

## INFLUENCE OF THE COEFFICIENT OF VAPORIZATION ON THE PARAMETERS OF THE GAS NEAR THE SURFACE

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*The dependence of the coefficient of concentration jump on the coefficient of vaporization for a diluted binary mixture, when the concentrations of the components are significantly different, has been investigated. The analytical expression of the concentration jump for the case where the frequency of collisions of molecules is in proportion to their velocity has been obtained.*

Growing interest in problems associated with allowance for the influence of the coefficient of vaporization on thermodiffusion processes in aerodisperse systems has been observed in recent times [1, 2]. We note that this influence related to the concentration jump at the gas–condensed body boundary was also considered earlier [3, 4] in a somewhat different formulation. The concentration jump in the case of a binary gas mixture was calculated earlier by approximate methods [5–7]. Up to then, there had been no analytical solution of the corresponding problem. The solution was realized just for a one-component gas [8] but this was insufficient for practical applications.

Different variants of boundary conditions in evaporation to a binary mixture, in which different dependences of the vaporization coefficient are presented, are used in a number of works [1–4]. Such a situation makes it necessary to construct an accurate quantitative theory of kinetic coefficients that would give a correct description of the dependence of the latter on the vaporization coefficient. This problem is the focus of the present work.

**Formulation of the Problem and Basic Equations.** We consider the process of evaporation from a plane surface to a binary gas mixture. It is assumed that the concentration of the evaporating component of the mixture  $n_1$  is much lower than the concentration of the nonevaporating component  $n_2$  (case of a diluted mixture). We note that this condition is fulfilled for the majority of the most important applications.

The Boltzmann equation for the binary gas mixture has the form [9]

$$\frac{\partial f_i}{\partial t} + \mathbf{v}_i \frac{\partial f_i}{\partial \mathbf{r}_i} = J_{ii} + J_{ij}, \quad i \neq j, \quad i, j = 1, 2; \quad J_{ij} = \int v_{ij} (f_i' f_j' - f_i f_j) d\sigma_{ij} d^3 p_j. \quad (1)$$

We note that  $J_{11} \sim n_1^2$ , and  $J_{12} \sim n_1 n_2$  (since  $f_i \sim n_i$ ). The quantity  $\varepsilon = n_1/n_2$  is a small parameter, since  $n_1 \ll n_2$ . It is evident that  $|J_{11}|/|J_{12}| \sim \varepsilon$ ; therefore, we may neglect  $J_{11}$  compared to  $J_{12}$  in the first approximation of  $\varepsilon$ . Furthermore, in this approximation, the action of the first component on the distribution function of the second may be disregarded. Consequently, under the conditions of the problem in question, the distribution function of the second component of the gas mixture may be considered to be equilibrium Maxwellian with average velocity  $\mathbf{U}_2 = 0$  and constant temperature  $T$  and concentration  $n_2$ .

The quantity  $J_{12}$  may be approximated by the kinetic model [10, p. 356] with a collision frequency proportional to the molecular velocity. Then with account for (1) the kinetic equation for the first component will take the form

$$\frac{\partial f_1}{\partial t} + \mathbf{v}_1 \frac{\partial f_1}{\partial \mathbf{v}_1} = \frac{v_1}{l} (f_1^* - f_1), \quad f_1^* = n_1^* \left( \frac{\beta_1}{\pi} \right)^{3/2} \exp(-\beta_1 v_1^2), \quad n_1^* = \sqrt{\pi \beta_1} \frac{1}{2} \int v f_1 d^3 v_1. \quad (2)$$

We can show [9] that  $D_{12} = 2l/(3\sqrt{\pi\beta_1})$ . Let us take a Cartesian coordinate system with its center on the surface from which evaporation occurs. We draw the  $x_1$  axis perpendicularly to the surface. In evaporation from the surface, there

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is a constant gradient of concentration of the first component  $g_n^1 = \left( \frac{dn_1}{dx_1} \right)_\infty$  at a large distance from it. We consider the evaporation to be weak, i.e., assume that the relative change in the concentration of the first component on the molecular free path length  $l$  is much less than unity:  $|G_n| \ll 1$  and  $G_n = lg_n^1/n_{1s}$ . Under these conditions, the problem allows linearization. The distribution function of the molecules of the first component  $f_1$  will be represented as

$$f_1 = f_s (1 + \psi), \quad f_s = n_{1s} (\beta_1/\pi)^{3/2} \exp(-\beta_1 v_1^2). \quad (3)$$

Taking account of the stationarity of the problem and of relation (3), we rewrite Eq. (2) in the form

$$v_{1x} \frac{\partial \psi}{\partial x_1} = \frac{v_1}{l} \left( \frac{\delta n_1^*}{n_{1s}} - \psi \right), \quad (4)$$

$$\delta n_1^*(x_1) = n_1^*(x_1) - n_{1s}, \quad \frac{\delta n_1^*(x_1)}{n_{1s}} = \frac{1}{2\pi} \int C \exp(-C^2) \psi(x_1, \mathbf{C}) d^3 C = \frac{1}{2} \int \psi(x_1, \mu) d\mu.$$

Let us consider a fairly well-known [11] boundary condition on the evaporation surface for the molecules of the first component; this boundary condition allows for the influence of the properties of the surface by introducing the vaporization (condensation) coefficient  $\alpha$ :

$$f_1(0, \mathbf{v}_1) = \alpha f_s(n_{1s}, v_1) + (1 - \alpha) f_0(n_0, v_1), \quad v_{1x} > 0, \quad f_0 = n_0 (\beta_1/\pi)^{3/2} \exp(-\beta_1 v_1^2). \quad (5)$$

The quantities  $\alpha$  and  $(1 - \alpha)$  are the probabilities that a molecule incident onto the wall is respectively condensed on it and is reflected from it without condensation. The quantity  $n_0$  is determined from the nonflow condition for molecules reflected from the surface without condensation on it:

$$(1 - \alpha) \int v_{1x} \left[ f_0(n_0, v_1) H_+(v_{1x}) + f(0, \mathbf{v}_1) H_+(-v_{1x}) \right] d^3 v_1 = 0.$$

With account for relation (3), we rewrite boundary condition (5) as

$$\psi(0, \mathbf{v}_1) = (1 - \alpha) \frac{n_0 - n_{1s}}{n_{1s}}, \quad v_{1x} > 0. \quad (6)$$

From the form of Eq. (4) and boundary condition (6), it follows that the function  $\psi$  is dependent just on the  $x_1$  component of the velocity  $\mathbf{v}$ , i.e.,  $\psi = \psi(x_1, v_{1x})$ . After introduction of the dimensionless coordinates  $x = x_1/l$  and the velocity  $\mu = v_{1x}/v_1$ , Eq. (4) is simplified:

$$\mu \frac{\partial \psi}{\partial x} + \psi(x, \mu) = \frac{1}{2} \psi(x, \mu') d\mu', \quad (7)$$

and condition on the wall (6) is transformed:

$$\psi(0, \mu) = (1 - \alpha) a, \quad a = \frac{n_0 - n_{1s}}{n_{1s}}, \quad 0 < \mu < 1. \quad (8)$$

At a large distance from the surface (outside the Knudsen layer of thickness of the order of the molecular free path length), the function  $\psi$  has the form (Chapman–Enskog distribution [9])

$$\psi_0 = G_n(x - \mu) + \varepsilon_n, \quad \varepsilon_n = \frac{\delta n_1(0)}{n_{1s}}, \quad \delta n_1(0) = n_1(0) - n_{1s}. \quad (9)$$

The quantity  $a$  is found from the nonflow condition. In this condition, we pass to the spherical coordinate system

$$\int_{-1}^1 \mu \left[ n_0 H_+(\mu) + n_{1s} (1 + \psi(0, \mu)) H_+(-\mu) \right] d\mu = 0,$$

whence we obtain the equation

$$\frac{a}{2} + \int_{-1}^1 \mu \psi(0, \mu) d\mu - \int_0^1 \mu \psi(0, \mu) d\mu = 0.$$

The replacement of the function  $\psi$  in the second integral by  $\psi_0$  yields

$$a = \frac{4}{3\alpha} G_n. \quad (10)$$

**Solution of the Problem.** The solution of Eq. (7) in problem (7)–(9) will be sought in the form

$$\psi_\eta(x, \mu) = \exp\left(-\frac{x}{\eta}\right) \Phi(\eta, \mu), \quad \int_{-1}^1 \Phi(\eta, \mu) d\mu = 1.$$

Using these equalities we obtain, from (7), the characteristic equation  $(\eta - \mu)\Phi(\eta, \mu) = \frac{1}{2}\eta$ . When  $\eta \in (-1, +1)$  we find [12] its eigenfunctions

$$\Phi(\eta, \mu) = \frac{1}{2} \eta^P \frac{1}{\eta - \mu} + \lambda(\eta) \delta(\eta - \mu).$$

Here  $Px^{-1}$  is the principal value of the integral of  $x^{-1}$  and  $\lambda(\eta)$  is the dispersion Case function [12]:

$$\lambda(z) = 1 + \frac{z}{2} \int_{-1}^1 \frac{du}{u - z}.$$

The solution of problem (7)–(9) is sought in the form of the expansion

$$\psi(x, \mu) = \varepsilon_n + G_n(x - \mu) + \int_0^1 \exp\left(-\frac{x}{\eta}\right) \Phi(\eta, \mu) A(\eta) d\eta,$$

where  $A(\eta)$  is the unknown function, and  $\varepsilon_n$  is the unknown constant. The coefficients  $G_n$  and  $\varepsilon_n$  are related by the linear relation  $\varepsilon_n = C_n^*(\alpha)G_n$ . We seek the function  $C_n^*(\alpha)$ .

Substitution of the eigenfunctions into the expansion leads to a singular integral equation with a Cauchy kernel [13]:

$$(1 - \alpha) a = \varepsilon_n - G_n \mu + \frac{1}{2} \int_0^1 \frac{\eta A(\eta) d\eta}{\eta - \mu} + \lambda(\mu) A(\mu) = 0, \quad 0 < \mu < 1.$$

We introduce the auxiliary function

$$N(z) = \frac{1}{2} \int_0^1 \frac{\eta A(\eta) d\eta}{\eta - z}.$$

Using the boundary values of the functions  $\lambda(z)$  and  $N(z)$  on the upper and lower edges of the cut  $(0, 1)$ , we reduce the singular equation to the boundary-value Riemann problem [13]

$$\lambda^+(\mu) \left[ N^+(\mu) + \varepsilon_n - G_n \mu - (1 - \alpha) a \right] = \lambda^-(\mu) \left[ N^-(\mu) + \varepsilon_n - G_n \mu - (1 - \alpha) a \right], \quad 0 < \mu < 1.$$

We consider the corresponding homogeneous problem [13]

$$\frac{X^+(\mu)}{X^-(\mu)} = \frac{\lambda^+(\mu)}{\lambda^-(\mu)}, \quad 0 < \mu < 1,$$

whose solution has the form [14]

$$X(z) = \frac{1}{z} \exp(-V(z)), \quad V(z) = \frac{1}{\pi} \int_0^1 \frac{\zeta(u) du}{u-z}, \quad \zeta(u) = \arctan \frac{2\lambda(u)}{\pi u} - \pi.$$

Using it we reduce the Riemann problem to that of determining of the analytical function from the zero jump:

$$X^+(\mu) \left[ N^+(\mu) + \varepsilon_n - G_n \mu - (1 - \alpha) a \right] = X^-(\mu) \left[ N^-(\mu) + \varepsilon_n - G_n \mu - (1 - \alpha) a \right], \quad 0 < \mu < 1,$$

the general solution of the problem has the form

$$N(z) = -\varepsilon_n + G_n z + (1 - \alpha) a - \frac{G_n}{X(z)}.$$

From the condition  $N(\infty) = 0$ , we find that

$$\varepsilon_n = G_n \left[ \sqrt{\pi} \frac{1 - \alpha}{\alpha} + V_1 \right], \quad V_1 = -\frac{1}{\pi} \int_0^1 \zeta(u) du = 0.710447.$$

Consequently, the function sought is

$$C_n^*(\alpha) = \sqrt{\pi} \frac{1 - \alpha}{\alpha} + V_1.$$

Passing to dimensional quantities, using (9) we obtain

$$\delta n_1(0) = C_n(\alpha) \sqrt{\beta_1} D_{12} g_n^1, \tag{11}$$

where

$$C_n(\alpha) = \frac{3}{2} \sqrt{\pi} C_n^*(\alpha)$$

is the sought coefficient of concentration jump. From formula (11), we find

$$D_{12} g_n^1 = \frac{1}{\sqrt{\beta_1}} K_n(\alpha) \delta n_1(0), \tag{12}$$

where

$$K_n(\alpha) = \frac{1}{C_n(\alpha)} = \frac{2\alpha}{\sqrt{\pi} [3V_1\alpha + 4(1 - \alpha)]}$$

is the sought coefficient reciprocal to  $C_n(\alpha)$ .

**Discussion of the Results.** In most works, the boundary condition has a form analogous to (11) [3, 6, 7]. It allows for the correction of the Knudsen number to the condition in the hydrodynamic description of evaporation processes. At the same time, a boundary condition of the type (12) for the concentration jump is used in [1, 2, 15] (in [1, 2], it is equivalent to condition (12) in form)). In these works (also, see [16]) Yalamov et al. give the following expression for the coefficient  $K_n(\alpha)$  (we denote it by  $K_n^1(\alpha)$ ):

$$K_n^1(\alpha) = \frac{\alpha}{2\sqrt{\pi}}. \quad (13)$$

We note that boundary condition (12) with the coefficient (13) is called the Hertz–Knudsen boundary condition [15]. In deriving it, we have used the methods of elementary kinetic theory.

Let us compare the result (12) of the analytic solution obtained to the Hertz–Knudsen number. When  $\alpha = 1$ , according to the Hertz–Knudsen condition (13), we have  $K_n^1(1) = 0.282095$ , whereas in accordance with the analytical solution (12)  $K_n(1)$  is equal to 0.529405. When  $\alpha \rightarrow 0$  we obtain, from expression (12), the following asymptotics:

$$K_n(\alpha) = \frac{1}{2\sqrt{\pi}} a = 0.282095\alpha,$$

which exactly coincides with the Hertz–Knudsen condition (13). Consequently, when the values of the vaporization coefficients are low, the coefficients  $K_n(\alpha)$  and  $K_n^1(\alpha)$  coincide.

In [17, 18], the problem on evaporation of a binary gas mixture was considered with the use of the model Krook equation with a constant frequency of molecular collisions. In the case of a diluted mixture ( $n_1 \ll n_2$ ) from the results given in these works, it follows that

$$K(\alpha) = \frac{\alpha}{2\sqrt{\pi} + 2\alpha(l_v(\infty) - \sqrt{\pi})}. \quad (14)$$

We note that the quantity  $l_v(\infty)$  is found numerically; just two of its values that fall within the interval permissible for this case were given in [17, 18]. From formula (14), it follows that an asymptotics exactly coincident with (13) is obtained for  $\alpha \rightarrow 0$ , whereas for  $\alpha = 1$  and  $m_1/m_2 = 0.05$  (and  $m_1/m_2 = 20$ )  $K(1)$  is equal to 0.526. The difference from our result —  $K(1) = 0.529$  — amounts to 0.6%. When  $\alpha = 1$  and  $m_1/m_2 = 0.268$  (and  $m_1/m_2 = 3.73$ ),  $K(1)$  is equal to 0.511, which differs from our result by 3.6%. From the given data, it is clear that the quantity  $K(\alpha)$  is weakly dependent on the ratio of the molecular weights of the gas mixture.

A comparison of the Hertz–Knudsen formula with the results of our work and with those of [17, 18] shows that, for a vaporization coefficient equal to unity, it yields a result understated by nearly half for the quantity  $K(\alpha)$ . At the same time, for a vaporization coefficient tending to zero, all the relations considered lead to the same result.

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## NOTATION

$A(\eta)$ , continuous-spectrum coefficient;  $a = (n_0 - n_{1s})/n_{1s}$ ;  $\mathbf{C} = \sqrt{\beta_1} \mathbf{v}_1$ , dimensionless velocity;  $C_n(\alpha)$  and  $C_n^*(\alpha)$ , coefficients of concentration jump;  $D_{12}$ , diffusion coefficient;  $d\sigma_{ij}$ , differential scattering cross section of the molecules of the  $i$ th and  $j$ th components;  $d^3C$ , volume element in the dimensionless-velocity space;  $d^3p_j$ , volume element in the momentum space;  $d^3v_1$ , volume element in the velocity space;  $f_i$ , distribution function of the  $i$ th component;  $f_i'$ , distribution function of the  $i$ th component after the collision;  $f_1^*$ , equilibrium Maxwellian distribution function for the first component;  $f_0$  and  $f_s$ , absolute Maxwellians;  $g_n$  and  $G_n$ , gradient and relative gradient of concentration of the first component;  $H_+(x)$ , Heaviside function,  $H_+(x) = 1$ ,  $x > 0$  and  $H_+(x) = 0$ ,  $x < 0$ ;  $J_{ii}$  and  $J_{ij}$ , integrals of collisions of the molecules of the  $i$ th component with each other and with the molecules of the  $j$ th component;  $k$ , Boltzmann constant;  $l$ , effective free path length for molecules;  $l_v(\infty)$ , constant [17, 18];  $m_1$ , weight of a molecule of the first component;

$n_1(0)$ , molecular concentration (extrapolated up to the surface) of the first component;  $n_{1s}$ , concentration of a saturated gas (first component) on the evaporation surface;  $n_1^*$ , quantity determined from the law of conservation of the number of molecules of the first component;  $N(z)$ , auxiliary function;  $p_i$ , momentum of the  $i$ th component;  $Px^{-1}$ , principal value of the integral of  $x^{-1}$ ;  $\mathbf{r}_i$ , coordinate of the molecules of the  $i$ th component of the mixture;  $T$ , temperature of the mixture;  $\mathbf{U}_2$ , velocity of the second component;  $\mathbf{v}_i$ , velocity of the molecules of the  $i$ th component of the mixture;  $v_{ij} = |v_i - v_j|$ ;  $V(z)$ , auxiliary function;  $X(z)$ , solution of the homogeneous boundary-value Riemann problem;  $\alpha$ , evaporation coefficient;  $\beta_1 = m_1/2kT$ ;  $\delta(x)$ , Dirac delta function;  $\varepsilon_n$ , relative jump of the molecular concentration of the first component of the mixture;  $\zeta(u)$ , angle;  $\zeta(u) = \arg \lambda^+(u) - \pi$ ;  $\lambda(z)$ , dispersion Case function;  $\mu = C_x/C$ , cosine of the angle between the  $x$  axis and the vector of velocity of molecules;  $\nu_1$ , frequency of mutual collisions of the molecules of the first component of the mixture;  $\Phi(\eta, \mu)$ , eigenfunction of the characteristic equation. Subscripts:  $i$  and  $j$ , Nos. of components in the mixture;  $s$ , surface;  $+(-)$ , boundary values of the functions of a complex variable on the upper (lower) edge of the cut;  $n$ , concentration;  $x$ , projection onto the  $x$  axis;  $\eta$ , continuous spectrum.

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