AN APPROXIMATE METHOD FOR CALCULATING
TRANSFER COEFFICIENTS FOR PARTIALLY
IONIZED GAS MIXTURES

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UDC 536.24

A universal method, economical in the number of calculations required, is proposed for calculating transfer coefficients for partially ionized gas mixtures with an unlimited number of components. Its use is illustrated with the example of calculating heat transfer in a flow of low-temperature plasma.

Calculating the heat and mass transfer in flows of low-temperature plasma requires data on the transfer coefficients of gas mixtures of various compositions over a wide range of temperature and pressure. Direct calculation of these values during solution of heat- and mass-transfer problems on permeable and impermeable surfaces is difficult because of the great complexity of the exact formulas of molecular theory and the limited capabilities of present computers.

Use of preexisting tabulations of viscosity and thermal conductivity coefficients is not always possible. Due to variability of the large number of parameters on which these quantities depend, the volume of the tables proves to be unusually large. Thus, there is a need for simplified methods of calculating transfer coefficients, based on semiempirical expressions for viscosity and frozen thermal conductivity. A detailed review of such expressions for neutral gas mixtures was presented in [1, 2]. Especially simple expressions can be obtained with the use of the bifurcation approximation for binary diffusion coefficients [3, 4].

In [5] the present authors proposed an approximate method for calculating multicomponent diffusion in partially ionized gas mixtures, based on the ambipolar approximation. A two-group bifurcation approximation was used for the binary diffusion coefficients. This allowed reduction of the solution of the system of equations describing multicomponent diffusion for an ν-component mixture to solution of a system of four linear equations.

This same approximation may be used to simplify the expressions for viscosity and frozen thermal conductivity.

The approximate formula for viscosity of a multicomponent gas mixture [2] has the following form:

$$\mu = \sum_{j=1}^{\nu} \frac{\mu_j x_j}{D_{jj} \sum_{k=1}^{\nu} \frac{x_k}{D_{jk}}} . \tag{1}$$

To calculate the frozen thermal conductivity it is desirable to use an analogous formula which is one variant of Vasil'eva's equation [1]

$$\lambda_f = \sum_{j=1}^{\nu} \frac{\lambda_{fj} x_j}{D_{jj} \sum_{k=1}^{\nu} \frac{x_k}{D_{jk}}} . \tag{2}$$

Simpler expressions for the thermal conductivity and viscosity coefficients of gas mixtures such as the formulas of Mann and Brokaw are not applicable under conditions of ionization [6].

The viscosity and thermal conductivity of individual components may be represented as follows:

$$\mu_j = \frac{5}{6} \cdot \frac{\rho D_{jj} M_j}{\bar{M} A_{jj}^*} , \qquad (3)$$

where

$$A_{jj}^* = \frac{\Omega_{jj}^{(2,2)}}{\Omega_{jj}^{(1,1)}} , \qquad (4)$$

$$\lambda_{jj} = \frac{5}{6} \cdot \frac{\rho D_{jj}}{\bar{M} A_{jj}^*} \left(c_{pj} + \frac{5}{4} R \right) . \qquad (5)$$

The latter expression uses Eiken's correction for internal degrees of particle freedom [1].

Calculations with Eqs.(1), (2) are made difficult by the presence of a double summation and the necessity of calculating all binary diffusion cross-coefficients, the general formula of which has the form:

$$D_{kl} = \frac{3}{8} \cdot \frac{kT}{p} \frac{\sqrt{\dfrac{\pi RT (M_k + M_l)}{2 M_k M_l}}}{\Omega_{kl}^{(1,1)}} . \qquad (6)$$

With increase in the number of components considered there is a progressive increase in the number of computations required and the memory space needed to retain the initial data required for calculation of $\Omega_{kl}^{(1,1)}$. These difficulties may be avoided if we use the two-group bifurcation approximation for the binary diffusion coefficient [5]. The two groups of components, neutrals and ions, correspond to three groups of binary diffusion coefficients: 1) neutral−neutral; 2) neutral−ion; 3) ion−ion.

For each component we introduce two factors which approximately characterize its properties in the diffusion process: F_j^n and F_j^i. The first of these refers to binary diffusion of the given component and any neutral component; the second, to binary diffusion of the given component and any ion. Thus, for the first group of diffusion coefficients we have the following approximate equality:

$$D_{kl} \approx \frac{D}{F_k^n F_l^n} , \qquad (7)$$

where D is the value of the diffusion coefficient for particles of unit molecular mass for unity value of the collision integral $\Omega_{kl}^{(1,1)}$. It has been shown [3] that for many systems of neutral components corresponding to gas mixtures often met in practice, the factors F_j^n may be selected such that Eq. (7) is satisfied with a sufficient degree of accuracy. This is due to the character of the dependence of the diffusion coefficient on molecular mass of the components and the presence of certain correlations between values of the collision integrals. Since the collision integrals for neutral particles are functions of temperatures the factors F_n^n will also be temperature dependent.

An analogous approach may be used in the presence of ionization.

For the second group of binary diffusion coefficients we use the following expression:

$$D_{kl} \approx \frac{D}{F_k^i F_l^n} . \qquad (8)$$

The subscript k here indicates a neutral component; l denotes an ion.

A special case is the diffusion of an atom and an ion of one and the same element. Upon collision of such particles resonant charge exchange occurs, which leads to relatively high values of the quantities $\Omega_{kl}^{(1,1)}$ [7], so that use of Eq. (8) is not desirable. For this case we take

$$D_{kr} = \frac{D}{\sqrt{M_k} \, \Omega_{kr}^{(1,1)}} , \qquad (9)$$

where r is the index of the particle collision with particle k which occurs with resonant charge exchange. The quantities $\Omega_{kl}^{(1,1)}$ for neutral−ion collisions, and consequently, the factors F_n^i, F_i^n are functions of temperature.

For the third group of binary diffusion coefficients

$$D_{kl} \approx \frac{D}{F_k^i F_l^i \Omega_{ii}^{(1,1)}} \, , \tag{10}$$

where $\Omega_{ii}^{(1,1)}$ is the collision integral for single charged ions. This form was chosen so that for positively charged ions $\Omega_{kl}^{(1,1)} = (z_k z_l)^2 \Omega_{ii}^{(1,1)}$ [8]. The quantities F_n^i in this case prove to be constant.

For a given system of components to be considered the factors F_j^n, F_j^i are selected such that the approximate equalities (7), (8), (10) have the smallest possible relative error. They may be calculated with the method of least squares. For example, for the first group of diffusion coefficients we use the condition

$$\sum_k \sum_l \left(\lg \frac{D}{D_{kl}} - \lg F_k^n - \lg F_l^n \right)^2 = \min. \tag{11}$$

The summation in Eq. (11) is performed over all neutral components. Differentiation of Eq. (11) produces a system of linear algebraic equations in $\ln F_j^n$, the solution of which gives F_n^n values in explicit form. The coefficients F_n^i, F_i^n and F_i^i are determined in an analogous manner. Substitution of approximations (7)-(10) in Eqs. (1), (2) with consideration of Eqs. (3)-(5) produces the following expressions for viscosity and frozen thermal conductivity:

$$\mu = \frac{5}{6} \cdot \frac{\rho D}{\overline{M}} \sum_{j=1}^{v-1} \frac{M_j x_j}{A_{jj}^*(T_j + R_j)} \, , \tag{12}$$

$$\lambda_f = \frac{5}{6} \cdot \frac{\rho D}{\overline{M}} \sum_{j=1}^{v-1} \frac{x_j \left(C_{pj} + \frac{5}{4} R \right)}{A_{jj}^*(T_j + R_j)} + \Delta \lambda_e, \tag{13}$$

$$\Delta \lambda_e = \frac{x_e \lambda_e}{D_{ee} \sum_{j=1}^{v} \frac{x_j}{D_{ej}}} \, , \tag{14}$$

where for neutrals

$$T_j = F_j^n B_{nn} + F_j^i B_{ni}, \tag{15}$$

for ions

$$T_j = F_j^n B_{in} + F_j^i B_{ii}, \tag{16}$$

for atoms and atomic ions

$$R_j = x_r (\sqrt{M_j} \, \Omega_{jr}^{(1,1)} - F_r^r F_r^j), \tag{17}$$

and for remaining particles

$$R_j = 0. \tag{18}$$

The quantities B_{kl} are defined as follows:

$$B_{nn} = \sum_n x_j F_j^n \tag{19}$$

$$B_{ni} = \sum_i x_j F_j^n \tag{20}$$

$$B_{in} = \sum_n x_j F_j^i \tag{21}$$

$$B_{ii} = \Omega_{ii}^{(1,1)} \sum_i x_j F_j^i. \tag{22}$$

In Eqs. (19), (21) summation is performed over all neutrals, and in Eqs. (20), (22), over all ions. The volume of calculations with Eqs. (12)-(22) is proportional to the number of components, which significantly simplifies

TABLE 1. Coefficients of Analytical Expressions for Approximated Factors

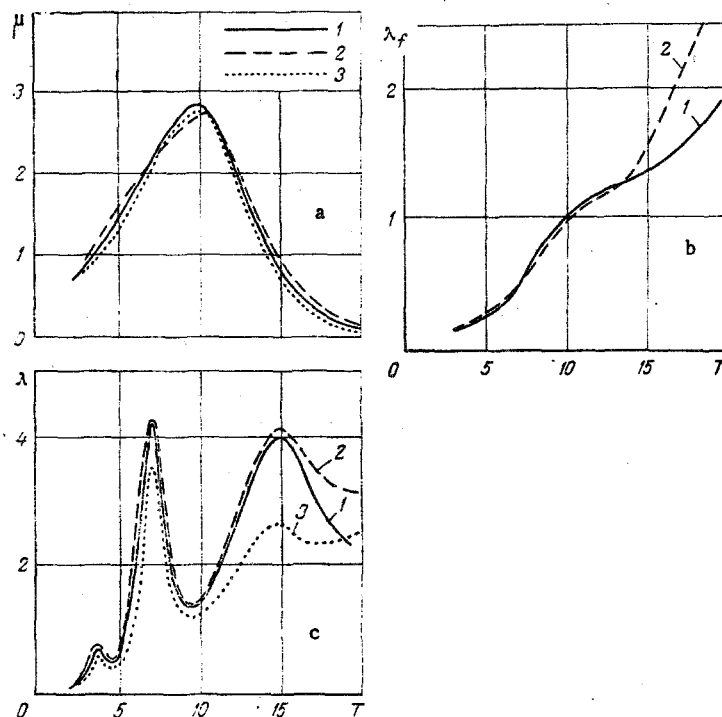| Compo-nent	F_j^n		F_j^i		Compo-nent	F_j^n		F_j^i	
	A	m	A	m		A	m	A	m
O_2	9,15	0,154	8,56	0,500	N	5,85	0,197	5,84	0,400
NO	8,93	0,098	8,46	0,500	NO^+	11,27	0,000	2,32	0,000
N_2	8,82	0,143	8,35	0,500	O^+	9,59	0,000	2,00	0,000
O	5,49	0,202	6,06	0,400	N^+	9,28	0,000	1,93	0,000

Fig. 1. Viscosity (10^{-4} N · sec/m²) (a), frozen thermal conductivity (W/m · °K) (b), and total thermal conductivity of air (W/m · °K) (c) versus temperature (10^{3} °K): 1) present study: 2) results of [8]; 3) [10].

calculations of transfer properties of mixtures with complex composition as compared to calculations with the original Eqs. (1)-(5). It is also significant that for calculations of transfer properties of mixtures with variable composition it is sufficient to retain in the computer memory a number of coefficients proportional to ν, appearing in the analytic expressions for F_j^n and F_j^i, or the values of these quantities for a number of temperatures. It is sufficient to determine the values of these coefficients once, before calculating the transfer coefficients.

To estimate the errors produced by the method described above, the transfer properties of equilibrium air at pressures of 0.1-10 atm were calculated. The total thermal conductivity of the equilibrium gas mixture was defined as the value of thermal flux generated by a unit temperature gradient. Moreover, the absence of diffusion flows of chemical element mass was required. This corresponds to Butler and Brokaw's definition of total thermal conductivity [9]. A quite detailed calculation of the transfer properties of air was performed by Sokolova [8], using formulas for higher approximations of Chapman—Enskog theory. For comparison, the resulting collision integral values were taken identical to those of [8]. The neutral—neutral and neutral—ion collision integrals in this case are power functions of temperature, which is very convenient in calculating F_j^n and F_j^i. The analytical expressions obtained for these quantities have the form
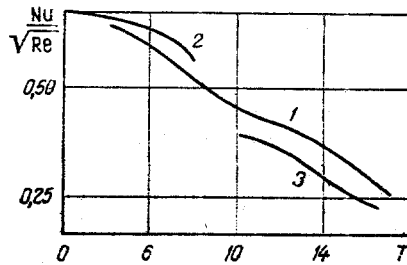
$$F_j = A_j (T \cdot 10^{-4})^{-m_j}. \tag{23}$$

Fig. 2. Dimensionless heat-transfer coefficient versus braking temperature ($10^{3\circ}$K): 1) present study; 2) Fay–Riddell calculation; 3) [12].

The values of the coefficients A_j and m_j are presented in Table 1. Then

$$D\left(\frac{M^2}{c}\right) = 0.0837\,\frac{T^{1.5}}{P}\,, \tag{24}$$

where P is in Pa.

Resulting values of the viscosity and thermal conductivity coefficients for a pressure of 1 atm are presented in Fig. 1a, b, c. Also shown are data obtained in [8, 10]. The greatest deviation of the present results from those of [8] occurs for the frozen thermal conductivity, but even in this case the error of the calculation by the approximate method does not exceed 15–20% up to temperatures producing 80% ionization. This also occurs at pressures differing from atmospheric. It has also been shown that the semiempirical expressions (1) and (2) are applicable not only for neutral gas mixtures, but also for partial ionization.

The method described herein was used to calculate heat transfer on an impermeable surface in the vicinity of the braking point of an axisymmetric blunt body in a flow of dissociated and partially ionized air. The gas composition was assumed to be in equilibrium. The flow in the boundary layer was described by the continuity equation, and conservation equations for momentum, energy, and chemical element mass in the following form:

$$\frac{\partial}{\partial x}(\rho u x) + \frac{\partial}{\partial y}(\rho v x) = 0, \tag{25}$$

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = -\frac{\partial P}{\partial x} + \frac{\partial}{\partial y}\left(\mu \frac{\partial u}{\partial y}\right), \tag{26}$$

$$\rho u \frac{\partial H}{\partial x} + \rho v \frac{\partial H}{\partial y} = \frac{\partial}{\partial y}\left(\lambda \frac{\partial T}{\partial y} - \sum_{j=1}^{v} J_j H_j\right), \tag{27}$$

$$\rho u \frac{\partial \alpha_k}{\partial x} + \rho v \frac{\partial \alpha_k}{\partial y} = -\frac{\partial}{\partial y}\sum_{j=1}^{v} \gamma_{kj} J_j. \tag{28}$$

Conditions on the external surface of the boundary layer have the form

$$H = H_e;\quad \alpha_k = \alpha_{k\infty};\quad \frac{\partial u}{\partial x} = \left(\frac{\partial u}{\partial x}\right)_e, \tag{29}$$

with boundary conditions on the wall

$$v = u = 0;\quad T = T_w;\quad \sum_{j=1}^{v} \gamma_{kj} J_j = 0. \tag{30}$$

Diffusion flows were calculated by the method of [5]. Temperature, gas composition, and the required derivatives of temperature and component concentration with respect to spatial coordinate were calculated for specified enthalpy, element concentrations, and derivatives of these quantities with respect to coordinates from conditions of thermodynamic equilibrium. The conservation equations were transformed to Dorodnitsyn–Lees variables [11, 12]. The numerical solution method is based on a finite difference scheme of second-order

accuracy. The difference equations were solved by Newton's method with matrix factorization. Results of the heat-transfer calculation for P_e = 1 atm, T_W = 2000°K are presented in Fig. 2, where

$$\frac{Nu}{\sqrt{Re}} = \frac{q_w Pr_w}{(H_e - H_w)\sqrt{\left(\frac{\partial u}{\partial x}\right)_e \rho_w \mu_w}} . \tag{31}$$

For comparison, Fig. 2 also shows calculations by the Fay−Riddell formula [11] for low braking temperatures (dissociation region) and Suslov's results [12] in the ionization region. In [12] the diffusion flows were calculated directly with the Stefan−Maxwell equation. The deviations which exist (up to 25%) are evidently due to differences in the collision integral values chosen.

On the whole the present results agree with those of [11, 12] in a completely satisfactory manner. The method of heat-transfer calculation described here may be used for gas mixtures other than air, in particular, in the presence of a draft of some other gas.

NOTATION

μ	is the viscosity;
λ_f	is the frozen thermal conductivity;
λ	is the total thermal conductivity;
ρ	is the density;
M_j	is the molecular mass;
$\overline{M}$	is the mean molecular mass;
D_{kl}	is the binary diffusion coefficient;
$\Omega_{kl}^{(1,1)}$	is the reduced collision integral;
x_j	is the molar concentration;
z_j	is the ionic charge multiplicity;
e	is the symbol for electron;
c_p	is the heat capacity;
R	is the universal gas constant;
T	is the temperature;
P	is the pressure;
k	is the Boltzmann's constant;
q	is the thermal flux;
J_j	is the diffusion flow;
α_k	is the mass concentration of element;
γ_{kj}	is the mass content of element k in component j;
H	is the enthalpy;
x, y	are the longitudinal and transverse boundary-layer coordinates;
u, v	are the longitudinal and transverse components of gas velocity in boundary layer.

Indices

e	is the braking condition;
w	is the conditions on wall;
∞	is the conditions in incident flow;
n	is neutral;
i	is the ion.

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RELATIONSHIP OF GAS PHASE MASS TRANSFER TO
THERMAL CONDUCTIVITY OF REFRACTORIES

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UDC 536.21

The problem of change in thermal resistance of pores and microcracks in refractories with occurrence of heterogeneous reactions and formation of gas with diffusion product transfer in the temperature gradient field is analyzed.

It has been demonstrated previously [1-3] that thermal resistance of the microcracks which have a marked influence on effective thermal conductivity and diffusivity of ceramics, refractories, and other porous materials is related to, among other factors, the intensity of mass-transfer processes in the gas phase. Such a process develops in microcavities filled by gas in the presence of a temperature gradient and is caused by the temperature dependence of equilibrium pressure of the gaseous products formed by heterogeneous chemical reactions and phase transformations. In this case the effective thermal conductivity of the microcracks must be supplemented by a term related to mass transfer:

$$\lambda = \sum_i j_i H_i \, \frac{\delta}{\Delta T} \, , \tag{1}$$

where j_i is the molar flow of the i-th gaseous component, H_i, its enthalpy; δ, gap thickness; ΔT, temperature change.

In [3] expressions were obtained for the effective mass flow and effective thermal conductivity of a microcrack for free-molecular (Knudsen) gas flow (λ^{Kn}). Such a regime is realized at high rarefactions in narrow gaps. However, it follows from analysis of the structure of many refractories that they contain a significant quantity of coarse pores and cracks, where at pressures of 10^2-10^5 N/m^2 gas product transfer is accomplished basically due to diffusion. The effective thermal conductivity of a microcrack in the diffusion regime λ^D is determined by the temperature and thermodynamic properties of the system, and in contrast to the parameter λ^{Kn} it is dependent on the diffusion coefficients of the molecules, their concentrations, the total gas pressure p, and the relationship between the flows j_i. In the simplest case of a binary mixture consisting of an "active" substance, i.e., one which liberates gas during a heterogeneous reaction or phase transition, and a "passive" gas, i.e., one not participating in these processes, the expression for λ^D has the form

$$\lambda^D = \frac{pp_A}{p - p_A} \cdot \frac{(\Delta H)^2}{R^2 T^3} \, , \tag{2}$$

where $D \sim p^{-1}$ is the binary diffusion coefficient; $p_A \sim \exp(-\Delta H/RT)$ is the pressure of active gas; ΔH, thermal effect of the process; R, gas constant; $T = \sqrt{T_1 T_2}$ (T_1 and T_2 are temperatures of hot and cold surfaces).

Equation (2) was obtained by solution of the diffusion equation in a plane-parallel gap with consideration of the Stefan flow [4], assuming the process occurs in equilibrium and that $\Delta T \ll T$. It is analogous to the expression for thermal conductivity of a chemically reacting gas mixture of [5], differing only by the factor $p_A/p - p_A$ produced by the Stefan mass flow.