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PROBLEMS OF THE RADIATION THEORY OF HEAT AND MASS TRANSFER IN SOLID AND LIQUID MEDIA

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A mechanism and foundations of the radiation theory of heat and mass transfer that are based on the transfer of energy by photons emitted and absorbed by particles of the substance are presented. Equations of heat and mass transfer that transform, in the limit, to known phenomenological equations, energy distribution functions of atoms and their degrees of freedom in diffusion processes, and expressions for the specific heat and the diffusion coefficient that yield, as particular cases, the known Debye, Arrhenius, and Einstein formulas have been found.

Kinetic processes in condensed bodies that are related to atomic migrations cause significant changes in their macro- and microproperties. To purposefully change these properties, it is necessary to have detailed knowledge of the processes themselves. These processes are characterized by the fact that their intensity is highly dependent on the temperature. For example, the diffusion coefficient of zinc in copper increases by a factor of 1014 as the temperature increases from 20 to 300°C [1].

Diffusion transfer in solids is usually related [1-5] to atomic-energy fluctuations, owing to which an atom can reach an energy level sufficient for breakage of the bonds with neighboring atoms and for migration into the surroundings of other atoms. It is suggested [2] that most of the time an atom is found in the "settled" state where it oscillates with a frequency $\nu = kT/h$, and from time to time it performs diffusion transitions when it is given the activation energy u. The duration of stay of the atom in the settled state between transitions is $\tau = \tau_0 \exp(u/kT)$, where τ_0 is a time of the order of the oscillation period of the lattice atoms that corresponds to the frequency ν ($\tau_0 = 10^{-13}$ sec). The diffusion coefficient D is determined by an expression that is analogous to the Arrhenius formula for the temperature dependence of the rate of macroscopically observed processes:

$$D = \alpha l^2/\tau = D_0 \exp(-u/kT)\,, \tag{1}$$

where l is the mean distance traversed by the atom in a diffusion transition, which is usually assumed to be equal to the distance between neighboring atoms of the body; α is geometric factor that depends on the kind of crystal lattice; D_0 is the preexponential factor, $D_0 = \alpha l^2/\tau_0$.

In solids, several diffusion mechanisms can occur; among them are exchange of places of atoms of the crystalline structure with its vacancies, migration of atoms over interstitial sites, simultaneous cyclic migration of several atoms, and exchange of places between two neighboring atoms. These mechanisms correspond to different values of the parameters D_0 and u [4, 5]. The diffusion coefficient is sometimes evaluated with the use of the Eyring theory of reaction rates, which also gives a dependence of the form of (1) with a preexponential factor $D_0 = A_0 kT/h$, where A_0 is the transmission coefficient. However, it does not agree with usual data [6]. In [7, 8], the temperature dependence of the diffusion coefficient of hydrogen and deuterium in niobium was obtained experimentally; with increase in the temperature one observes an accelerated increase in D, which cannot be described with the use of one exponent.

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The theory of diffusion in liquids has been developed in three main directions. The first of them is based on an analogy between the structures of a liquid and a solid and on the mechanism of migrations of molecules [2] with an activation energy lower than the activation energy in solids. The second direction starts from the general principles of statistical physics and the concept of local equilibrium [9, 10]. The density of molecules in each component is considered as a hydrodynamic variable changing slowly in space and time. Statistical equilibrium is established initially in macroscopically small volumes, and then the entire system switches to a state of equilibrium at a rate proportional to the gradient of the concentration of the components. The diffusion coefficient is defined in terms of a correction to the local equilibrium distribution function.

In the third direction, the diffusion of molecules in liquids is considered as a migration of small particles with friction. This migration can be described using the Einstein equation to relate the diffusion coefficient of Brownian particles to their mobility:

$$D = bkT\,, \tag{2}$$

where b is the mobility of the diffusing particles, determined as the coefficient of proportionality between the velocity of a particle and the motive force in steady motion. For spherically symmetric particles, in accordance with the Stokes law, $b = 1/(6\pi\mu r_{\mathrm{p}})$, where μ is the viscosity of the medium and r_{p} is the radius of the particle.

In the works of Nikitenko [11-14], a radiation theory of heat conduction that is based on the mechanism of energy transfer by photons emitted and absorbed by particles of the substance has been constructed. In it Nikitenko obtained an integro-differential equation of energy transfer that makes it possible to explain the known discrepancies between the classical theory of heat conduction and experimental data and, in the limit, becomes: the Fourier equation of heat conduction; the fundamental law of spectral-radiation intensity of microparticles of a body, from which the Planck formula for the emissive power of a blackbody as well as known and certain new functions energy distribution of particles follow; the potential of interatomic interaction representing a function of particle energy; an equation of state of bodies from which Hooke's law, the law of thermal expansion, and the Grüneisen law follow.

In this work, a mechanism and foundations of the radiation theory of heat and mass transfer in condensed media are presented. A system of equations of heat and mass transfer that, in the limit, transforms to the equations of the phenomenological theory of the thermodynamics of irreversible processes has been derived. Energy distribution functions of atoms and their degrees of freedom in diffusion processes have been found, and based on them the temperature dependences of the specific heat and the diffusion and thermodiffusion coefficients of the components of a body have been obtained.

The dynamics of diffusion processes in multicomponent condensed systems in a changing temperature field is determined by energy distribution functions of the atoms and an intensity function of their transition from a given energy level to the next higher level in these processes. The indicated functions can be found based on the law of spectral-radiation intensity.

Let us consider a condensed body consisting of B components. Each atom of the body corresponds to three degrees of freedom, and it can emit and absorb photons of three different frequencies ν. Assume that in a unit volume of a condensed body there are $n_{\beta\nu i}$ degrees of freedom of atoms of the component β, which have an energy $E_{i\nu} = ih\nu$, i.e., are found at the i-th energy level with respect to the frequency ν. Then, in accordance with the law of spectral-radiation intensity, the energy emitted by these degrees of freedom with the same probability in all directions in unit time comprises [11]

$$q_{\beta i\nu} = \varepsilon_{\beta\nu}\, n_{\beta i\nu}\, E_{i\nu} = \varepsilon_{\beta\nu}\, n_{\beta i\nu}\, ih\nu\,, \quad i = 1, 2, \dots, I_{\beta\nu}\,, \tag{3}$$

where $\varepsilon_{\beta\nu}$ is the emission coefficient of photons $h\nu$; $I_{\beta\nu}$ is the limiting energy level at which the degree of freedom of a β-component atom can be found, determined from the condition $I_{\beta\nu}h\nu < u_{\beta} \le (I_{\beta\nu} + 1)h\nu$; u_{β} is the activation energy at which the β-component atom performs a diffusion transition. Since in emission, the degree of freedom shifts to a zero energy level, emitting i quantums $h\nu$, the number of degrees of freedom leaving the level in unit time is $\dot{n}_{\rho i\nu} = q_{\rho i\nu}/ih\nu = \varepsilon_{\beta\nu} n_{\beta i\nu}$. In a diffusion transition the atom gives up its energy $(I_{\beta\nu} + 1)h\nu$ and is brought to a zero energy level in a neighboring cell.

If the density of photons $h\nu$ is χ_ν, then the energy absorbed in unit time $n_{\beta i\nu}$ by the degrees of freedom [11] is $q'_{\beta i\nu} = n_{\beta i\nu}\sigma_{\beta\nu}c\chi_\nu h\nu$, where $\sigma_{\beta\nu}$ is the effective cross section of absorption of photons $h\nu$ by a β-component atom; $\varepsilon_{\beta\nu}/\sigma_{\beta\nu} \neq f(\beta)$ [11]. The intensity function of the transition of the degrees of freedom of atoms in unit volume from the given energy level i to the level $i + 1$ as a result of absorption of the energy $q_{\beta i\nu}$ by them has the form

$$\dot{n}'_{\beta i\nu} = q'_{i\nu}/h\nu = n_{\beta i\nu}\,\sigma_{\beta\nu}\,c\chi_\nu\,, \quad i = 1, 2, \ldots, I_{\beta\nu}\,. \tag{4}$$

All the degrees of freedom of β-component atoms in unit volume $n_{\beta\nu} = \sum_i n_{\beta i\nu}$ absorb the energy $q'_{\beta\nu} = n_{\beta\nu}\sigma_{\beta\nu}c\chi_\nu h\nu$ and emit the energy $q_{\beta\nu} = \sum_i q_{\beta i\nu} + (I_{\beta\nu} + 1)h\nu\dot{n}_{\beta I_{\beta\nu}\nu}$ in unit time. Under steady-state conditions the number of degrees of freedom at the level i remains constant, i.e., $\partial n_{\beta i\nu}/\partial t = \dot{n}'_{\beta i-1,\nu} - \dot{n}'_{\beta i\nu} - \dot{n}_{\beta i\nu} = 0$ and $q_{\beta\nu} = q'_{\beta\nu}$. Going from the function $n_{\beta i\nu}$ to the probability $w_{\beta i\nu}$ that a β-component atom is found, with respect to the frequency ν, at the i-th level $w_{\beta i\nu} = n_{\beta i\nu}/n_{\beta\nu}$ and taking into account the normalization condition $\sum_i w_{\beta i\nu} = 1$, we obtain

$$w_{\beta i\nu} = \left[1 - \exp\left(-\frac{h\nu}{kT}\right)\right]\left[1 - \exp\left(-\frac{(I_{\beta\nu} + 1)\,h\nu}{kT}\right)\right]^{-1} \exp\left(-\frac{E_{i\nu}}{kT}\right), \tag{5}$$

$$\chi_\nu = \frac{\varepsilon_{\beta\nu}}{c\sigma_{\beta\nu}}\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]^{-1}, \tag{6}$$

$$e_{\beta\nu} = h\nu\left[1 - (I_{\beta\nu} + 1)\, w_{\beta I_{\beta\nu}\nu}\right]\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]^{-1}. \tag{7}$$

Here the function $w_{\beta i\nu} = 0$ at $i > I_{\beta\nu}$; $e_{\beta\nu}$ is the mean energy of the degree of freedom of the atom, determined from the relation $e_{\beta\nu} = h\nu\sum_i in_{\beta\nu i}/\sum_i n_{\beta\nu i}$. When $I_{\beta\nu} >> 1$ the function $w_{\beta i\nu}$ transforms to the Maxwell–Boltzmann distribution, and $e_{\beta\nu}$ transforms to the expression for the mean energy of a quantum oscillator $e_\nu = h\nu\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]^{-1}$; by analogy with χ_ν, the quantity e_ν is independent of the kind of component.

The quantity χ_ν determines the total number of photons $h\nu$ in unit volume that transfer in different directions and form N_ν standing waves. The energy of one standing wave is $U_{\mathrm{st}\nu} = \chi_\nu h\nu/N_\nu$. Since, according to classical physics, the frequency density distribution function of standing waves in a blackbody is $g(\nu) = 8\pi\nu^2 d\nu/c^3$, the number of frequencies in the interval from ν to $\nu + d\nu$ comprises $8\pi\nu^2 d\nu/(c^3 N_\nu)$. In this case, the density of the energy of the black-radiation field is

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

Comparing this expression with the Rayleigh–Jeans formula, we find that $\varepsilon_{\beta\nu}/(c\sigma_{\beta\nu}N_\nu) = 1$. In this case formula (8) coincides with the Planck formula.

In general, the distribution function of atoms by energies can be obtained if the of the distribution functions of their degrees of freedom by frequencies ν and over the energy levels are known. In this case, the probability w^{a} that an atom has an energy E when the state of its degrees of freedom is characterized by the parameters ν_1, i_1, ν_2, i_2, ν_3, and i_3 (here, $i_1h\nu_1 + i_2h\nu_2 + i_3h\nu_3 = E$) is determined by the product of the probabilities that the degrees of freedom of the atom are found in the corresponding states. The probability w^{a} that an atom has an energy E is found by summation of the values of w^{a} for all possible atomic states fitting this energy.

For solids, the function $g(\nu)$, in general, is unknown; this being so, approximate representations of it are used. At a high and a usual temperature, when $kT >> h\nu_{\max}$, the Einstein hypothesis of the existence of a unique characteristic frequency ν' for each substance is a fairly good approximation of the function $g(\nu)$ [6]. In this approximation, the probability that an atom is found at the i-th energy level when its degrees of freedom occupy levels i_1, i_2, and i_3 satisfying the condition $i = i_1 + i_2 + i_3$ is

$$\overline{w}^{a}_{\beta i} = w_{\beta i_1\nu}\, w_{\beta i_2\nu}\, w_{\beta i_3\nu} = \frac{\left[1-\exp\left(\frac{h\nu'}{kT}\right)\right]^3}{\left[1-\exp\left(-\frac{(i+1)\,h\nu'}{kT}\right)\right]^3}\exp\left(-\frac{E_{i\nu'}}{kT}\right).$$

The probability that a β-component particle has an energy $ih\nu$ is $w^{a}_{\beta iz} = \omega_{\beta iz}\overline{w}^{a}_{\beta i}$, where $\omega_{\beta iz}$ is the statistical weight of the particle state, which is defined as the number of ways in which i quanta $h\nu'$ can be distributed over z_β degrees of freedom, $\omega_{\beta iz} = (i + z_\beta - 1)\,!/[i\,!\,(z_\beta - 1)\,!]$. With diffusion transitions, the probability that a particle is found at a zero energy level is determined, in accordance with the normalization condition, by the expression $w^{a}_{\beta 0z} = 1 - \sum_{i=1}^{l_{\beta\nu}} w^{a}_{\beta iz}$. At $l_{\beta\nu} >> 1$

$$w^{a}_{\beta i\nu} = \omega_{\beta iz}\left[1-\exp\left(-\frac{h\nu'}{kT}\right)\right]^z \exp\left(-\frac{E_{i\nu'}}{kT}\right). \tag{9}$$

For an atom with three degrees of freedom ($z = 3$), it follows from (9) that

$$w^{a}_{\beta i} = \frac{(i+1)\,(i+2)}{2}\left[1-\exp\left(\frac{h\nu'}{kT}\right)\right]^3 \exp\left(-\frac{ih\nu'}{kT}\right).$$

It can be shown that

$$\sum_{i=0}^{\infty} \frac{(i+z)\,!}{i\,!}\,q^{i} = \frac{z\,!}{(1-q)^{z+1}}$$

and, correspondingly, $\sum w^{a}_{\beta iz} = 1$, and the mean energy of an atom is $e^{a}_{\nu'} = \sum ih\nu w^{a}_{\beta iz} = ze_{\nu'}$. It is seen from Fig. 1 that the energy distribution functions of the atoms and their degrees of freedom differ markedly. Whereas for the degrees of freedom of the atoms the distribution function has a maximum at $i = 0$ and monotonically decreases independently of the temperature, for the atoms this function has a maximum at $i > 0$ at fairly high temperatures. Analogously, we can find the energy distribution functions in the case of diffusion of molecules and groups of atoms.

Since the probable number of diffusion transitions performed by an atom of kind β in unit time is $\dot{n}_\beta/n_\beta$ and in each transition the atom traverses a distance l_β, its mean velocity is $v_\beta = l_\beta\dot{n}_\beta/n_\beta$. The value

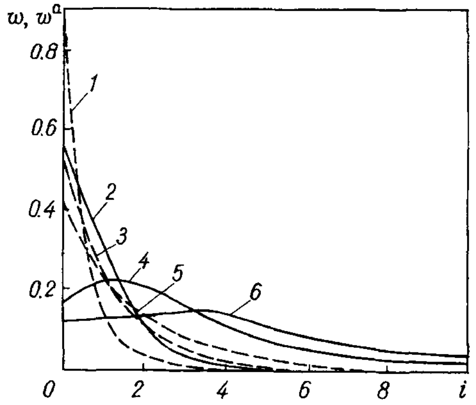

Fig. 1. Change in distribution functions of atoms w^a (solid curves) and their degrees of freedom w (dashed curves) over the energy levels i at different temperatures: 1, 2) T = 573 K; 3, 4) 1145; 5, 6) 1753.

of l_β is determined by the parameters of an elementary crystalline cell, and therefore we can consider that $l_\beta \neq f(n_\beta, T)$.

According to elementary kinetic theory [10], the density of the diffusion flux of atoms of kind β passing through the z plane in the positive direction comprises $j_\beta^+ = \frac{1}{6} n_\beta(z - l_\beta) v_\beta(z - l_\beta) = \frac{1}{6} l_\beta \dot{n}_\beta(z - l_\beta)$, and in the opposite direction, $j_\beta^- = \frac{1}{6} l_\beta \dot{n}_\beta(z + l_\beta)$. Consequently, the resulting density of the diffusion flux of atoms of kind β in the z direction is

$$j_\beta = j_\beta^+ - j_\beta^- = -\frac{1}{3} l_\beta^2 \frac{\partial \dot{n}_\beta}{\partial z} = -\frac{1}{3} l_\beta^2 \sigma_{\beta\nu'} c \frac{\partial}{\partial z} (n_{\beta\nu'} w_{\beta i\nu'} \chi_{\nu'}) . \tag{10}$$

Since the mechanism of transformation of activation energy in a diffusion transition of an atom is not understood yet, we considered two criteria for this transition: a) attainment of the activation energy u_β by one of the degrees of freedom of the atom; b) attainment of the energy u_β by the atom.

Substituting expression (10) into the equation of conservation of mass for the component β [11, 15] $d\rho_\beta/dt = -\text{div}\,(J_\beta)$, where $\rho_\beta = m_\beta n_\beta$ and $J_\beta = m_\beta j_\beta$, m_β is the mass of a β-component atom, we obtain, with account for relations (4)-(6), an equation of mass transfer that can be represented in the form

$$\frac{\partial \rho_\beta}{\partial t} = \text{div}\,(D_\beta\,\text{grad}\,\rho_\beta) + \text{div}\left(\frac{K_\beta}{T}\,\text{grad}\,T\right), \tag{11}$$

where D_β and K_β are the diffusion and thermodiffusion coefficients of the β-component particles,

$$D_\beta = \frac{1}{3} l_\beta^2 \sigma_{\beta\nu} c w_{\beta i\nu} \chi_\nu , \quad K_\beta = T\rho_\beta \frac{\partial D_\beta}{\partial T} = \frac{1}{3} T\rho_\beta l_\beta^2 \sigma_{\beta\nu} c \frac{\partial (w_{\beta i\nu} \chi_\nu)}{\partial T} . \tag{12}$$

Equation (11) is analogous in form to the equation of mass transfer that follows from the phenomenological theory of the thermodynamics of irreversible processes [11, 15]. In the case of realization of the first criterion, in accordance with (5), (6), and (12), the diffusion and thermodiffusion coefficients are equal to

$$D_\beta = \frac{1}{3} l_\beta^2 \varepsilon_\beta \left[\exp\left(\frac{(I_{\beta\nu} + 1) h\nu}{kT}\right) - 1\right]^{-1} = \frac{1}{3} l_\beta^2 \varepsilon_\beta \left[\exp\left(\frac{u_\beta}{kT}\right) - 1\right]^{-1} , \tag{13}$$

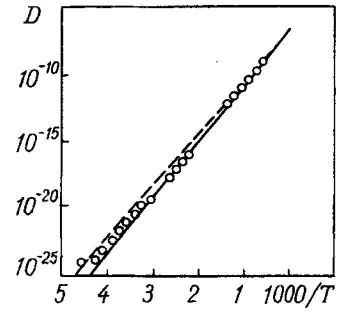

Fig. 2. Diffusion coefficient D of carbon in Armco iron vs. temperature. The solid line shows a calculation by formula (13); the dashed line shows a calculation by formula (15); the points show experiment [1]. D, m/sec; T, K^{-1}.

$$K_\beta = \frac{1}{3}\rho_\beta l_\beta^2 \varepsilon_\beta \frac{u_\beta}{kT}\exp\left(\frac{u_\beta}{kT}\right)\left[\exp\left(\frac{u_\beta}{kT}\right) - 1\right]^{-2} . \tag{14}$$

In the limit at $u/kT >> 1$ expression (13) transforms to the Arrhenius formula (1), and $D_0 = l_\beta^2\varepsilon_\beta/3$, and at $u/kT << 1$ this expression transforms to the Einstein formula (2), and $b = l_\beta^2\varepsilon_\beta/(3u_\beta)$. As is evident from Fig. 2, formula (13) agrees well with experimental data on the diffusion coefficient of carbon in Armco iron obtained by different authors [1] in the temperature range from –40 to 800°C at $l_\beta^2\varepsilon_\beta = 0.466\cdot 10^{-5}$ m^2/sec and $u_\beta/k = 1.01\cdot 10^4$ K. Note that according to the Einstein formula for the heat capacity, the characteristic frequency for carbon atoms is $\nu' \approx 1065$ k/h. Here, $I_{\beta\nu'} = 9$.

When the second criterion is realized, as a result of absorption of a photon $h\nu'$, a diffusion transition can be performed by an atom for which the total energy of the degrees of freedom is $I_{\beta\nu}h\nu'$. The number of these transitions in unit volume in unit time is determined by the formula $\dot{n}_{\beta\nu'}^{a} = 3n_{\beta\nu'}^{a} w_{\beta, I_{\beta\nu},\nu'}^{a} \sigma_{\beta\nu'} c\chi_{\nu'}$. According to (5), (8), and (12), the diffusion coefficient is

$$D_\beta^a = l_\beta^2 \varepsilon_\beta \frac{(I_{\beta\nu'} + 1)(I_{\beta\nu'} + 2)}{2} \frac{\left[1 - \exp\left(-\frac{h\nu'}{kT}\right)\right]^2 \exp\left(-\frac{(I_{\beta\nu'} + 1)h\nu'}{kT}\right)}{\left[1 - \exp\left(-\frac{(I_{\beta\nu'} + 1)h\nu'}{kT}\right)\right]^3} . \tag{15}$$

At $u_\beta/kT >> 1$, it follows from (15) that

$$D_\beta^a = \frac{1}{2} l_\beta^2 \varepsilon_\beta \frac{u_\beta}{h\nu'}\left(\frac{u_\beta}{h\nu'} + 1\right)\left[1 - \exp\left(-\frac{h\nu'}{kT}\right)\right]^2 \exp\left(-\frac{u_\beta}{kT}\right). \tag{16}$$

It is seen from Fig. 2 that formulas (15) and (16) agree well with experiment at $l_\beta^2\varepsilon_\beta = 0.52\cdot 10^{-6}$ m^2/sec and $u_\beta/k = 1.01\cdot 10^4$ K.

According to the radiation theory of heat transfer, the equation of heat transfer for a multicomponent system under diffusion conditions can be written in the form

$$\frac{\partial U(r, t)}{\partial t} = -Q_{\text{em}} + Q_{\text{abs}} + Q_{\text{dif}} + Q_{\text{s}} + Q_{\text{el}} . \tag{17}$$

Here Q_{em} is the power of photons emitted at the instant t by particles of a unit volume whose position is characterized by the radius vector r; Q_{abs} is the power of photons absorbed by particles of a unit volume and emitted by other particles of the considered system; Q_{dif} and Q_{s} are the powers supplied to the considered unit volume as a result of diffusion of particles and the action of external and internal energy sources; Q_{el} is the power spent to change the electromagnetic-energy density. The problem of changing the form of the equation of transfer for the case of convective motion of a medium was considered in [11].

The expressions for the functions entering into (17) were found under the following assumptions: the β-component atoms can emit and absorb photons whose frequency does not exceed a certain limiting value ν_β^*; in the frequency range $0 \le \nu \le \nu_\beta^*$ standing waves are distributed with a density $8\pi\nu^2 d\nu/c^3$; the probable number γ_β of degrees of freedom of β-component atoms forming a standing wave is independent of its frequency, i.e., $n_{\beta\nu}/N_\nu = \gamma_{\beta\nu} = \gamma_\beta$. The frequency ν_β^* was found from the condition that the total number of degrees of freedom of β-component atoms participating in oscillations is equal to triple the number n_β of these atoms:

$$\frac{8\pi}{c^3}\int\limits_0^{\nu_\beta^*} \gamma_\beta \nu^2\, d\nu = 3n_\beta\,. \tag{18}$$

It follows from (18) that $\nu_\beta^* = [9n_\beta c^3/(8\pi\gamma_\beta)]^{1/3}$. The specific energy U_β of the component β of a multicomponent body is

$$U_\beta = \frac{8\pi}{c^3}\int\limits_0^{\gamma_\beta^*} \gamma_\beta\, \nu^2\, e_\nu d\nu = 9kT^4\,\frac{n_\beta}{\vartheta_\beta^3}\int\limits_0^{\vartheta_\beta/T}\frac{z^3 dz}{e^z - 1}\,, \tag{19}$$

where $\vartheta_\beta = h\nu_\beta^*/k$. The specific internal energy U of a multicomponent body is

$$U = 9kT^4 \sum_{\beta=1}^{B} \frac{n_\beta}{\vartheta_\beta^3}\int\limits_0^{\vartheta_\beta/T}\frac{z^3 dz}{e^z - 1}\,. \tag{20}$$

The specific heat capacity per unit volume of a body is

$$c_V = \frac{\partial U}{\partial T} = 9K \sum_{\beta=1}^{B} n_\beta \left\{4\,\frac{T^3}{\vartheta_\beta^3}\int\limits_0^{\vartheta_\beta/T}\frac{z^3 dz}{e^z - 1} + \frac{T}{\vartheta_\beta^3}\left[\exp\left(\frac{T}{\vartheta_\beta^3}\right) - 1\right]^{-1}\right\}. \tag{21}$$

If the change in the parameter ν_β^* in the process of formation of a multicomponent system is negligibly small, the functions U and c_V are additive quantities, i.e., $U = \sum\limits_\beta U_\beta \rho_\beta$ and $c_V = \sum\limits_\beta c_\beta \rho_\beta$. It should be noted that such dependences are widely used to describe heat processes in alloys and solutions. At low temperatures, the heat capacity is proportional to the cube of the temperature, $c_V = 2.4\pi^4 kT^3 \sum\limits_\beta n_\beta/\vartheta_\beta^3$, and at high temperatures $c_V = 3nk$, where $n = \sum\limits_\beta n_\beta$. These dependences are found to be in accordance with experimental data. In the particular case of a single-component body ($B = 1$), when $\gamma_\beta = 3(c/v_{\mathrm{sound}})^3/2$, where v_{sound} is the velocity of sound, relation (20) becomes the Debye formula. The latter was obtained under the assumption that the change in the energy of solid-body particles is due to the propagation of elastic waves in its bulk, and each wave is realized by one degree of freedom of an atom [6]. However, according to present views, an elastic wave arises as a result of collective oscillations of the atoms.

According to the law of spectral-radiation intensity (3), the function Q_{em} is

$$Q_{\mathrm{em}}(r,t)=\frac{8\pi}{c^3}\sum_{\beta}\int_{\nu}\frac{1}{N_\nu}\varepsilon_{\beta\nu}\,n_{\beta\nu}(r,t)\,e_\nu(r,t)\,\nu^2\,d\nu\,. \tag{22}$$

The energy flux $J_{s\beta\nu}(r,\ t)$ of photons $h\nu$ that are absorbed by a β-component particle with a radius vector r at the instant t and are emitted by an s-component particle with a radius vector $r+\eta$ at the instant $t-|\eta|/c$ is found from the relation

$$J_{s\beta\nu}(r,t)=\sigma_{\beta\nu}\,\varepsilon_{s\nu}\,e_\nu\,(r+\eta,\,t-|\eta|/c)\,G_\nu(\eta)\,. \tag{23}$$

Here $G_\nu(\eta)$ is a function that determines the decrease in the energy flux in the case where the distance η increases as a result of radial divergence of the emitted photons and their absorption by other particles of the body [11]:

$$G_\nu(\eta,t)=\frac{\mu_\nu}{4\pi\eta^2}\exp\left[-\left|\int_0^{\eta}\mu_\nu\sum_{\beta}\sigma_{\beta\nu}\,n_{\beta\nu}\left(r+\xi,\,t-\frac{|\xi|}{c}\right)d\xi\right|\right], \tag{24}$$

where μ_ν is the coefficient of overlapping of some particles by others, $0<\mu_\nu<1$, and for amorphous bodies $\mu_\nu\approx 1$. According to (23) and (24), the function Q_{abs} can be represented in the form

$$Q_{\mathrm{abs}}=\frac{8\pi}{c^3}\int_V\sum_{\beta}\int_{\nu}\frac{1}{N_\nu}\varepsilon_{\beta\nu}\,n_{\beta\nu}\left(r+\eta,\,t-\frac{|\eta|}{c}\right)e_\nu\left(r+\eta,\,t-\frac{|\eta|}{c}\right)G_\nu(\eta)\,\times$$

$$\times\sum_{\beta}\sigma_{\beta\nu}\,n_{\beta\nu}(r,t)\,\nu^2\,d\nu\,dV\,. \tag{25}$$

The power of the energy sources (sinks) was assumed to be a prescribed function $Q_s=Q_s(r,\ t,\ T)$. The quantities Q_{dif} and Q_{el} are determined by the expressions

$$Q_{\mathrm{dif}}=\sum_{\beta}U_\beta J_\beta\,;\quad Q_{\mathrm{el}}=\frac{\partial}{\partial t}\left(\int_{\nu=0}^{\nu^+}\rho_\nu^{\mathrm{rad}}(r,t)\,d\nu\right),\quad \nu^+=\max\,(\nu_\beta^*)\,. \tag{26}$$

The function $G_\nu(\eta)$ decreases rapidly with increase in the distance η; this being so, in the neighborhood of the point r we can single out a subregion $\eta<\eta'=\mathrm{const}$ outside of which the value of the integrand in (24) and (25) can be neglected. If η' is much smaller than the characteristic dimension of the body, in determining Q_{ab} the integration can be performed in an arbitrary region that includes the sphere $\eta=\eta'$, in particular, in an unbounded region. Converting to Cartesian coordinates, expanding the function $\varphi(x+\eta_x,\ y+\eta_y,\ z+\eta_z,\ t-|\eta|/c)$, where $\varphi=e_\nu,\ n_{\beta s\nu}$, in a Taylor series in the neighborhood of the point $(x,\ y,\ z,\ t)$, and retaining terms up to third order in η, we are led, after calculations analogous to the calculations presented in [11], from the integro-differential equation of heat transfer (17) to the hyperbolic equation

$$\left(1+\frac{8\varepsilon}{Fc}\right)\frac{\partial U}{\partial t}+\frac{4}{Fc}\frac{\partial^2 U}{\partial t^2}=\nabla\left(\frac{\varepsilon}{3F^2}\nabla U\right)+Q_{\mathrm{dif}}+Q_s+Q_{\mathrm{el}}\,,$$

where ε and F are averaged values of ε_ν and the expression entering into (24): $\mu_\nu\sum_{\beta}\sigma_{\beta\nu}n_{\beta\nu}=F_\nu$. When $c\to\infty$ and $\rho_\beta=\mathrm{const}$ this equation becomes the Fourier equation of heat transfer, which incorporates the assumption that the velocity of propagation of thermal disturbances is infinite [11, 15]. The expression for the thermal conductivity $\lambda = c_V \varepsilon / 3F^2$ that follows from this limiting transition agrees with the well-known Debye approximate formula [11].

NOTATION

U, specific internal energy of the multicomponent body; t, time; h, Planck constant; $\sigma_{\beta\nu}$, effective cross section of absorption of photons $h\nu$ by a β-component atom; $q_{\beta i\nu}$, specific radiation intensity of the degrees of freedom of β-component atoms oscillating with a frequency ν and found at the i-th energy level; $q_{\beta\nu}$, specific spectral-radiation intensity of the degrees of freedom of β-component atoms oscillating with a frequency ν; g, frequency density distribution function of standing electromagnetic waves; ρ_β, density of the component β; c_V, specific heat capacity per unit volume of the component β; c, velocity of light; $\varepsilon_{\beta\nu}$, radiation coefficient; $n_{\beta i\nu}$, density of particles oscillating with a frequency ν and found at the i-th energy level; $\dot{n}_{\beta i\nu}$ and $\dot{n}'_{\beta i\nu}$, numbers of degrees of freedom leaving the energy level i in unit time as a result of emission and absorption of photons $h\nu$; k, Boltzmann constant; r, radius vector; η, radius vector connecting a given point with an arbitrary point of the body; T, temperature; $E_{i\nu}$, energy of the degree of freedom of an atom oscillating with a frequency ν and found at the i-th energy level; $I_{\beta\nu}$, limiting energy level at which the degree of freedom of the atom can be found; u, activation energy of the atom; χ_ν, density of photons of frequency ν; $w_{\beta i\nu}$, probability that a β-component atom oscillates with a frequency ν and is found at the i-th energy level; $e_{i\nu}$, mean energy of the degree of freedom of the atom; λ, thermal conductivity. Subscripts: β and s, ordinal numbers of the body components; ν, frequency of oscillations of the degree of freedom of the atom; i, ordinal number of the energy level.

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