MASS TRANSFER IN A HIGHLY RAREFIED GAS

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Equations of mass exchange in closed high-vacuum systems are obtained on the basis of the analogy between processes of transfer of molecular particles in a highly rarefied gas and processes of radiation.

The wide application of high-vacuum systems in different areas of science and technology requires the development of analytical methods for the study of their functional characteristics and particularly the mass transfer characteristics.

A high-vacuum system consits of an enclosed volume filled with a highly rarefied gas ($Kn \gg 1$) and bounded by surfaces at which there exists a heterogeneous field of temperatures and partial pressures. The processes of mass exchange in such systems are closely connected with irreversible processes of transfer of mass, energy, and momentum based on the respective fundamental conservation laws.

The realization of transfer processes in a highly rarefied gas is accomplished through the interaction of the free-molecular flux with the surfaces bounding the vacuum space. Either the reflection of the moleclar particles from the surface or the sorption of these particles by the surface occurs in this case. The exchange of mass, energy, and momentum between the molecular flux and the surface is characterized by the appropriate coefficients of exchange (accomodation) α_m, α_e, and α_p and of reflection R.

For the determination of the macroscopic characteristics of the interaction of a free-molecular flux with a surface there are kinetic equations for the distribution function $f(\bar{u}, \bar{r}, \tau)$, which represents the probability density of the number of particles with velocity $\bar{u}$ at the point of space with radius vector $\bar{r}$ at the time τ, with allowance for the boundary conditions at the solid surface. As was shown in [1], however, owing to the reflections of the particles during their interaction with the boundary in a closed system the distribution function $f(\bar{u}, \bar{r}, \tau)$ is connected not only with the initial distribution function or with the distribution function at one point of the surface but also with the distribution function at infinitely many points of the surfaces of the system. A distribution function of this type and the kinetic equations based on it are extremely complicated and very laborious for solution in engineering practice and moreover they have so far been obtained only for the simplest geometries, such as for two parallel plates [2].

For an analysis of the process of mass transfer in a real high-vacuum system bounded by a finite number of surfaces we will use the analogy between the transfer laws of molecular particles and of radiation in a highly rarefied gas (diathermal medium). For the radiation in this case one can start from corpuscular concepts, considering the radiation as a flux of photons.

It was shown in [3] that the macroscopic equations of mass transfer in a rarefied gas and the macroscopic equations of radiation transfer in a diathermal medium have a single foundation: the microscopic Boltzmann equations for a gas and for photons. Therefore, with certain assumptions for the molecular particles it appears to be possible to use the solutions and method of analysis of the macroscopic radiation equations for the solution and analysis of the macroscopic equations of mass transfer.

For subsequent considerations we will assume that incident and reflected molecular fluxes having a Maxwell distribution interact with any surface of the high-vacuum system. The molecular fluxes generated (desorbed) by the surface are distributed in accordance with Lambert's law. The mean velocities, kinetic energy, and momentum of the particles correspond to the temperature of the surface.

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Let us take the surface density of the molecular flux as the determining physicoenergetic parameter of the mass transfer. In this case the proper (desorbed), incident, reflected, and absorbed molecular flux densities are interconnected by the generalized relationships for the densities of the effective and resultant molecular fluxes [4, 5]

$$M_e = M_p + M_r = M_p + \overline{R}\cdot M_s,\ M_t = M_p - M_a = M_p - \overline{B}\cdot M_s,\ \overline{R} + \overline{B} = 1, \tag{1}$$

where $\overline{R}$ and $\overline{B}$ are generalized sorption characteristics of the surface.

We will solve the problem of mass transfer under conditions of a highly rarefied gas on the basis of the integral equations of radiation transfer. These equations give a sufficiently strict analytical description of the transfer process. The approximate methods of solving these equations (generalized zonal methods [5, 6]) for closed systems bounded by a finite number of surfaces (zones) with constant (continuous) and with constant-discrete optical (sorption–desorption) and energy characteristics permit one: to take into account the physical nature of the phenomena; to determine not only the characteristics of the radiation (mass emission) field averaged over the individual zones but also the local characteristics; to use the existing analytical expressions for the local and average angular radiation transfer coefficients.

Let us consider a closed system filled with a rarefied gas and bounded by a sufficiently smooth surface F at all parts of which the mass emission density field is given.

The mass exchange in such a closed system can be described with sufficient accuracy by the integral equation

$$M_e(P) = M_\alpha(P) + \overline{R}(P)\int_F M_e(N)\,K(P,\ N)\,dF_N, \tag{2}$$

where $K(P,\ N) = \cos\Theta(P)\cos\Theta(N)/\pi r^2$ is the kernel of Eq. (2) and $P \in F$, $N \in F$.

Depending on the formulation of the problem the generalized function $M_\alpha(P)$ reflects the proper or the resultant mass emission field.

The solution of Eq. (2) has the form

$$M_e(P) = M_\alpha(P) + \overline{R}(P)\int_F M_\alpha(N)\,\Gamma(P,\ N)\,dF_N. \tag{3}$$

Here the resolvent $\Gamma(P,\ N)$ of the kernel $K(P,\ N)$ allows for multiple reflections of the particles of the molecular flux from the surfaces of the system and is determined from the integral equation

$$\Gamma(P,\ N) = K(P,\ N) + \int_F \overline{R}(Q)\,K(P,\ Q)\,\Gamma(Q,\ N)\,dF_Q. \tag{4}$$

If the boundary surface F is given in the form of a set of homogeneous sorption–desorption zones $F_n = \sum_{i=1}^{n} F_i$ and if $R(P_i) \to R_i$ and $M_\alpha(P_i) \to M_{\alpha i}$ are given in the form of stepwise functions for each i-th zone, where $i = 1,\ 2,\ \dots,\ n$, then Eq. (2) for the set of surfaces takes the form

$$M_e(P_i) = M_{\alpha i} + R_i\sum_{j=1}^{n}\int_{F_j} M_e(P_i)\,K(P_i,\ N_j)\,dF_{Nj}. \tag{5}$$

We can write the solution of this system of equations with allowance for multiple reflections of the particles of the molecular flux from the surfaces F_n in the form

$$M_e(P_i) = M_{\alpha i} + R_i\sum_{j=1}^{n} M_{\alpha j}\int_{F_j}\Gamma(P_i,\ N_j)\,dF_{Nj}. \tag{6}$$

The integral $\int_{F_j}\Gamma(P_i,\ N_j)\,dF_{Nj}$ represents the resolvent angular transfer coefficient $\Phi(P_i,\ F_j)$ a sorption–geometrical indicator, which by analogy with [5] takes into account the geometrical properties of its surfaces, and multiple reflections at the boundary.

The resolvent (local or average) angular transfer coefficient is determined by calculating the matrix $\Gamma(P_i,\ N_j)$ of the resolvent, determined by the system of equations

$$\Gamma(P_i,\ N_j) = K(P_i,\ N_j) + \sum_{k=1}^{n} R_k\int_{F_k} K(P_i,\ Q_k)\,\Gamma(Q_k,\ N_j)\,dF_{Qk}. \tag{7}$$

The analytical solution of (7) comes down to the determination of the sum of an infinite converging functional series. An approximate method of determining the resolvent angular transfer coefficients exists [6], according to which (7) is approximated by a finite system of algebraic equations

$$\Phi(P_i, F_j) \cong \varphi(P_i, F_j) + \sum_{k=1}^{n} R_k \varphi_{kj} \Phi(N_i, F_k), \tag{8}$$

where j = 1, 2, ..., n; i = 1, 2, ..., n.

Here the geometrical (local or average) angular transfer coefficients φ are determined on the basis of well-known rules [5] or from the results of problems of radiation transfer solved earlier for systems of specific geometries.

A summary table of analytical dependences of geometrical angular transfer coefficients for the surfaces of the most common geometries in high-vacuum systems is presented in [7].

It must be noted that in addition to the well-known reciprocal relations the resolvent angular mass transfer coefficients are interconnected by an additional relation based on the law of conservation of mass:

$$\sum_{i=1}^{n} \Phi_{ik} \mu_k = 1, \text{ where } k = 1, 2, \ldots, n. \tag{9}$$

Finally, the system of equations (6) with allowance for (8) is converted to the form

$$M_e(P_i) - R_i \sum_{j=1}^{n} M_{\alpha j} \Phi(P_i, F_k) = M_{\alpha i}, \tag{10}$$

where k = 1, 2, ..., n; i = 1, 2, ..., n.

The generalized function $M_{\alpha i}$, as indicated earlier, has the form

$$M_{\alpha i} = \begin{cases} M_{pi}, & R_i = 1, \\ -M_{ti}, & R_i = 1 - B_i. \end{cases} \tag{11}$$

In mass transfer problems the function M_{pi} characterizes the mass flux density generated by the i-th surface of the high-vacuum system due to the independent processes of desorption from the surface and diffusion of gas particles from the volume of the solid, evaporation or sputtering of atoms from the surface of the solid, and the penetration of molecular particles through the surface bounding the vacuum space.

The processes enumerated are determined by the temperature of the surface, the physicoenergetic parameters of the particles of the external medium, and by the properties, composition, and structure of the solid. Since there does not yet exist a single generalized characteristic of the mass emission of materials in a high vacuum at different temperatures and other conditions, experimental average characteristics for each process are used as a rule to estimate the desorption molecular fluxes, for example, of the type

$$M_{p(T)} = M_{p(0)} + A \exp\left(-\frac{C}{T}\right), \tag{12}$$

where $M_{p(0)}$ is the initial (at T = 300°K) desorption flux; A and C are experimental coefficients for the specific materials, temperatures, and pressures.

Surfaces with equal and uniformly distributed characteristics M_{pi} will be called isodesorption surfaces.

Unfortunately, at present there are only a few reports available in which data on the desorption properties of the materials of high-vacuum systems are systematized.

The function M_{ti} represents the resultant molecular flux density and is determined in accordance with (1), where M_{ai} characterizes the absorptivity of the i-th surface, determined by the processes of adsorption– chemisorption or condensation of the moleclar particles.

The proportionality coefficient B_i in mass exchange problems depends on the physicochemical and thermodynamic properties of the surface and is the sticking probability μ_i for the case of interaction of gas particles with the surface and is the condensation coefficient α_{Ti} for the case of the interaction of condensing (vapor) particles. For quasi-surfaces joining the evacuated space with the evacuation elements the parameter B_i characterizes the capture coefficient Θ.

We should note that surfaces with equal and uniformly distributed values of μ_i and α_{Ti} will be considered as isosorption surfaces.

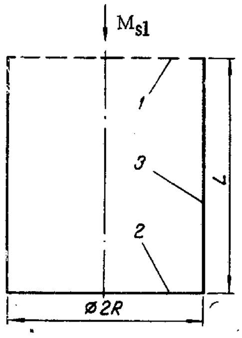

Fig. 1

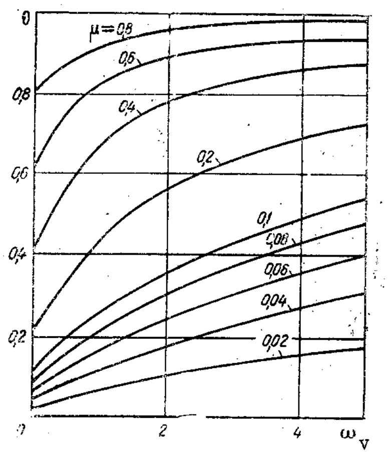

Fig. 2

Fig. 1. Diagram of a cylindrical evacuation cell with sorbing walls: 1) quasi-surface; 2, 3) sorbing surface.

Fig. 2. Dependence of effective capture coefficient Θ_V of a cylindrical evacuation cell on its relative depth ω_V and the sticking probability μ of the sorbing walls.

Summary data on the sticking probabilities (condensation coefficients) of different gases at different temperatures of the molecular particles and surfaces are presented in [7].

It follows from (1) and (10) that the local density of the incident molecular flux is determined by the equation

$$M_s(P_i) = \frac{M_e(P_i) - M_{pi}}{R_i} = \sum_{j=1}^{n} M_{pj}\Phi(P_i, F_k), \tag{13}$$

$$i = 1, 2, \ldots, n; \quad k = 1, 2, \ldots, n.$$

Although Eqs. (10), (11), and (13) are written for a homogeneous gas they can easily be generalized to the case of a mixture of gases.

The solution of the system of Eqs. (10) and (13) and the subsequent analysis make it possible to obtain a qualitative and quantitative picture of the distribution of molecular fluxes in a high-vacuum system. As a result one can determine the capture coefficients and evacuation rates of different gases, the fields of partial pressures along the length and over cross sections of the system, the pressure of any gas at any point of the surface of the system which is difficult to reach for measurement by scaling the experimentally obtained results, and the optimum geometry of the system providing for its highest efficiency.

As an example we will show the determination of the capture coefficient for a cylindrical evacuation cell with sorbing walls, a diagram of which is presented in Fig. 1.

The effective capture coefficient of the cell is determined as the ratio of the molecular flux absorbed by the cell to the molecular flux incident on the cell through the quasi-surface (1), i.e.,

$$\Theta_V = \frac{\overline{M}_{av}}{\overline{M}_{sl}}, \tag{14}$$

where

$$\overline{M}_{av} = \sum_{i=2}^{3} \overline{M}_{ai} = \sum_{i=2}^{3} M_{si} A_i \mu_i; \quad \overline{M}_{sl} = M_{sl} \cdot A_1. \tag{15}$$

In accordance with (13)

$$M_{si} = M_{sl}\Phi_{i1}. \tag{16}$$

After transformations using the dimensionless depth $\omega_V = L/R$ and assuming that the surfaces of the cell are only sorbing and isosorption surfaces, i.e., $\mu_i = \mu = \text{const}$, and do not generate molecular fluxes, we obtain

$$\Theta_V = \mu(2\omega_V\Phi_{31} + \Phi_{21}). \tag{17}$$

We determine the values of Φ_{21} and Φ_{31} from (8), constructing a matrix of equations for Φ_{ik} and solving it on a computer for different values of μ and ω_V. The results of the calculation are shown in Fig. 2. It follows from the graph that for an evacuation cell with sorbing walls ($\mu_i = \mu$) there always exists the relationship

$$\Theta_v > \mu \text{ when } \omega_v > 0, \quad \Theta_v = \mu \text{ when } \omega_v = 0, \tag{18}$$

which, as we will show in the future, is of prime value in the planning and operation of high-vacuum systems.

NOTATION

M	is the molecular flux density, mole/cm^2·sec;
$\bar{M}$	is the molecular flux, mole/sec;
Kn	is the Knudsen number;
A	is the surface, cm^2;
R	is the reflection coefficient;
n	is the number of zones in system;
T	is the absolute temperature, °K;
Θ	is the effective capture coefficient;
ω	is the relative depth.

Subscripts

s	incident;
e	effective;
t	resultant;
a	absorbed;
p	proper;
r	reflected;
v	evacuation cell.

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