THE THERMAL CONDUCTIVITY OF GAS MIXTURES AT LOW TEMPERATURES. II

A. G. Shashkov and T. N. Abramenko

UDC 536.23

This article provides a review of the theoretical and experimental references devoted to the thermal conductivity of gas mixtures at low temperatures. We discuss the influence of quantum effects on the thermal conductivity of gas mixtures.

In investigating the thermal conductivity of gas mixtures under conditions in which the effect of thermal oscillations is particularly weakened we note unique quantum properties which enable us to ascertain a number of new effects whose observation would be impossible at higher temperatures.

At low temperatures, in calculating the thermal conductivity of a mixture, we must take these quantum effects into consideration. Deviation from the results of classical theory is a result of:

1) diffraction effects whose contribution to the thermal conductivity of the mixture is a function of the de Broglie wavelength $\tilde{\lambda} = h/2\pi\sqrt{\mu kT}$ as a ratio of the molecular diameter;

2) the symmetry effects whose contribution to the thermal conductivity of the mixture is a function of the de Broglie wavelength as a ratio of the molecular mean free path.

The diffraction effects are not significant in the temperature range 200-300°K, and the effects of symmetry are not significant above 2°K.

The state of the ν-component gas mixture is completely described by the distribution function $f(\mathbf{r}, \mathbf{v}, t)$ which is a solution of the Boltzmann equation and which, with consideration of the quantum effects of the gas mixture, has the form [2]

$$\frac{\partial f_i}{\partial t} + \mathbf{v}_i \frac{\partial f_i}{\partial \mathbf{r}} = 2\pi \sum_j \int\int [f'_i f'_j (1 + \theta_i f_i)(1 + \theta_j f_j) - f_i f_j (1 + \theta_i f'_i)(1 + \theta_j f'_j)]\, \alpha (g_{ij}, \chi) \sin \chi d\chi d\mathbf{v}_j. \tag{1}$$

Having solved this equation, we can derive the expression for the thermal conductivity of the gas mixture in terms of the collision integrals. Both in the classical and quantum theory, the integrals $\Omega^{(n,t)}$ are found from the expression

$$\sqrt{\frac{2\pi\mu}{kT}}\ \Omega^{(n,t)} = \int_0^\infty e^{-\gamma^2} \gamma^{2t+3} Q^{(n)} d\gamma. \tag{2}$$

In the classical theory $\gamma^2 = \mu g^2/2kT$; in the quantum theory $\gamma^2 = h^2\varkappa^2/8\pi^2\mu kT$.

In classical theory the basic problem which arises in the calculations of the transfer processes is the determination of the deflection angle $\chi(b, g)$ as a function of the collision parameter b and the initial relative velocity g.

In the quantum theory of transfer processes the basic problem is the determination of the radial-wave phase-shift function $\eta_l(\varkappa)$, with the phase shift serving as the only characteristic of collision included in the formulas for the transfer coefficients.

Institute of Heat and Mass Transfer of the Academy of Sciences of the Belorussian SSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 17, No. 1, pp. 65-71, July, 1969. Original article submitted January 21, 1969.

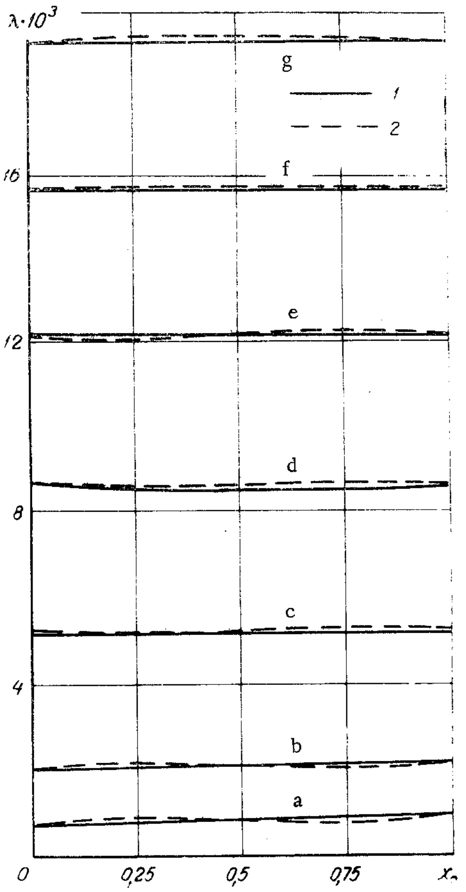

Fig. 1. Thermal conductivity of the pH_2-OH_2 mixture (W/m · deg) at various temperatures: a) 1.85°K; b) 3.7°K; c) 7.4°K; d) 11.1°K; e) 14.8°K; f) 18.5°K; g) 22.2°K; 1) data derived from (6); 2) data derived from (7).

In first approximation [2] the phase shift is derived in the form

$$\eta_l^{[1]}(\varkappa) = \frac{\pi}{2}\sqrt{l(l+1)} - \varkappa r_m + \int_{r_m}^{r} \left(\sqrt{\varkappa^2 - f_l(r)} - \varkappa\right) dr. \qquad (3)$$

Let us transform the quantity $\eta_l^{[1]}$, determined from (3):

$$\eta_l^{[1]}(\varkappa) = \frac{\pi}{2} p\varkappa - r_m\varkappa + $$

$$+ \int_{r_m}^{r} \sqrt{\left(\frac{\pi}{\Lambda^*}\right)^2 \frac{E}{\varepsilon\sigma^2} - \frac{l(l+1)}{r^2} - \left(\frac{2\pi}{\Lambda^*}\right)^2 \frac{\varphi(r)}{\varepsilon\sigma^2}}\, dr$$

$$- \int_{r_m}^{r} \sqrt{\left(\frac{2\pi}{\Lambda^*}\right)^2 \frac{E}{\varepsilon\sigma^2}}\, dr = \varkappa \lim_{r\to\infty} \left[\int_{r_m}^{r} F(r)\, dr - \int_{p}^{r} \sqrt{1 - \frac{p^2}{r^2}}\, dr\right]. \qquad (4)$$

Here $p = \sqrt{l(l+1)}/\varkappa$; $\varkappa = \frac{2\pi\mu g}{h}$; $\varkappa^2 = \left(\frac{2\pi}{\Lambda^*}\right)^2 \frac{E}{\varepsilon\sigma^2}$; $f_l(r) = \frac{l(l+1)}{r^2} + \left(\frac{2\pi}{\Lambda^*}\right)^2 \frac{\varphi(r)}{\varepsilon\sigma^2}$; $F(r) = 1 - \frac{\varphi(r)}{E} - \frac{p^2}{r^2}$; and $\Lambda^* = \frac{h}{\sigma\sqrt{\mu\varepsilon}}$ is the de Bour parameter.

When the effective potential $\varphi_{\text{eff}}(r) = \varphi(r) + (1/2)(\mu g^2 p^2/r^2)$ is negative, formula (4) must be presented [3] in the form

$$\eta_l^{[1]}(\varkappa) = \varkappa \lim_{r\to\infty} \left\{ \int_{r_m}^{p} F(r)\, dr + \int_{p}^{\infty} [F(r) - (1 - p^2/r^2)^{1/2}] dr \right\} \qquad (5)$$

or by means of a similar formula, if $p < r_m$ (here p = b, the analog of the impact parameter in quantum mechanics).

The quantum effects are taken into consideration in the collision integrals in the expression for the cross section $Q^{(n)}$.

There are several references devoted to the calculation of the quantum collision integrals [4-6]. Reference [4] presents the quantum collision integrals for the 12: 6 Lennard–Jones potential

$$\varphi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

for the range of variations in the de Bour parameter from 0 to 3.5. In [5] we find the quantum collision integrals for the Lennard–Jones potential for He^4 ($\Lambda^* = 2.67$), $He^4 - He^3$ ($\Lambda^* = 2.88$), and He^3 ($\Lambda^* = 3.08$).

In [6] we find the quantum collision integrals for the Morse potential

$$\varphi(r) = \varepsilon\left\{\exp\left[-2(C/\sigma)(r - r_s)\right] - 2\exp\left[-(C/\sigma)(r - r_s)\right]\right\},$$

where $r_s/\sigma = 1 + \ln 2/C$.

A number of papers have been devoted to experimental and theoretical investigations of the thermal conductivity of gas mixtures at low temperatures.

Reference [7] gives theoretical data on the thermal conductivity of the pH_2-oH_2 mixture at temperatures of 1.85-22.2°K. These data were derived from the formula for the thermal conductivity of a mixture of monatomic gases:

$$\frac{1}{\lambda} = [x_1^2(L_1/\lambda_1) + 2x_1x_2(L_{12}/\lambda_{12}) + x_2^2 L_2/\lambda_2][x_1^2 L_1 + 2x_1x_2 M_{12} + x_2^2 L_2]^{-1}. \qquad (6)$$

It should be noted that the diffraction effects are identical for the molecules of the components making up this mixture ($\Lambda_1^* = \Lambda_2^* = 1.72$). The pH_2 molecules (spin zero) and the oH_2 (spin equal to 1) are subject to Bose–Einstein statistics. Figure 1 shows data on the thermal conductivity of pH_2-oH_2.

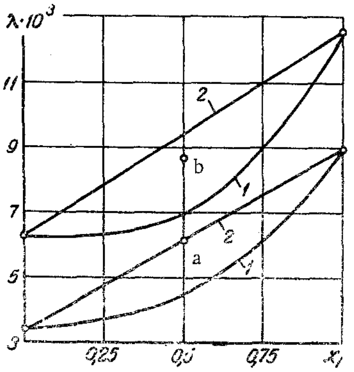

Fig. 2

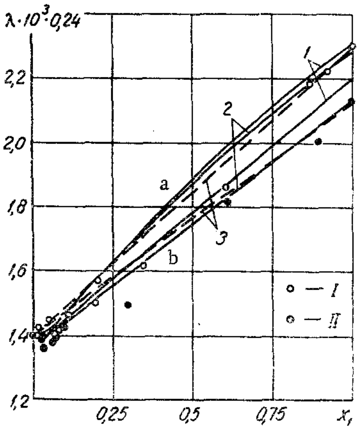

Fig. 3

Fig. 2. Thermal conductivity of an He^3-He^4 mixture (W/m · deg) at temperatures of 1.522°K (a) and 3.009°K (b): 1) data derived from (6); 2) data derived from (7); the points denote experiments.

Fig. 3. Thermal conductivity of N_2-Ar (a) and O_2-Ar (b) mixtures (W/m · deg) at a temperature of 90°K: I) experimental values for (a); II) experimental values for (b); 1) calculation according to (8); 2) the same, but with $\lambda_i = \lambda_{i\text{trans}} (1 - \delta_f + \delta_f c_p/c_{pf})$, $\delta_f = \rho D c_{pf}/\lambda_{i\text{trans}}$, where $c_{pf} = 5/2 R$; 3) calculation according to (7).

In [8] we find the theoretical values for the thermal conductivity of an He^3-He^4 mixture at temperatures below 4.09°K. The thermal conductivity of the mixture was calculated in accordance with (6). For an He^3-He^4 isotope mixture we have $\Lambda_1^* = 3.08$, $\Lambda_2^* = 2.67$, and $\Lambda_{12}^* = 2.88$. The He^3 molecules are subject to Fermi–Dirac statistics (molecular spin of 1/2); the He^4 molecules are subject to the Bose–Einstein statistics (molecular spin equal to 0).

In [9] we find experimental data on the isotope equimolar He^3-He^4 mixture for the temperature range 0.531-3.009°K. The experimental data were derived by the method of a plane horizontal layer. The experimental conditions were such that the de Broglie wavelength was smaller than the molecular mean free path by a factor of at least 100.

Figure 2 presents a comparison of the theoretical and experimental results in connection with the thermal conductivity of an He^3-He^4 mixture; the theoretical values were derived from (6) and from the following formula [1, 10]:

$$\lambda = \frac{\lambda_1}{1 + A_{12}x_2/x_1} + \frac{\lambda_2}{1 + A_{21}x_1/x_2}, \tag{7}$$

where

$$A_{ij} = \frac{D_{ii}}{D_{ij}} = \sqrt{2}\left(\frac{\sigma_{ij}}{\sigma_i}\right)^2\left(\frac{M_{ij}}{M_i + M_j}\right)^{1/2} \frac{\Omega_{ij}^{(1,1)*}(T_{ij}^*)}{\Omega_i^{(1,1)*}(T_i^*)}.$$

The thermal conductivity of N_2-Ar and O_2-Ar mixtures at a temperature of 90°K is investigated in [11]. Figure 3 shows a comparison of the experimental data and the data derived [2] with the Hirschfelder formula

$$\lambda = \lambda^* + \frac{\lambda_1^{\text{eik}} - \lambda_{1\text{trans}}}{1 + \frac{D_{11}}{D_{12}}\frac{x_2}{x_1}} + \frac{\lambda_2^{\text{eik}} - \lambda_{2\text{trans}}}{1 + \frac{D_{22}}{D_{21}}\frac{x_1}{x_2}} \tag{8}$$

and formula (7).

We see that for gas mixtures characterized by weak diffraction effects (N_2-Ar: $\Lambda_1^* = 0.226$, $\Lambda_2^* = 0.186$, $\Lambda_{12}^* = 0.209$; O_2-Ar: $\Lambda_1^* = 0.201$, $\Lambda_2^* = 0.186$, $\Lambda_{12}^* = 0.198$) at moderately low temperatures we can use the classical Hirschfelder formula, with the collision integral calculated for the classical Boltzmann equation

$$\frac{\partial f_i}{\partial t} + \mathbf{v}_i \frac{\partial f_i}{\partial \mathbf{r}} = \sum_j \iiint (f_i' f_j' - f_i f_j)\, g_{ij} b\, db\, d\varepsilon\, d\mathbf{v}_j.$$

Reference [12] presents data on the thermal conductivity of an He^4-H_2 mixture at a temperature of 90.2°K. The experimental data are compared with the theoretical data derived from the Hirschfelder formula. The overstated theoretical values for the thermal conductivity of the mixture, in comparison with the experimental data, are a result of the overestimation of the thermal conductivity of the mixture as a consequence of translational degrees of freedom. The use of experimental thermal-conductivity values for fewer components in the theoretical Hirschfelder formula yields better agreement between the experimental and theoretical results.

Analysis of experimental data on the thermal conductivity of the He^4-H_2 mixture at temperatures of 273.76°, 195.56°, 158.76°, 128.76°, and 77.96°K [13] demonstrate that it is highly unlikely that such a minimum would be observed in the relationship between the thermal conductivity of this mixture and the concentration.

It should be noted that the experimental data cited in [11, 12] were derived by the heated-filament method, whereas the data in [13] were derived by a coaxial-cylinder method.

In [10] we find a discussion of the influence exerted by the quantum effects on the thermal conductivity of mixtures at low temperatures.

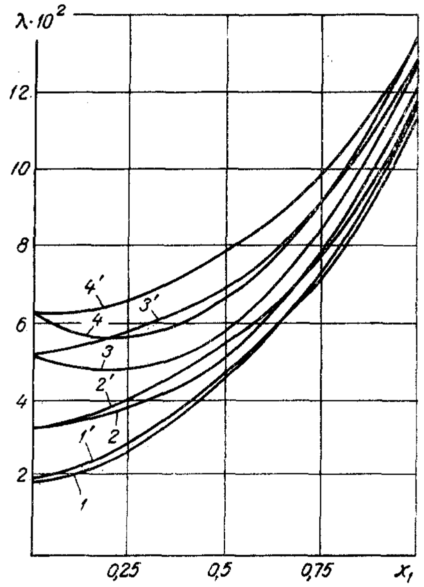

Fig. 4. Thermal conductivity of He^4-N_2 mixture (W/m · deg) at a temperature of 196.66°K and at various pressures: 1) 0.1 Mn/m²; 2) 10.1 Mn/m²; 3) 20.2 Mn/m²; 4) 30.3 Mn/m²; 1-4) experiment; 1', 2', 3', 4') calculation according to (7).

Figure 4 shows a comparison of experimental and theoretical values for the thermal conductivity of the He^4-N_2 mixture at a temperature of 196.66°K and at pressures of 0.1, 10.1, 20.2, and 30.3 Mn/m². The experimental data have been taken from [14]; the theoretical data were derived in accordance with (7). We see that with a rise in pressure there is an increase in the divergence between the experimental and theoretical results.

We know that for dense gases those assumptions which have been adopted for rarefied gases (consideration exclusively of the pairwise molecular collisions, neglecting the molecular diameter) are not satisfied. For dense gases and their mixtures the following Boltzmann equation [2] is valid:

$$\frac{\partial f_i}{\partial t} + \mathbf{v}_i \frac{\partial f_i}{\partial \mathbf{r}} = \sum_j \iiint \left[Y\left(r + \frac{1}{2} d\mathrm{k}\right) f_i(\mathbf{r}, \mathbf{v}_i') f_j(\mathbf{r} + d\mathrm{k}, \mathbf{v}_j') - Y\left(\mathrm{r} - \frac{1}{2} d\mathrm{k}\right) f_i(\mathbf{r}, \mathbf{v}_i) f_j(\mathbf{r} - d\mathrm{k}, \mathbf{v}_j) \right] g b\, db\, d\varepsilon\, d\mathbf{v}_j,$$

where $Y = 1 + 0.625 b_0/\tilde{V} + 0.2869 (b_0/\tilde{V})^2 + 0.115 (b_0/\tilde{V})^3 + \ldots$, $b_0 = 2/3\pi \tilde{N} d^3$, and the collision integrals for this equation will therefore be different from the collision integrals for Eq. (1) and for the classical Boltzmann equation.

It should be noted that the theoretical values for the thermal conductivity of the mixtures, presented in this paper, were calculated for the 12 : 6 Lennard–Jones potential by means of the quantum collision integrals given in [4].

NOTATION

h	is the Planck constant;
k	is the Boltzmann constant;
μ	is the reduced molecular mass;
$\eta_l(\varkappa)$	is the phase shift;
l	is the orbital quantum number;
$\varkappa$	is the wave number characterizing the overall relative energy of the colliding molecule pair;

r_m	is the classical point of rotation;
r	is the intermolecular distance;
γ	is the reduced initial relative velocity;
λ	is the thermal conductivity of the mixture;
λ^*	is the thermal conductivity of the mixture as a consequence of translational degrees of freedom;
λ_{itrans}	is the thermal conductivity of the i-th component as a consequence of the translational degrees of freedom;
x_i	is the molar concentration of the i-th component;
T^*	is the reduced temperature
ε and σ	are the parameters of the 12 : 6 Lennard–Jones potential;
d	is the molecular diameter;
v	is the molecular velocity;
t	is the time;
k	is the unit vector directed from the center of one molecule to the center of another molecule at the instant of molecular contact on collision;
b_0	is the second virial coefficient for a gas of solid spheres with the diameter d;
$\tilde{N}$	is the Avogadro number;
$\tilde{V}$	is the molar volume;
E	is the energy.

LITERATURE CITED

1. A. G. Shashkov and T. N. Abramenko, Inzhen.-Fiz. Zh., 16, No. 6 (1969).
2. J. Hirschfelder, Ch. Curtiss, and R. Bird, The Molecular Theory of Gases and Liquids [Russian translation], IL (1961).
3. F. J. Smith, Physica, 30, No. 3 (1964).
4. R. J. Munn, F. J. Smith, and E. A. Mason, Journ. Chem. Phys., 42, No. 2 (1965).
5. L. Monchick, E. A. Mason, R. J. Munn, and F. J. Smith, Journ. Chem. Phys., 43, No. 4A (1965).
6. F. J. Smith and R. J. Munn, Journ. Chem. Phys., 41, No. 11 (1964).
7. E. J. D. Cohen, M. J. Offerhaus, and J. M. J. van Leeuven, Physica, 22, No. 9 (1956).
8. E. G. D. Cohen, M. J. Offerhaus, and J. de Boer, Physica, 20, No. 8 (1954).
9. K. Fokkens, W. miss Vermeer, K. W. Taconis, and R. de Bruyn Ouboter, Physica, 30, 2153-2174 (1964).
10. A. G. Shashkov and T. N. Abramenko, Inzhen.-Fiz. Zh., 13, No. 4 (1967).
11. R. Mukhopadhyay and A. K. Barua, Brit. Journ. Appl. Phys., 18, 1307 (1967).
12. P. Mukhopadhyay and A. K. Barua, Brit. Journ. Appl. Phys., 18, 635 (1967).
13. I. F. Golubev and E. A. Rychkova, Gazovaya Promyshlennost', No. 11 (1966).
14. Z. A. Rychkova and I. F. Golubev, Gazovaya Promyshlennost', No. 7 (1967).