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APPLICATION OF THE THIRD APPROXIMATION OF THE CHAPMAN–ENSKOG THEORY TO CALCULATING THE THERMAL CONDUCTIVITY OF BINARY MIXTURES OF MONATOMIC GASES AND ESTIMATING THE INFLUENCE OF THE DIFFUSIONAL THERMOEFFECT

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UDC 536.22.083

The coefficient of thermal conductivity and the contribution of the diffusional thermoeffect to the thermal conductivity of binary mixtures of monatomic gases are calculated within the framework of the second and third approximations of the strict kinetic theory. The theoretical results are compared with experimental results.

Inert gases and their mixtures represent the most suitable subjects for testing the strict Chapman–Enskog molecular–kinetic theory, since it treats phenomena occurring in the interactions of molecules without internal degrees of freedom.

Within the framework of this theory the first nonzero approximation for one or another of the transfer coefficients is designated as the first approximation. This is not very convenient, since to obtain the lowest approximations of the transfer coefficients in expansions by Sonine polynomials one must allow for different numbers of series terms: one term is enough for the coefficients of viscosity and diffusion but two terms of the expansion must be taken for the coefficients of thermal conductivity and thermodiffusion. Below, by series approximation we understand the number of series terms in the expansion by Sonine polynomials, it being assumed that the gradients of all the physical quantities are small, i.e., the heat flux and temperature gradient are connected by a linear relation. Thus, the lowest approximation for the coefficient of thermal conductivity is the second: $[\lambda_\infty]_2$.

An adequate amount of experimental data on the transfer properties of nonpolar gases [2-6] and of their binary mixtures [7-13] has appeared in the last decade. Some of the data have an accuracy within 0.1% limits for the viscosity [12] and the thermal conductivity [14], 0.2% limits for the interdiffusion [7, 8], and 1.0% for the thermodiffusion [9]. In a number of reports [15-17] it is shown that a second approximation is inadequate for a more precise analysis of experimental data on the thermophysical properties of gas mixtures. Calculations from higher approximations are especially necessary in the case of mixtures containing very light components [18], as well as when estimating the thermophysical properties of ionized gases [15]. Replacing the first approximation by the second for the coefficient of ordinary diffusion improves its accuracy. But the use of the same approximation for the coefficients of thermal conductivity and thermodiffusion leads to errors of up to 57% for the coefficient of thermodiffusion for an ionized gas [15]. The reason for the considerable disagreement between these data for gas mixtures evidently is the close interrelationship between the processes of heat conduction and thermodiffusion, as well as the use of too low approximations in the theoretical expressions. Nevertheless, there are very few reports devoted to calculations from higher approximations [18,20,21].

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TABLE 1. Interaction Force Constants for the (exp—6) Potential

Mixture	σ, Å	α	ε/k, k
He—Ne	3,143	13,46	18,71
He—Ar	3,488	13,21	33,4
He—Xe	3,65	12,55	52,3
Ne—Ar	3,443	14,17	73,7
Ar—Xe	4,108	13,44	178,5
Kr—Xe	4,251	12,65	191,0

The results of calculations of the coefficients of thermal conductivity of six monatomic gas mixtures, He—Ne, He—Ar, He—Xe, Ne—Ar, Ar—Xe, and Kr—Xe, within the framework of the second and third approximations of the Chapman—Enskog theory are presented below, and the magnitudes of the contribution of the diffusional thermoeffect to the thermal conductivities of these mixtures in the temperature range of $90 \le T \le 2000$°K and the concentration range of $0.1 \le x_1 \le 0.9$ at a pressure of 1 atm are also estimated. All the calculations are made for the (exp — 6) potential parameters of [19], presented in Table 1.

The second approximation of the coefficient of thermal conductivity for binary mixtures of monatomic gases was calculated from the equation

$$[\lambda_\infty]_2 = [\lambda_0]_2 - \frac{R^2 T x_1 x_2 [D_1^T]_2^2}{p\,[D_{12}]_1}\left(\frac{1}{x_1 M_1} + \frac{1}{x_2 M_2}\right)^2,$$

where $[\lambda_0]_2$ is the second approximation of the coefficient of thermal conductivity of a binary gas mixture without allowance for the diffusional thermoeffect; $[D_{12}]_1$ and $[D_1{}^T]_2$ are the lowest approximations of the coefficients of ordinary diffusion and thermodiffusion, respectively; M_1 and x_1 are the molecular weight and the molar fraction of the light component of the mixture.

In the case of the third approximation the expression for the higher approximations of the coefficient of thermal conductivity suggested by Devoto [17] is written in the form

$$[\lambda_\infty]_3 = -\frac{75k}{8}\,\frac{(2\pi kT)^{1/2}}{\begin{vmatrix} q_{ij}^{11} & q_{ij}^{12} \\ q_{ij}^{21} & q_{ij}^{22} \end{vmatrix}}\begin{vmatrix} q_{ij}^{11} & q_{ij}^{12} & n_i \\ q_{ij}^{21} & q_{ij}^{22} & 0 \\ \dfrac{n_j}{m_j^{1/2}} & 0 & 0 \end{vmatrix},$$

where n_j is the number density; m_j is the mass of the j-th component of the mixture.

The contribution of the third approximation to the thermal conductivities of the above-indicated mixtures is estimated from the equation

$$\delta = \frac{[\lambda_\infty]_3 - [\lambda_\infty]_2}{[\lambda_\infty]_2}\cdot 100,\ \%. \tag{1}$$

The calculations showed that, as a rule, the contribution of the third approximation grows with the increase in temperature, with the quantity δ changing sign in the low-temperature region for some mixtures (He—Ar, He—Xe, Ne—Ar, Kr—Xe). The concentration dependences of the ratio (1) have a complicated character. A maximum is observed for the He—Ne and Ar—Xe mixtures (Fig. 1a, b), a minimum for the Ne—Ar and He—Xe mixtures (Fig. 1d, f), and a maximum and a minimum for the He—Ar and Kr—Xe mixtures (Fig. 1e, c). It is interesting to note that the points of the maxima correspond to a higher percentage content of the light component in the mixtures while the points of the minima are always shifted toward a higher content of the heavy component. With an increase in temperature all the extremal points (both max and min) shift toward a lower content of the light component in the mixtures. From an analysis of the behavior of the quantity δ it is seen that it can become appreciable for mixtures containing a very light component (He—Ne). In this case the contribution of the third approximation can reach an amount on the order of 12% even at the lowest temperature of 90°K, which is a correction which cannot be neglected.

As is known, the coefficient of thermal conductivity λ_∞ calculated with allowance for the diffusional thermoeffect corresponds to the quantity determined in experiments by steady-state methods. To estimate

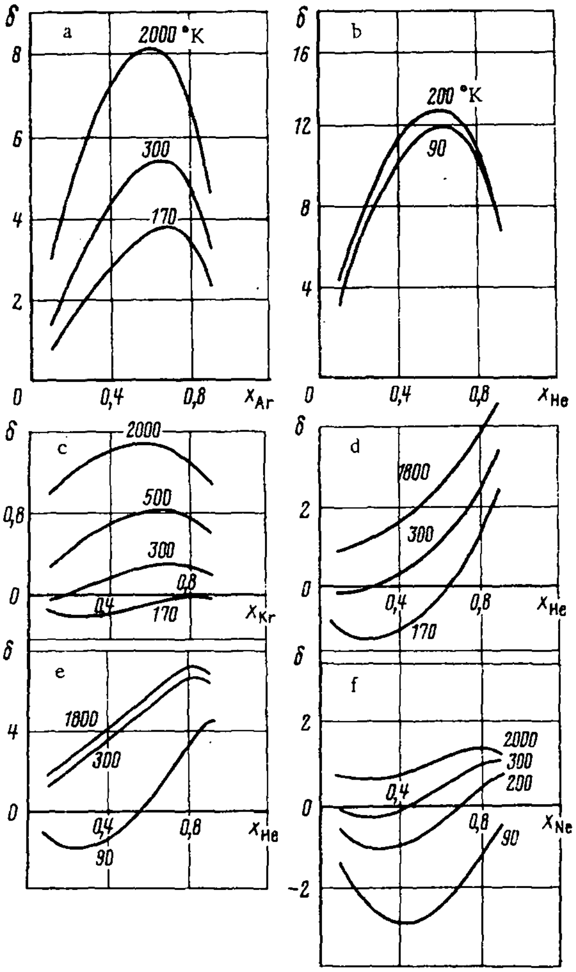

Fig. 1. Disagreement (%) between values of thermal conductivity for mixtures, obtained from the second and third approximations of the Chapman — Enskog theory, as a function of the concentration for different temperatures: a) Ar—Xe; b) He—Ne; c) Kr—Xe; d) He—Xe; e) He—Ar; f) Ne—Ar. δ, %.

the contribution of the diffusional thermoeffect to the thermal conductivity of gas mixtures one must calculate λ_0, the coefficient of thermal conductivity of a uniformly mixed gas mixture, i.e., a mixture in which a temperature gradient has not yet lead to the appearance of nonuniformity in the spatial distribution of the concentrations of the components. An expression for λ_0 up to the fourth approximation is presented in [15]; for the third approximation, in particular, one can write

$$[\lambda_0]_3 = -\frac{75k(2\pi kT)^{1/2}}{8}\,\frac{q_3'}{q_3},$$

where

$$q_3' = \begin{vmatrix} q_{ij}^{00} & q_{ij}^{01} & q_{ij}^{02} & 0 \\ q_{ij}^{10} & q_{ij}^{11} & q_{ij}^{12} & n_i \\ q_{ij}^{20} & q_{ij}^{21} & q_{ij}^{22} & 0 \\ 0 & \frac{n_j}{m_j^{1/2}} & 0 & 0 \end{vmatrix}.$$

The determinant q_3 is obtained from q_3' by deletion of the last column and the last row.

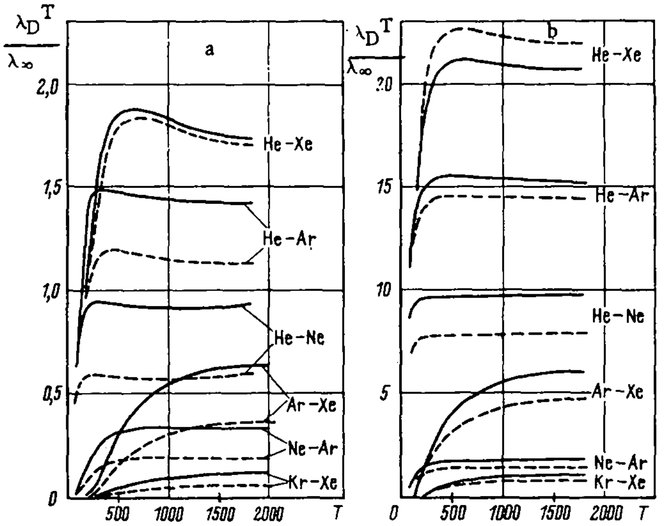

Fig. 2. Contribution of the diffusional thermoeffect to the thermal conductivity of gas mixtures (equimolar concentrations). Solid line) calculation from second approximation; dashed line) from third approximation; a) in the coordinate system of the average-hourly velocity (isochoric processes); b) of average-mass velocity (isobaric processes). $\lambda_D{}^T/\lambda_\infty$, %; T, °K.

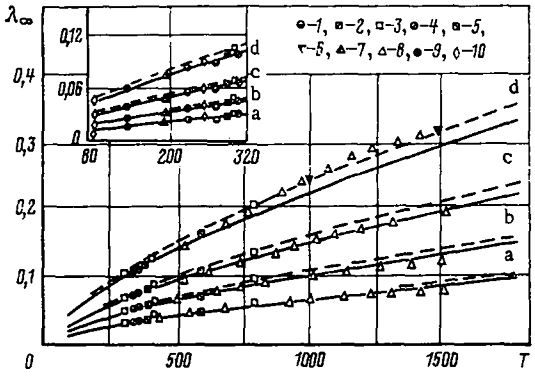

Fig. 3. Thermal conductivity of He–Ar mixture as a function of temperature at helium concentrations $x_1 = 0.2$ (a), $x_1 = 0.4$ (b), $x_1 = 0.6$ (c), and $x_1 = 0.8$ (d). Dashed curves) calculation from third approximation. Experimental data: 1) [22]; 2) [23]; 3) [24]; 4) [25]; 5) [26]; 6) [27]; 7) [28]; 8) [29]; 9) [30]; 10) [31]. λ_∞, W/m·°K; T, °K.

An estimate of the contribution of the diffusional thermoeffect from the equation

$$\frac{\lambda_{DT}}{\lambda_\infty} = \frac{\lambda_n - \lambda_\infty}{\lambda_\infty} \cdot 100, \ \%.$$

showed that for all the mixtures investigated this quantity reaches a maximum at equimolar concentrations and grows with an increase in the difference between the molecular weights of the components of the mixture. If all the mixtures are placed in order of increase in the ratio M_2/M_1 then the values of $\lambda_D{}^T/\lambda_\infty$ will be arranged in the same sequence, namely: Kr–Xe, Ne–Ar, Ar–Xe, He–Ne, He–Ar, He–Xe. For isochoric processes,

$$\lambda_{DT} = \frac{pD_{12}}{T} \alpha_T k_T,$$

the contribution of the diffusional thermoeffect to the thermal conductivity of gas mixtures is slight (Fig. 2a). For isobaric processes [32],

$$\lambda_{DT} = \frac{pD_{12}}{T} k_T \left(\alpha_T c_1 \frac{\partial \bar{\mu}_1}{\partial c_1} + \frac{\partial h}{\partial c_1} \right),$$

the contribution of $\lambda_D{}^T$ to λ_∞ reaches a significant amount for the He—Xe, He—Ar, and He—Ne mixtures, while for mixtures with components close in molecular weights (Ne—Ar and Kr—Xe) the contribution of the diffusional thermoeffect does not exceed 2% even at the highest temperatures (Fig. 2b).

A comparison of the available experimental data with the theoretical data calculated both from the second and the third approximation of the Chapman—Enskog theory showed that in the majority of the cases the experimental data for mixtures having a large content of the light component agree better with those calculated from the third approximation, whereas for mixtures having a low content of the light component the second approximation gives better results. The results of a comparison of the theoretical and experimental data for the He—Ar mixture are shown in Fig. 3 as an example.

NOTATION

R, universal gas constant; p, pressure; T, temperature; k, Boltzmann's constant; α_T, thermodiffusion constant; k_T, thermodiffusion ratio; ρ, density of mixture; c_i, mass concentration; q_{ij}^{mp}, a function of the number density, masses of component molecules, potential parameters, and collision integrals.

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TEMPERATURE DEPENDENCE OF MAGNETIC SUSCEPTIBILITY IN THREE NEMATIC LIQUID CRYSTALS

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Results are presented of an experimental study of temperature dependence of magnetic susceptibility in the isotropic state and mesophase of nematic liquid crystals by Gui's relative method.

The change in magnetic susceptibility of nematic liquid crystals in the mesophase with temperature is quite significant. This occurs because of changes in the ordering of molecules which have high anisotropy. The relationship between $\Delta\chi$ and molecular ordering permits determination of the degree of order [1], which is one of the most important characteristics of nematic liquid crystals [2], and is employed in a number of theories of the liquid crystal state. At the present time this quantity can be determined by various methods [3, 4]; however, the most reliable values of degree of order are considered to be those obtained by experimental measurement of anisotropy in magnetic susceptibility [4]. Using $\Delta\chi$ values and the Fredericks phenomenon, one can determine elastic constants, which are of great significance in the further development of continuum theory [4, 5].

In the present study χ was measured by Gui's relative method. Analysis of the results obtained with the apparatus and technique described in [6] revealed that the zero position of the balance beam, and thus, the distance between the coil and the suspension system magnet varies even for constant bridge unbalance. The cause of this is a change in the optical properties of the glass belljar covering the scales each time it is installed, together with time and temperature changes in the characteristics of the photosensors and illuminator. The relative error in determination of magnetic susceptibility thus reached 2%. The major contribution to this error comes from variation in the distance between coil and magnet for repeated measurements, while a contribution an order of magnitude smaller is produced by uncertainty in the position of the ampul between the electromagnet pole pieces.

To eliminate this shortcoming, a copper calibration weight was employed. By using special equipment it was possible to weigh this weight before each measurement without uncovering the scale. Then by choosing the zero position of the balance beam at the point where the current flowing through the coil is constant while the calibration weight is being weighed, we preserve the distance between coil and magnet, and the position of the ampul between the polepieces is unchanged. Since changes in ampul position between the polepieces have an insignificant effect on measurement accuracy, for convenience such changes may be neglected over the course of a single experiment (the error then does not exceed 0.1%, while the change in distance between coil and magnet may be considered, if in the computation formula instead of the current passing through the coil and the proportional force acting on the specimen, we take the ratio of this current force to the current force existing during weighing of the calibration weight. Evaluation of results from measurements performed with the calibration weight indicate that the maximum relative error in χ determination does not exceed 0.5% and is produced by the error in measurement of the force acting on the empty ampul (0.1%), on the ampul with specimen (0.1%), and by calibration error.

Degasified double distilled water was used as a reference substance. Its magnetic susceptibility at 20°C was taken equal to $0.720 \cdot 10^{-7}$ $\mathrm{cm}^3 \cdot \mathrm{g}^{-1}$. The temperature change of the water χ agreed with the results of [7].

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