# THERMAL CONDUCTIVITY OF BINARY GAS MIXTURES AT LOW TEMPERATURES

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A method is proposed for the calculation of the thermal conductivity of gas mixtures at low temperatures. The theoretical values of the thermal conductivity are compared with experimental data.

At moderate temperatures molecules are not ionized nor excited; the thermal motion is limited exclusively to the translational motion of the molecules.

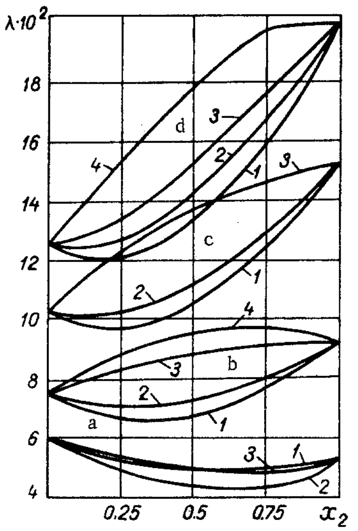


Fig. 1. Thermal conductivity (Wx/m · deg) of the mixture helium-hydrogen at temperature 77.96° K: 1) Experimental data; 2) calculated from formula (1) (constants $A_{ij}$, calculated from formula (2), collision integrals are calculated for Eq. (3)); 3) the same, collision integrals are calculated for Eq. (6); 4) calculated from formula (7): a) P = 1 MN/m², b) 10, c) 30, d) 50.

There exists a temperature range within which the thermal motion of a molecular gas is made up exclusively of translational and rotational motion.

Molecular vibrations are excited at higher temperatures (several hundreds and thousands of degrees).

At low temperatures the molecules in a molecular gas are set into rotation. The energies of the rotational quanta, expressed in degrees (divided by the Boltzmann constant k), are small (2.1° K for oxygen, 2.9° K for nitrogen, etc., with the exception of hydrogen molecules, 85.4° K). At room temperature (and even more so at high temperatures) the quantum effects play no role whatsoever.

At low temperatures, the thermal conductivity of the gas mixture cannot be presented as the sum of two terms governed by the presence of translational and intrinsic degrees of freedom.

The thermal conductivity of the gas mixture at low temperatures is achieved by means of the "diffusion" of quanta. There is a difference between the diffusion of molecules and the "diffusion" of quanta. Molecules do not disappear on collision, but change the direction of their motion. Quanta, however, after covering a certain distance, are absorbed by the substance. At the point of absorption new quanta of various frequencies are emitted in all directions.

The thermal conductivity of the mixture at low temperatures can be calculated from the formula [5]

$$\lambda = \lambda_1\left(1 + A_{12}\frac{x_2}{x_1}\right)^{-1} + \lambda_2\left(1 + A_{21}\frac{x_1}{x_2}\right)^{-1}, \quad (1)$$

where

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

$$\frac{\partial f_i}{\partial t} + \left(\mathbf{v}_i\frac{\partial}{\partial \mathbf{r}} f_i\right) = 2\pi\sum_{j=1}^{\nu}\iint [f_i' f_j' (1 + \theta_i f_i)(1 + \theta_j f_j) - f_i f_j (1 + \theta_i f_i')(1 + \theta_j f_j')]\,\alpha(g_{ij}, \chi)\sin\chi\, d\mathbf{v}_j, \quad (3)$$

The collision integrals $\Omega_{ij}^{(1,1)*}(T_{ij}^*)$ and $\Omega_i^{(1,1)*}(T_i^*)$ in expression (2) are determined from the Boltzmann equation for the case of a gas mixture at low temperatures [1]

where $\theta_i = (h/m_i)^3\,(\delta/G_i)$; $G_i$ is the statistical weight of the i-th particle, equal to the number of independent quantum states in which a particle of the same intrinsic energy may be found; $\delta = -1;\ 0;\ 1$ (for Fermi-Dirac, Boltzmann and Bose-Einstein statistics); $\alpha(g_{ij}, \chi)$ is the scattering cross section.

The collision integrals for (3) differ from the corresponding collision integrals for the classical Boltzmann equation because consideration is given to the quantum effects governed by the wave-like nature of the particles (diffraction effect) and by the statistics of the particles (the effects of symmetry).

Let us calculate the collision integrals for intermediate temperatures by means of the potential of intermolecular interaction $\varphi(r) = 4\varepsilon\left(\frac{\sigma}{r}\right)^{12}$, representing a part of the Lennard-Jones (12-6) potential for the forces of repulsion.

The collision integrals have the form

$$\Omega_{ij}^{(1,1)} = 0.3458\sqrt{\frac{\pi kT}{\mu_{ij}}}\left(\frac{6}{T_{ij}^*}\right)^{1/3}\times$$

$$\times\,\sigma_{ij}^2\cdot 2.66\left(1-6\cdot 10^{-3}\frac{\Lambda_{ij}^{*2}}{T_{ij}^{*5/6}}+\ldots\right),$$

$$\Omega_{i}^{(1,1)} = 0.3458\sqrt{\frac{\pi kT}{\mu_{i}}}\left(\frac{6}{T_{i}^*}\right)^{1/3}\times$$

$$\times\,\sigma_{i}^2\cdot 2.66\left(1-6\cdot 10^{-3}\frac{\Lambda_{i}^{*2}}{T_{i}^{*5/6}}+\ldots\right), \quad (4)$$

where $\Lambda^* = h/(\sigma\sqrt{2\mu\varepsilon})$; $T^* = kT/\varepsilon$; $\sigma$ and $\varepsilon$ are the parameters of the potential function; and $\mu_{ij}$ is the reference molecular mass equal to

$$\mu_{ij}^{-1} = m_i^{-1} + m_j^{-1}.$$

Since all the collision integrals are of the same order,

$$\Omega_{ij}^{(1,1)*}/\Omega_{i}^{(1,1)*} = \Omega_{ij}^{(1,1)}/\Omega_{i}^{(1,1)}. \quad (5)$$

Let us compare the theoretical values for the thermal conductivities of the He-$H_2$ mixture, calculated from (1) for a number of temperatures and pressures, with the experimental data presented in [2].

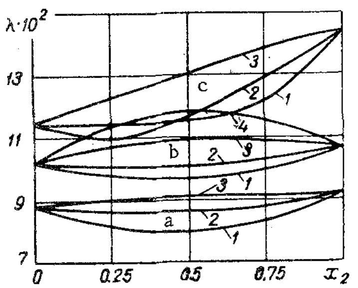


Fig. 2. Thermal conductivity of mixture helium-hydrogen at pressure 0.1 MN/m²: (a) T = 128.76° K, b) 158.76, c) 195.56): 1) Experimental data; 2) calculated from formula (1) (constants $A_{ij}$ are calculated from formula (2), collision integrals are calculated for Eq. (3)); 3) the same, collision integrals are calculated for Eq. (6); 4) calculated from formula (1) with constants calculated from formula (7).

Figure 1 shows the thermal conductivity of the helium-hydrogen mixture as a function of hydrogen concentration at a temperature of 77.96° K and various pressures. The experimental values are compared with the theoretical values derived according to formula (1) with the constants $A_{ij}$ calculated: a) with consideration of the quantum correction factors and, b) without consideration of the quantum correction

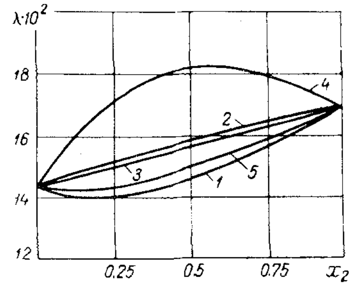


Fig. 3. Thermal conductivity of mixture helium-hydrogen at temperature 273.76° K and pressure 50 MN/m²: 1) Experimental data; 2) calculated from formula (1) (constants $A_{ij}$ are calculated from formula (2), collision integrals are calculated from Eq. (3)); 3) the same, collision integrals are calculated from Eq. (6); 4) calculated from formula (1) with constants calculated from formula (7); 5) calculated from formula (8) with constants $A_{ij}$ calculated from formula (10), and $B_{ij}$ calculated from formula (11).

factors (the collision integrals are calculated for the classical Boltzmann equation)

$$\frac{\partial f_i}{\partial t} + \left(\mathbf{v}_i\frac{\partial}{\partial \mathbf{r}}f_i\right) =$$

$$= \sum_{j=1}^{\nu}\iiint (f_i' f_j' - f_i f_j)\, g_{ij} b\, db\, d\varepsilon\, d\mathbf{v}_j, \quad (6)$$

c) according to the Maison formula [3]

$$A_{ij} = \frac{1.065}{2\sqrt{2}}\left(1+\frac{M_i}{M_j}\right)^{-1}\times$$

$$\times\left[1+\left(\frac{\lambda_i}{\lambda_j}\right)^{1/2}\left(\frac{M_i}{M_j}\right)^{1/4}\right]^2. \quad (7)$$

Figure 2 shows a comparison of the theoretical and experimental data for a helium-hydrogen mixture at temperatures of 128.76, 158.76, and 195.56° K and a pressure of 0.1 MN/m².

Figure 3 shows a comparison of the theoretical and experimental data for a helium-hydrogen mixture at a temperature of 273.76° K and a pressure of 50 MN/m². In this case, the data derived from (1) with constants $A_{ij}$, calculated by means of the classical Boltzmann equation (6), are in better agreement with the experimental results than the data derived from (1) with the constants $A_{ij}$, calculated with consideration of the quantum correction factors.

The data derived from (1) with the constants $A_{ij}$, calculated according to (7), yield poorer agreement with experimental results. Expression (1) for the calculation of the thermal conductivity of the helium-hydrogen mixture at the given temperature must be presented in the form

$$\lambda = \lambda_1 \left( 1 + A_{12} \frac{x_2}{x_1} \right)^{-1} + $$
$$+ \lambda_{2\text{const}} \left( 1 + A_{21} \frac{x_1}{x_2} \right)^{-1} + \lambda_{2\text{ext}} \left( 1 + B_{21} \frac{x_1}{x_2} \right)^{-1}, \quad (8)$$

where

$$\lambda_{2\text{const}} = 1.99 \cdot 10^{-4} \frac{\sqrt{T/M_2}}{\sigma_2^2 \Omega_2^{(2,2)*} (T_2^*)}. \quad (9)$$

Further,

$$\lambda_{2e} = \lambda_{2\exp} - \lambda_{2\text{const}},$$

$$A_{ij} = \left[ 1 + \left( \frac{\lambda_{i\text{const}}}{\lambda_{j\text{const}}} \right)^{1/2} \left( \frac{M_i}{M_j} \right)^{1/4} \right]^2 \times$$
$$\times \left[ 1 + 2.41 \frac{(M_i - M_j)(M_i - 0.142 M_j)}{(M_i + M_j)^2} \right]^{-1}, \text{ [4]}, \quad (10)$$

$$B_{ij} = D_{ii}/D_{ij}. \quad (11)$$

Good agreement exists between the experimental and theoretical values derived from (8) with constants calculated according to (9)–(10).

The thermal conductivity of the gas mixtures at low temperatures may thus be calculated according to the Vasil'eva Formula (1). The constants $A_{ij}$ should be calculated with consideration of the quantum correction factors. The divergence of the calculation results from the measured values of the thermal conductivity can be explained by inaccuracies in the calculation of the collision integrals for the Boltzmann equation (3) in the case of low temperatures.

This conclusion is drawn on the basis of experimental data for a helium-hydrogen mixture. The absence of experimental data for other mixtures makes it impossible completely to ascertain the mechanism of the heat-conduction process at low temperatures.

Subsequent development and refinement of both theory and methods for the calculation of the thermal conductivities of mixtures at low temperatures must therefore proceed along the lines of accumulating experimental data and comparing these with the predictions of the theory.

## NOTATION

h is the Planck constant; $m_i$ is the mass of the i-th molecule; $g_{ij}$ is the initial relative velocity of two interacting particles; $\chi$ is the deviation angle of two interacting particle paths; $\lambda_i$ is the thermal conductivity of the i-th component; $x_i$ is the mole fraction of the i-th component; $M_i$ is the molecular weight of the i-th component; v is the particle velocity; $f(r, v, t)$ is the distribution function; $D_{ii}$ is the self-diffusion coefficient of the i-th component; $D_{ij}$ is the mutual diffusivity; k is the Boltzmann constant; b is the impact parameter; $\Omega^{(l,s)*}$ is the collision integral predicted for molecular model of solid spheres. Quantities referring to particles after coupled collisions are marked by (').

## REFERENCES

1. J. Hirschfelder, C. Curtiss, and R. Bird, Molecular Theory of Gases and Liquids [Russian translation], IL, 1961.

2. I. F. Golubev and Z. A. Rachkova, Gazovaya promyshlennost, no. 11, 1966.

3. N. V. Tsederberg, The Thermal Conductivity of Gases and Liquids [in Russian], Gosenergoizdat, 1963.

4. R. S. Brokaw, NASA, TR, R-81, 1961.

5. A. Wassiljewa, Phys. Zeitschr., 5, 737, 1904.

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