obtain the values of the gradients of the kilogram-mole fractions of the dependent and independent components, respectively:

$$\operatorname{grad} x_j = \frac{1}{RT^2\Delta}\sum_{p=1}^{\mu}\sum_{i=1}^{\mu}\Delta H_p\left[(-1)^{i+p} x_j \Delta_{pi}\left(\frac{RT}{p\mathcal{D}_{ij}} - \sum_{k=\mu+1}^{\nu}\frac{RT}{p\mathcal{D}_{kj}} n_{ik}\right) - (-1)^{j+p}\Delta_{pj}\sum_{a=1}^{\nu}\frac{RT}{p\mathcal{D}_{aj}} x_a\right]\operatorname{grad} T + \frac{n x_j Z_j e}{p}\mathrm{E} \quad (22)$$

$$(j = 1,\ 2,\ \ldots,\ \mu);$$

$$\operatorname{grad} x_l = \frac{1}{RT^2\Delta}\sum_{p=1}^{\mu}\sum_{i=1}^{\mu}(-1)^{p+i}\Delta H_p\Delta_{pi}\left[x_l\left(\frac{RT}{p\mathcal{D}_{il}} - \sum_{k=\mu+1}^{\nu}\frac{RT}{p\mathcal{D}_{kl}} n_{ik}\right) + \sum_{a=1}^{\nu}\frac{RT x_a}{p\mathcal{D}_{al}} n_{il}\right]\operatorname{grad} T + \frac{n x_l Z_l e}{p}\mathrm{E} \quad (23)$$

$$(l = \mu + 1,\ \mu + 2,\ \ldots,\ \nu),$$

where Δ is the determinant in the denominator of the expression (19) for the W_i and the Δ_{ji} are its minors.

If the quasineutrality condition is not satisfied, relations (22) and (23) must be changed. Their right sides must be supplemented by the terms

$$-\frac{n x_j m_j}{p\rho}\left(\sum_{b=1}^{\nu} n_b Z_b e\right)\mathrm{E} \text{ and } -\frac{n x_l m_l}{p\rho}\left(\sum_{b=1}^{\nu} n_b Z_b e\right)\mathrm{E},$$

respectively.

3. If there is no external electric field, there is in the plasma an internal electric field caused by the separation of charges that takes place as a result of the unequal diffusion velocities of particles with different masses.

In the stationary case, when there is no leakage of charge to the walls, the vector of the density of the electric current j is equal to zero and the value of the external electric field intensity is found from the following relation [10]:

$$\mathrm{E} = \kappa T\,\frac{\sum\limits_{a=1}^{\nu}\sum\limits_{b=1}^{\nu} Z_a M_a D_{ab}\operatorname{grad} x_b}{\sum\limits_{a=1}^{\nu}\sum\limits_{b=1}^{\nu} Z_a M_b D_{ab} x_b Z_b e}. \quad (24)$$

In this case the gradients of the concentrations of the plasma components are determined by the temperature gradients.

Substituting the expressions (24) into the relations (14), we obtain a linear system of ν equations in the ν unknowns grad x_b ($b = 1, 2, \ldots, \nu$):

$$\sum_{b=1}^{\nu} B_{ab} \operatorname{grad} x_b = \mathbf{A}_a \quad (a = 1, 2, \ldots, \nu), \tag{25}$$

where

$$\mathbf{A}_a = \sum_{b=1}^{\nu} \frac{RT}{p\mathcal{D}_{ab}} (x_a \mathbf{W}_b - x_b \mathbf{W}_a) \quad (a = 1, 2, \ldots, \nu), \tag{26}$$

$$B_{ab} = \delta_{ab} - \frac{n\kappa T}{p} x_a Z_a \frac{\sum\limits_{c=1}^{\nu} Z_c M_b D_{cb}}{\sum\limits_{c=1}^{\nu}\sum\limits_{d=1}^{\nu} Z_c Z_d M_d x_d D_{cd}} \tag{27}$$

$$(a, b = 1, 2, \ldots, \nu).$$

When $a \neq b$, $B_{ab} \neq B_{ba}$; if the particles of component are not charged, then $B_{ab} = 0$ when $a \neq b$ and $B_{aa} = 1$.

The solution of the system of equations (25) can be written in the form

$$\operatorname{grad} x_a = \frac{\begin{vmatrix} B_{11} \ldots B_{1,a-1} A_1 B_{1,a+1} \ldots B_{1\nu} \\ B_{21} \ldots B_{2,a-1} A_2 B_{2,a+1} \ldots B_{2\nu} \\ \ldots\ldots\ldots\ldots\ldots \\ B_{\nu 1} \ldots B_{\nu,a-1} A_\nu B_{\nu,a+1} \ldots B_{\nu\nu} \end{vmatrix}}{\begin{vmatrix} B_{11} B_{12} \ldots B_{1\nu} \\ B_{21} B_{22} \ldots B_{2\nu} \\ \ldots\ldots \\ B_{\nu 1} B_{\nu 2} \ldots B_{\nu\nu} \end{vmatrix}} \tag{28}$$

$$(a = 1, 2, \ldots, \nu).$$

If we denote the determinant in the denominator of the right side of relation (28) by the symbol $\Delta^{(\nu)}$ and its minors by the symbols $\Delta_{bc}^{(\nu)}$ and make use of the expressions (4), (22), and (23), we can transform formula (28) to the form

$$\operatorname{grad} x_a = -\frac{1}{RT^2} \frac{\begin{vmatrix} A_{11} \ldots A_{1\mu} \Delta H_1 \\ \ldots\ldots\ldots \\ A_{\mu 1} \ldots A_{\mu\mu} \Delta H_\mu \\ G_{1a} \ldots G_{\mu a}\ 0 \end{vmatrix}}{\begin{vmatrix} A_{11} \ldots A_{1\mu} \\ \ldots\ldots \\ A_{\mu 1} \ldots A_{\mu\mu} \end{vmatrix}} \operatorname{grad} T \tag{29}$$

$$(a = 1, 2, \ldots, \nu),$$

where

$$G_{ia} = \frac{RT}{p\Delta^{(\nu)}} \sum_{b=1}^{\nu} (-1)^{b+a} \Delta_{ba}^{(\nu)} x_b \left[\frac{1 - (-1)^{i-b} \Delta_{ia}^{(\nu)} / \Delta_{ba}^{(\nu)}}{\mathcal{D}_{ib}} - \sum_{k=\mu+1}^{\nu} \frac{1 - (-1)^{k-b} \Delta_{ka}^{(\nu)} / \Delta_{ba}^{(\nu)}}{\mathcal{D}_{kb}} n_{ik} \right] \tag{30}$$

$$(i = 1, 2, \ldots, \mu;\ a = 1, 2, \ldots, \nu).$$

Formula (29) will be true even if the quasineutrality condition is not satisfied. Only the form of the coefficients B_{ab} is changed; instead of relations (27) we have

$$B_{ab}=\delta_{ab}-\frac{n\kappa T}{p}x_a\left(Z_a+\frac{m_a}{\rho}\sum_{c=1}^{\nu}n_cZ_c\right)\frac{\sum\limits_{d=1}^{\nu}Z_dM_bD_{db}}{\sum\limits_{c=1}^{\nu}\sum\limits_{d=1}^{\nu}Z_cZ_dM_dx_dD_{cd}} \qquad (31)$$

$$(a,\ b=1,\ 2,\ \ldots,\ \nu).$$

From the above-determined concentration gradients grad x_a ($a = 1, 2, \ldots, \nu$) we can calculate the mass fluxes M_aW_a in the plasma for the stationary case:

$$M_a\mathbf{W}_a=\frac{p^2}{\rho R^2T^2}\sum_{b=1}^{\nu}M_aM_bD^*_{ab}\,\mathrm{grad}\,x_b \quad (a=1,\ 2,\ \ldots,\ \nu), \qquad (32)$$

where the D^*_{ab} are the effective coefficients of diffusion of the multicomponent mixture, given by the relations

$$D^*_{ab}=D_{ab}-\frac{\left(\sum\limits_{c=1}^{\nu}M_cD_{ac}x_cZ_c\right)\left[\sum\limits_{c=1}^{\nu}Z_c\left(D_{cb}-\frac{M_a}{M_b}D_{ca}\right)\right]}{\sum\limits_{c=1}^{\nu}\sum\limits_{d=1}^{\nu}Z_cZ_dM_dD_{cd}x_d} \qquad (33)$$

$$(a,\ b=1,\ 2,\ \ldots,\ \nu).$$

NOTATION

p, pressure; T, absolute temperature; k, Boltzmann constant; R, universal gas constant; n, total concentration of particles; n_a, m_a, and M_a, concentration of particles of component a, mass of a particle, and weight of a kilogram-mole of component a, respectively; ρ, average density of the plasma; e, absolute value of the elementary charge; Z_a, charge of a particle of component a in units of e; V_a, W_a, and H_a, diffusion velocity, vector of kilogram-mole flux, and enthalpy of 1 kilogram-mole of component a, respectively; x_a, kilogram-mole fraction of component a; λ_r and q_r, components of thermal conductivity and heat flux resulting from the chemical reactions in the plasma; X^k, X^l, and X^m, chemical symbols of independent components k, l, and m, respectively; X^i, X^j, X^p, chemical symbols of reaction-product components i, j, and p, respectively; n_{ik}, stoichiometric coefficient of component k in reaction number i; ΔH_i and K_{pi}, heat of reaction and equilibrium constant of reaction number i; $\mathscr{D}_{ab}$, coefficient of diffusion of a binary mixture of components a and b; D_{ab}, mutual diffusion coefficient of a multicomponent gas mixture for components a and b; **E**, vector of electric field intensity in the plasma; $\mathbf{F}_a$, force acting on a particle of component a.

LITERATURE CITED

1. W. Finkelburg and G. Mecker, Electric Arcs and Thermal Plasma [Russian translation], IL, Moscow (1961).
2. V. Lokhte-Khol'greven, Usp. Fiz. Nauk, 72, No. 3, 521 (1960).
3. F. Burhorn, Z. Phys., 155, No. 1, 42 (1952).
4. H. Pelzer, Proceedings of the Fifth International Conference on Ionization Phenomena in Gases, Vol. 1, Amsterdam (1962), p. 846.
5. I. A. Krinberg, Teplofiz. Vys. Temp., 3, 838 (1965).
6. J. N. Butler and R. S. Brokaw, J. Chem. Phys., 26, 1636 (1957).
7. Peng Tsai-cheng and A. L. Pindrokh, Vopr. Raketn. Tekh., No. 12, 3 (1962).
8. P. P. Kulik and N. V. Ermokhin, "Thermophysical properties of liquids and gases at high temperatures and plasma," in: Proceedings of the All-Union Conference on Thermophysical Properties of Substances at High Temperatures [in Russian], Vol. 2, Novosibirsk (1966), p. 347.
9. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, Wiley (1964).

10. W. J. Lick and H. W. Emmons, Transport Properties of He from 200°K to 50,000°K, Cambridge University Press (1965).

INVESTIGATION OF THE IONIZATION RATE IN A LOW-TEMPERATURE NONEQUILIBRIUM PLASMA FLUX

G. V. Babkin, A. V. Potapov,
V. V. Proshkin, and L. E. Tsvetkova

UDC 533.9.07

Results are presented of a determination of the ionization rate constants of a low-temperature lithium plasma on the basis of measuring the plasma parameters in a longitudinal discharge and of numerical processing of the experimental data.

The flow of a low-temperature plasma in the channel of a magnetogasdynamic accelerator is characterized by an essential separation of the electron temperature from the heavy-particle temperature and by spoilage of the ionization equilibrium. Taking account of the ionization and recombination kinetics is a distinctive singularity of methods of computing plasma fluxes which yield the most confident information about the parameters of the working process. Progress in the development of such methods is slowed down because of the lack of information about the characteristics of the fundamental physical processes in a low-pressure nonequilibrium plasma and on the surface of the accelerator channel. Among these processes, a special place is occupied by volume ionization, since it is primarily one of the causes of ion generation. Evaluation of the volume ionization rate constant K in the formula for the change in charged particle concentration obtained in the ionization–recombination process

$$\frac{\partial n_e}{\partial t} = Kn_a n_e - \gamma n_e^3, \quad (n_e = n_i), \tag{1}$$

is a very complex problem whose correct solution requires the presence of reliable data over the sections of the elementary processes in addition to the production of a correct theoretical model. Since information about these quantities is limited and of inadequate confidence at this time, an experimental determination of K acquires special value. The accumulation of appropriate experimental material is also the foundation for a critical analysis of existing theoretical developments on the question under consideration and of the selection of the logical physical model of the process. It should be noted that even an estimate of the coefficients to order-of-magnitude accuracy acquires great practical value in connection with the lack of experimental data on the plasma ionization rate constants for many substances.

A method of determining the coefficient K for ionized vapors of substances with a high boiling point, based on measurements of the partial profiles of the parameters and on the integrated discharge characteristics with a subsequent special numerical processing of these data, is elucidated briefly in this paper. The method is checked out in an example of a lithium plasma.

A coaxial plasmatron of the type in [3-4] with up to 10 kW power (Fig. 1) including a hollow tungsten cathode and a nozzle-anode separated by a boron carbonitride(BCN) insulator was used to obtain the plasma flux. The plasma jet is bounded by the wall of a thin-walled ($\delta \sim 2 \cdot 10^{-4}$ m) molybdenum tube 4 ($\varnothing 3.2 \cdot 10^{-2}$ m) heated by direct heat, and joined to the nozzle-anode 2 through the insulator 3. The main purpose of the cylindrical tube ($L \approx 0.1$ m) is assurance of a steady plasma flow characterizing the preferred change in the parameters in the radial direction.

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 29, No. 4, pp. 716-721, October, 1975. Original article submitted January 2, 1975.