INVESTIGATION OF THE DYNAMICS OF EVAPORATION OF CONDENSED BODIES ON THE BASIS OF THE LAW OF SPECTRAL-RADIATION INTENSITY OF PARTICLES[*]

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The fundamentals of radiation theory and the mechanism of evaporation of condensed bodies are presented. The distribution functions of particles of a body by energies and by the intensity of their transition from one energy level to another in the process of evaporation have been obtained based on the law of spectral-radiation intensity of the body particles. The temperature dependence of the resulting vapor flow on the outer surface of a massive condensed body and a thin layer in equilibrium and nonequilibrium states, which, in the limit, transforms to the known Hertz–Knudsen formula, has been found.

Study of the kinetics of the process of evaporation of a liquid is a topical problem for a number of modern industries. At present, the phenomenological approach is usually used in the theory of heat exchange for description of evaporation and other processes of phase transformations [1]. However, a purely empirical study of phase transformations limits significantly the possibility of determining the general mechanisms of these processes. In a number of works, the evaporation process has been investigated with the use of indirect information on the kinetics of condensation and heat and mass transfer in a vapor-gas medium external relative to the condensed body [2, 3]. Sometimes, it is possible to obtain this information using the methods of the kinetic theory of gases [4]. However, with this approach, it is difficult to take into account the influence of the geometric, structural, and thermophysical parameters of a condensed body on the evaporation kinetics, because this requires the introduction of simplifying assumptions. For example, the Hertz–Knudsen formula for the resulting flow of a condensed one-component saturated vapor is derived without regard for the difference between the velocity distributions of the vapor molecules moving toward the liquid and from it and the condensation coefficient is considered to be independent of the pressure. At the same time, experimental data show that this coefficient is a function of the state: it is close to unity at low pressures and decreases in the region of higher pressure [1, 5, 6]. Relaxation phenomena in the case of nonstationary evaporation of a liquid have been investigated in [7].

The attractive forces acting between the molecules of a condensed body contain them in the body. For the molecules in a liquid or solid body to go to vapor after certain fluctuation processes, they must reach an energy level sufficient to perform the work required for their breaking-away from the condensed body. However, the physical nature of these fluctuation processes and the mechanism of breaking-away of molecules are still not clearly understood.

In [8–11], the radiation theory of heat conduction, which is based on the mechanism of energy transfer using carriers emitted and absorbed by the particles of a substance, has been derived. Within the framework of this theory, the following laws have been obtained: the fundamental law of spectral-radiation intensity of microparticles of a body, which yields the Planck formula for the blackbody emissive power and the known and some new energy distribution functions of particles; the integro-differential equation of energy transfer, which allows one to explain the existence of the final velocity of propagation of energy carriers, the boundedness of the heat flux in the case of increase in the temperature gradient to infinity, the influence of the scale factor on heat conduction, and, in the limit, the transformation to the Fourier equation of heat conduction.

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[*] The article is published by way of discussion.

The theory of transfer processes is further developed in the recent radiation theory of heat-and-mass transfer [12–14]. Within the framework of this theory, the energy distribution function of particles of a multicomponent condensed body has been obtained and the formula for the temperature dependence of the diffusion coefficient, which, in the limiting cases, becomes the Arrhenius formula for a solid body and the Einstein formula for a liquid, has been found.

Below we describe the mechanism and the fundamentals of the radiation theory of evaporation. The energy-distribution functions of particles of a body and the intensities of their transition from one energy level to another in the process of evaporation have been found. The expressions for the temperature dependences of the intensity of evaporation of a condensed body and the saturated vapor pressure, which agree with the known experimental data and the known Hertz–Knudsen formula, have been obtained.

The parameters characterizing the dynamics of the process of evaporation of condensed bodies are found from the energy-distribution functions of atoms and from the intensity of their transition from one energy level to another in this process. The indicated functions can be obtained using the law of spectral-radiation intensity of particles of the body, which has been derived in [8] on the basis of the conservation laws, the phenomenological law of heat conduction, and some experimental data, starting from the fact that the energy transfer as well as the transfer of the mass of a substance or of the field are performed by material carriers emitted and absorbed by the particles of the substance. This law can be formulated as follows. The degrees of freedom of the particles of a unit volume of a body, found at the ith energy level in frequency ν, emit energy $q_{i\nu}$ by quanta $h\nu$ in a unit time. The value of this energy is proportional to the energy level i, the energy of the quantum $h\nu$, and the density of the degrees of freedom of the particles found at this level $n_{i\nu}$, i.e.,

$$q_{i\nu} = \varepsilon_\nu n_{i\nu} i h \nu , \qquad (1)$$

where ε_ν is the emissivity of photons of frequency ν, $\varepsilon_\nu \neq f(i)$. It has been established that, on condition that (1) is consistent with the laws of blackbody radiation and the Maxwell–Boltzmann law of energy distribution of particles of a body, the degree of freedom of an atom, found at the ith energy level in frequency ν, emits i photons at the moment of emission and passes to the zero energy level.

Let us consider a closed equilibrium system consisting of a single-component condensed body and its vapor. For the simplicity of presentation, we will assume that to every degree of freedom of a particle of the body corresponds an arbitrary particle (a quasiparticle) emitting and absorbing photons of only the frequency ν. The quasiparticles are distributed over the energy levels $i = 1, 2, ..., I$, where I is the limiting energy level for the frequency ν, at which a quasiparticle can be found. The quantity I is related to the activation energy A by the relation $\{Ih\nu < A \leq (I+1)h\nu\}$. The particles found at the energy level I, after the absorption of the photon $h\nu$, give up their energy $(I+1)h\nu$ to other particles of the body by way of emission. In this case, the particles that are positioned near the free surface of the condensed body can break away from it, while the other particles, after some displacements, pass to the zero level without leaving the body. On condition that the system is equilibrium, the total values of the number and momentum of evaporated and condensed particles can be considered to be the same.

Let us assume that in a unit volume of a body there are $n_{i\nu}$ quasiparticles with energy $E_{i\nu} = i h \nu$. Then, in accordance with the law of spectral-radiation intensity of particles, the energy emitted by these quasiparticles is $q_{i\nu} = \varepsilon_\nu n_{i\nu} E_{i\nu}$, $i = 1, 2, ..., I$, and the change in their number at the level i in a unit time, caused by the emission, is

$$\dot{n}_{i\nu} = q_{i\nu}/(ih\nu) = \varepsilon_\nu n_{i\nu} , \quad i = 1, 2, ... , I . \qquad (2)$$

where $\dot{n}_{i\nu}$ is the number of particles of the unit volume leaving the energy level i in a unit time because of the emission of photons $h\nu$.

If the density of the photons $h\nu$ in the body is χ_ν, the energy absorbed by $n_{i\nu}$ quasiparticles in a unit time [18] is $q'_{i\nu} = n_{i\nu}\sigma_\nu c\chi_\nu h\nu$, where σ_ν is the effective cross section of absorption of the photons $h\nu$ by an atom; as follows from the energy-balance equation for a system of particles under equilibrium conditions, the ratio $\varepsilon_\nu/\sigma_\nu$ is independent of the type of atoms. Since every quasiparticle of the energy level i that absorbed the photon $h\nu$ passes to the $(i+1)$th level, the number of particles that will pass from level i to level $i+1$ in a unit time because of the absorption of the energy $q'_{i\nu}$ will be

$$\dot{n}'_{iv} = \dot{q}'_{iv}/h\nu = n_{iv}\sigma_v c\chi_v\,, \quad i = 0.\ 1,\ ...\ ,\ I\,, \tag{3}$$

where $\dot{n}'_{iv}$ is the number of particles of the unit volume, which leave the energy level i in a unit time because of the absorption of the photons $h\nu$. In the same time interval, $\dot{n}'_{i-1,v} = n_{i-1,v}\sigma_v c\chi_v$ particles will pass from level $i-1$ to level i.

Under the equilibrium conditions of the system, the number of quasiparticles at the level i remains unchanged, i.e.,

$$\frac{dn_{iv}}{dt} = \dot{n}'_{i-1,v} - \dot{n}'_{iv} - \dot{n}_{iv} = 0\,, \quad i = 1, 2, ...\ ,\ I\,. \tag{4}$$

Equation (4) can be solved, with account for relation (2) and (3), as

$$w_{iv} = w_{0v}\left(1 + \frac{\varepsilon_v}{c\sigma_v\chi_v}\right)^{-E_{iv}/h\nu} = w_{0v}s^i\,, \quad i = 0, 1, ...\ ,\ I\,. \tag{5}$$

Here $w_{iv} = n_{iv}/n_v$ is the probability of existence of a quasiparticle oscillating with frequency ν at the ith energy level;

$$s = \left(1 + \frac{\varepsilon_v}{c\sigma_v\chi_v}\right)^{-1}\,. \tag{6}$$

For the equilibrium system, it follows from the condition of conservation of the number of quasiparticles n_v that

$$\sum_{i=0}^{I} w_{iv} = w_{0v}\sum_{i=0}^{I} s^i = w_{0v}\frac{1 - s^{I+1}}{1 - s} = 1 \tag{7}$$

and, consequently, $w_0 = (1 - s)/(1 - s^{I+1})$.

The mean energy of a quasiparticle oscillating with frequency ν is determined by the expression

$$e_v = \sum_{i=0}^{I} E_{iv}n_i \Big/ \sum_{i=0}^{I} n_i = h\nu w_{0v}\sum_{i=0}^{I} is^i = h\nu\frac{s}{(1 - s)(1 - s^{I+1})}[1 - s^I - Is^I(1 - s)]\,. \tag{8}$$

Since $s < 1$, the mean energy of a quasiparticle increases as the value of I increases. When $I \to \infty$, its mean energy is

$$e_v^{\infty} = h\nu\frac{s}{1 - s}\,. \tag{9}$$

When the system is equilibrium, the energy emitted by quasiparticles of the unit volume in a unit time,

$$J_{\text{imet}} = \sum_{i=0}^{I} \varepsilon_v n_i ih\nu + (I + 1)\,n_I h\nu c\sigma_v\,\chi_v\,, \tag{10}$$

is equal to the energy J_{abs} which is absorbed by them in the same time interval:

$$J_{\text{abs}} = \sum_{i=0}^{I} h\nu n_{iv}c\sigma_v\,\chi_v = h\nu n_v c\sigma_v\,\chi_v\,. \tag{11}$$

From (10) and (11) we find, with account for (9), that

$$\chi_\nu = \frac{\varepsilon_\nu}{c\sigma_\nu} \frac{s}{1-s} = \frac{\varepsilon_\nu}{c\sigma_\nu} \frac{e_\nu^\infty}{h\nu}. \tag{12}$$

The dependence of the quantities s, e_ν, and χ_ν on the temperature T can be obtained in the following way. We represent the function $w_{i\nu}$ in the form

$$w_{i\nu} = \frac{1-s}{1-s^{I+1}} s^i = \exp\left(\frac{\Psi - E_{i\nu}}{\theta}\right), \tag{13}$$

where

$$\theta = -\frac{h\nu}{\ln s} = \frac{h\nu}{\ln\left(1 + \dfrac{\varepsilon_\nu}{c\sigma_\nu \chi_\nu}\right)}; \quad \Psi = \theta \ln\left(\frac{1-s}{1-s^{I+1}}\right). \tag{14}$$

Substituting (13) into the equation of conservation of the number of particles, written in the form $\sum\limits_{i=1}^{I} w_i = 1$, and then differentiating it with respect to θ, we arrive at the equation

$$\sum_{i=1}^{I} \frac{1}{\theta^2}\left[\theta\frac{\partial\Psi}{\partial\theta} - (\Psi - E_{i\nu})\right]\exp\frac{\Psi - E_{i\nu}}{\theta} = 0. \tag{15}$$

Taking into account that the quantities θ and ψ are independent of i, we find from Eq. (15) that

$$\theta\frac{\partial\Psi}{\partial\theta} = \Psi - e_\nu. \tag{16}$$

This expression is a Gibbs–Helmholtz thermodynamic equation for the system in which the single oscillation frequency ν is realized; the function Ψ is the free energy attributed to a single particle, and $\theta = bT$, $b \neq b(T)$. Then it follows from (12) that

$$\chi_\nu = \frac{\varepsilon_\nu}{c\sigma_\nu}\left[\exp\left(\frac{h\nu}{bT}\right) - 1\right]^{-1}. \tag{17}$$

The quantity χ_ν determines the total number of photons $h\nu$ in the unit volume, which move in different directions and form N_ν standing waves. The energy of one standing wave is $U_{st\nu} = \chi_\nu h\nu/N_\nu$. According to classical physics, in a blackbody, the number of standing waves in a unit volume with frequencies from ν to $\nu + d\nu$ is determined by the relation $dg(\nu) = 8\pi\nu^2 d\nu/c^3$; then the number of frequencies in this interval is $8\pi\nu^2 d\nu/(c^3 N_\nu)$. In this case, the volume density of the energy of the blackbody-radiation field is

$$\rho_\nu = U_{st\nu}\frac{8\pi\nu^2}{c^3} = \frac{8\pi h\nu^3}{c^3}\frac{\varepsilon_{\beta\nu}}{c\sigma_{\beta\nu}N_\nu}\left[\exp\left(\frac{h\nu}{bT}\right) - 1\right]^{-1}. \tag{18}$$

Comparing the expression obtained to the Wien thermodynamic law and the Rayleigh–Jeans classical formula, we find that $b = k$ and $\varepsilon_{\beta\nu}/(c\sigma_{\beta\nu}N_\nu) = 1$. In this case, formula (18) coincides with the Planck formula

$$\rho_\nu = \frac{8\pi h \nu^3}{c^3}\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]^{-1}, \tag{19}$$

and the expressions for the photon density χ_ν and the function s take the form

$$\chi_\nu = \frac{\varepsilon_\nu}{c\sigma_\nu}\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]^{-1}, \quad s = \exp\left(-\frac{h\nu}{kT}\right). \tag{20}$$

It is easily seen that in the case of an infinite upper limit of the spectrum of energy states of a quasiparticle (when $I \to \infty$), the function $w_{i\nu}$ transforms to the Maxwell–Boltzmann distribution $w_{i\nu} = \left[1 - \exp\left(-\frac{h\nu}{kT}\right)\right]\exp\left(-\frac{E_{i\nu}}{kT}\right)$, while e_ν transforms to the expression for the mean energy of a quantum oscillator $e_\nu = e_\nu^\infty = h\nu\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]^{-1}$; just as χ_ν, the value of e_ν^∞ is independent of the chemical composition of the body. For the case where $I = 1$, it follows from (13) that $w_{0\nu} = 1/(1 + s)$ and $w_{1\nu} = s/(1 + s)$. In this case, the probability of existence of a quasiparticle in the state, which corresponds to the energy of $h\nu$, is $w_{1\nu} = 1 \Big/ \left[\exp\left(\frac{h\nu}{kT}\right) + 1\right]$, i.e., for this case, distribution (13) coincides with the Fermi–Dirac distribution.

The probable number of particles of the unit volume of a condensed body, oscillating with a frequency ν, which reach the activation energy per unit time, is

$$G_{A\nu} = w_I c\sigma_\nu \chi_\nu n_\nu = \varepsilon_\nu n_\nu \frac{s^{I+1}}{1 - s^{I+1}} = \varepsilon_\nu n_\nu\left[\exp\left(\frac{A}{kT}\right) - 1\right]^{-1}. \tag{21}$$

Summing (21) over all the electromagnetic wave frequencies realized in the condensed body, we find the probable number of particles of the unit volume which reach the activation energy in a unit time:

$$G_A = \varepsilon n\left[\exp\left(\frac{A}{kT}\right) - 1\right]^{-1}, \tag{22}$$

where ε is the value of ε_ν averaged over the oscillation frequencies of the particles; $n = \sum_\nu n_\nu$.

Not all the particles that received the energy $(I + 1)h\nu$ break away from the body. This is explained by the fact that on the way to the free surface a particle, overcoming the resistance of the surrounding particles, loses energy E_l that is proportional to the length of the path traversed by the particle after reaching the activation energy and to the particle density n, i.e., $E_l = \xi nl$, where $\xi = \text{const}$. A particle can break away from the body on condition that $E_l \le (I + 1)h\nu$. Hence it follows that the maximum distance of the particle from the free surface, at which the particle can leave the body, is

$$\delta^* = \frac{(I + 1)\,h\nu}{\xi n} \approx \frac{A}{\xi n}. \tag{23}$$

The quantity δ^* can be considered as the thickness of the boundary layer adjacent to the free surface of a fairly massive condensed body in which the evaporation process occurs.

Let us find the flux of particles that evaporate from a condensed-body layer of thickness δ reckoned from the free surface along its inner normal η. To do this, we consider the elementary layer $d\eta$ which is at a distance η from the free surface ($\eta = 0$). The number of particles contained in the elementary layer is $dn = nd\eta$. In accordance with

(22), the probable number of particles of the elementary layer of unit area which reach the activation energy per unit time is

$$dG_A = G_A d\eta . \tag{24}$$

Each of these particles has a chance to break away from the body. The probability of their evaporation is determined in the following way. A spherical surface of radius δ^* with a center coincident with the center of the particle is constructed. This surface is positioned in the elementary layer considered, and it reached the activation energy. This particle can break away from the body only at those points of its free surface which are positioned inside the indicated sphere. If, as a result of the transformation of activation energy, this particle obtains a momentum whose direction is equiprobable, the probability of its evaporation w_e is equal to the ratio between the solid angles $\omega_{f.s}$ and ω_{sph} which are bound by a part of the free surface positioned inside the sphere and by the entire sphere. For the case of a plane free surface, the solid angle $\omega_{f.s}$ is determined as the ratio of the area of the spherical segment cut off by the free surface $\eta = 0$ from the sphere to the square of its radius, i.e.,

$$\omega_{f.s} = 2\pi \left(1 - \frac{\eta}{\delta^*}\right), \quad \omega_{sph} = 4\pi, \quad w_e = \frac{1}{2}\left(1 - \frac{\eta}{\delta^*}\right).$$

In this case, the probable number of particles evaporated from the elementary layer of unit surface in a unit time is

$$dG_e = \frac{1}{2}\left(1 - \frac{\eta}{\delta^*}\right) G_A d\eta . \tag{25}$$

The specific flow rate of particles evaporated from the free surface G_e is determined by integrating (25) over the thickness of the layer considered, $0 < \eta < \delta$, if $\delta < \delta^*$ or over the thickness of the sublevel $0 < \eta < \delta^*$ if $\delta > \delta^*$. With account for (21) and (23), the formula for the specific intensity of evaporation of a condensed body can be written in the following form:

$$G_e = \frac{\bar{\delta}}{2}\left(1 - \frac{\bar{\delta}}{2}\right)\frac{\varepsilon A}{\xi}\left[\exp\left(\frac{A}{kT}\right) - 1\right]^{-1}, \quad 0 < \bar{\delta} \leq 1, \tag{26}$$

where $\bar{\delta} = \delta/\delta^*$. It follows from formula (26) that the intensity of evaporation of a condensed body depends on only one state parameter, i.e., the temperature of the body. For a massive body whose geometric characteristics are much larger than δ^*, formula (26) takes the form

$$G_e = \frac{\varepsilon A}{4\xi}\left[\exp\left(\frac{A}{kT}\right) - 1\right]^{-1}. \tag{27}$$

If the thickness of the boundary layer δ^* is a relatively small quantity, the intensity of evaporation can arbitrarily be considered as a function of the temperature of the outer boundary of the condensed body.

The flow of vapor molecules G_c from the gas phase, incident on the interface of unit area between the condensed and gas phases and condensed on it, is determined by the expression

$$G_c = \frac{1}{2} f n_v \bar{V}_\eta . \tag{28}$$

Here f is the condensation coefficient [1], which represents the ratio of the number of molecules caught by the surface of the liquid to the total number of vapor molecules incident on the surface of the condensate and n_v is the density of vapor molecules in the gas phase, which, for an ideal gas, is related to the partial pressure of the vapor P_v and its temperature T_v by the relation following from the Mendeleev–Clapeyron relation

$$n_v = \frac{P_v}{kT_v} \, ; \tag{29}$$

$\overline{V}_\eta$ is the component of the mean thermal velocity of molecules normal to the surface of the condensed body which, for the case of the Maxwell distribution of them by velocities, is determined by the expression

$$\overline{V}_\eta = \sqrt{\frac{2kT_v}{\pi m}} \, . \tag{30}$$

The factor 1/2 in (28) is due to the fact that of n_v molecules only half approach the phase interface and can condense. Substituting expressions (29) and (30) into (28), we obtain

$$G_c = \frac{f}{\sqrt{2\pi km}} \frac{P_v}{\sqrt{T_v}} \, . \tag{31}$$

When the system condensed body–gas phase is under heat-equilibrium conditions, the phase temperatures and the mass flows of the evaporated and condensed molecules are equal, i.e., $T_v = T$ and $G_e = G_c$, and the vapor pressure P_v is equal to the saturated vapor pressure P_s. Under these conditions, from formulas (27) and (31) we find the functional dependence of the saturated vapor pressure on the temperature:

$$P_s = N \sqrt{T} \left[\exp\left(\frac{A}{kT}\right) - 1 \right]^{-1} , \quad N = \frac{\overline{\delta}}{2} \left(1 - \frac{\overline{\delta}}{2} \right) \frac{\varepsilon A \sqrt{2\pi km}}{f\xi} \, . \tag{32}$$

The dependence between the temperature of the liquid T and the pressure of the saturated vapor P_s which is in thermodynamic equilibrium with the massive liquid layer has been found experimentally for a number of liquids, and it is presented in the literature [15] in the form of tables of a saturated vapor and a liquid on the saturation line. Because of this, one can compare the found dependence (32) to experimental data, for example, for water and ammonia. Broadly speaking, the quantities A, f, and ξ can undergo certain changes in the temperature range in which the liquid can exist. However, in separate regions of this range, the quantities A and N can be considered to be constant. The values of A and N can be found by way of solution of the system of two equations obtained as a result of representation of Eq. (32) for two points on the saturation line, which correspond, respectively, to the values of T_1, P_{s1} and T_2, P_{s2} in the table of a saturated vapor and water. The calculations have shown that the use of only two points on the saturation line for determining the dependence of P_s on T throughout the entire temperature range of existence of water (from 273 to 647 K) produces an error in the pressure P_s calculated from (32) as compared to its tabulated value (at the same temperature). The maximum value of this error was approximately $\Pi_{max} = 11.9\%$, while the mean error was $\Pi_m = 7.3\%$. The subdivision of the interval of existence of water into two regions $273 < T < 373$ K and $373 < T < 647$ K made it possible to obtain the errors $\Pi_{max} = 3.4\%$ and $\Pi_m = 2.1\%$ at $A^{'} = 0.4206 \cdot 10^8$ J/(kmole) and $N = 0.4361 \cdot 10^{10}$ kg/(m·sec^2·K$^{0.5}$) for the first region and $\Pi_{max} = 2.6\%$ and $\Pi_m = 1.2\%$ at $A^{'} = 0.3689 \cdot 10^8$ and $N = 0.8514 \cdot 10^9$ for the second region. These errors are close to the errors in the tabulated data. Here $A^{'} = A N_A$; N_A is the Avogadro number. The calculations of the dependence $P_s = F(T)$ for ammonia have shown that the subdivision of the temperature interval $203 < T < 323$, for which the tabulated data on the parameters of the saturated vapor on the saturation line are available in the literature [15], into two regions $203 < T < 243$ K and $243 < T < 323$ K makes it possible to obtain the errors $\Pi_{max} = 1.28\%$ and $\Pi_m = 0.56\%$ at $A^{'} = 0.2367 \cdot 10^8$ J/kmole and $N = 0.9821 \cdot 10^{10}$ kg/(m·sec^2·K$^{0.5}$) for the first region and $\Pi_{max} = 1.31\%$ and $\Pi_m = 0.76\%$ at $A^{'} = 0.2194 \cdot 10^8$ and $N = 0.4187 \cdot 10^9$ for the second region. As is seen from the figure, the calculated dependence is in good agreement with the tabulated data in this case, which indicates that the dependence of the state parameters on the saturation line can be described based on Eq. (32).

Starting from expressions (26) and (31), it can be shown that in the case of the equilibrium system threshold mixture–nonevaporated condensed body, on the latter there arises a liquid layer whose thickness is $\delta = \delta^*(1 - \sqrt{1 - \psi})$.
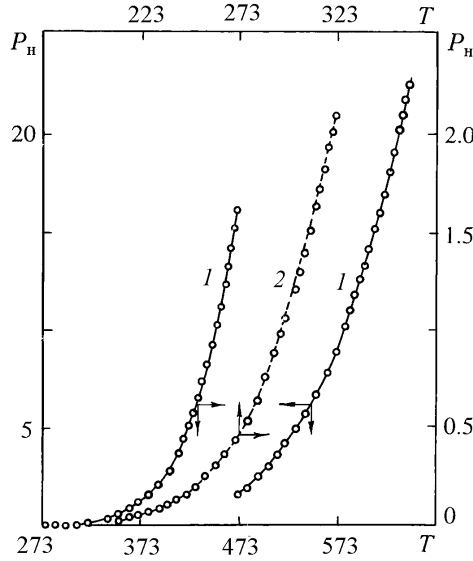
Fig. 1. Comparison of the dependences of the pressure P_s of the saturated vapor on the temperature T for water (curves 1) and ammonia (curve 2) calculated from Eq. (32) to the tabulated data (points). P_s, MPa; T, K.

Let us consider the nonequilibrium process of interaction of a condensed body with a vapor-gas mixture, which is realized, for example, in the case of flow of a gas around the body. We mentally separate a Knudsen layer near the surface of the condensed body in the gas phase, i.e., a layer having a thickness equal to the mean free path of the vapor molecules in order of magnitude. We denote the gas temperature and the partial pressure of the vapor at the outer boundary of the Knudsen layer as T_g and P_v. In this case, the specific flow rate of the molecules evaporated from the free surface of the condensed body is determined by formula (26). The flow of condensing vapor molecules passing through the outer boundary of the Knudsen layer has been found, in accordance with (29) and the condition of equality of the evaporation and condensation flows in the case of the equilibrium system, from the formula

$$G_c = \frac{f}{\sqrt{2\pi km}}\frac{P_s\psi}{\sqrt{T_g}} = \frac{\bar{\delta}}{2}\left(1 - \frac{\bar{\delta}}{2}\right)\frac{\varepsilon A\psi}{\xi}\left[\exp\left(\frac{A}{kT_g}\right) - 1\right]^{-1},$$ (33)

where ψ is the degree of saturation of the vapor-gas mixture at a given temperature, $\psi = P_v/P_s(T_g)$.

The resulting specific flow of vapor molecules from the condensed body

$$G = G_e - G_c = \frac{\bar{\delta}}{2}\left(1 - \frac{\bar{\delta}}{2}\right)\frac{\varepsilon A}{\xi}\left\{\left[\exp\left(\frac{A}{kT}\right) - 1\right]^{-1} - \psi\left[\exp\left(\frac{A}{kT_g}\right) - 1\right]^{-1}\right\}.$$ (34)

For the case of the single-component condensation of a saturated vapor on a massive condensed body where $\psi = 0$ and $G_e = G_c$, it follows from (34) that the resulting mass flow of the condensate $G_m = Gm$ is determined by the expression

$$G_m = f\sqrt{\frac{m}{2\pi k}}\left[\frac{P_s(T_g)}{\sqrt{T_g}} - \frac{P_s(T)}{\sqrt{T}}\right],$$ (35)

which represents the known Hertz–Knudsen formula [1].

The specific heat flux $Q = -\lambda\partial T/\partial\eta\,|_{\eta=0}$ which is delivered to the boundary surface of the condensed body due to the processes of evaporation, condensation, and convective heat exchange can be found on the basis of the energy conservation law:

691

$$Q = \frac{\overline{\delta}}{2}\left(1 - \frac{\overline{\delta}}{2}\right)\frac{\varepsilon A m}{\xi}\left\{r\left(T\right)\left[\exp\left(\frac{A}{kT}\right) - 1\right]^{-1} - \psi r\left(T_g\right)\left[\exp\left(\frac{A}{kT_g}\right) - 1\right]^{-1}\right\} - \alpha\left(T_g - T\right), \tag{36}$$

where r is the heat of the phase transition of the condensed body to the vapor ($r = r(T)$) and α is the coefficient of convective heat exchange. Equation (36) can be used as the condition of heat exchange between the evaporating body and the environment.

NOTATION

A, activation energy; c, velocity of light; e, mean energy per degree of freedom of an atom; $E_{i\nu}$, energy per degree of freedom of an atom found at the ith energy level in frequency ν; G_A, probable number of particles in a unit volume, which reach the activation energy in a unit time; G_e, specific intensity of evaporation of particles from the free surface of the condensed body; G_c, specific flow of vapor molecules from the gas phase, which are condensed from the free surface of the body; G_m, resulting mass flow of the condensate; h, Planck constant; k, Boltzmann constant; m, mass of vapor molecules; n, density of particles (quasiparticles); N_ν, number of standing waves of frequency ν in a unit volume of the body; P, pressure; P_v, partial pressure of the vapor; q, spectral-radiation power of the degrees of freedom of particles in a unit volume of the body; Q, specific heat flux; t, time; T, temperature; V, velocity of travel of vapor particles in the environment; $\overline{\delta}$, relative thickness of the condensed-body layer; δ^*, thickness of the near-boundary layer in which the evaporation process occurs; ε, emissivity; η, normal to the free surface of the body; λ, thermal-conductivity coefficient; σ, effective cross section of the absorption of photons by a particle of the body; χ, photon density; ξ, coefficient of resistance to the movement of a particle. Subscripts: e, evaporation; c, condensation; s, saturated vapor; v, vapor; i, serial number of energy level; ν, frequency of oscillations of the degree of freedom of an atom; emit, emission; abs, absorption; st, standing; f.s, free surface; m, mean; g, gas.

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