QUESTION OF THE HEAT CONDUCTIVITY OF INERT GASES
AT LOW TEMPERATURES

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Theoretical and experimental data on the heat conductivity of inert gases at temperatures below 273°K are shown to be in agreement.

Systematic experimental investigations performed in [1, 2] on the heat conductivity of monatomic gases at low temperatures (90–273°K) and atmospheric pressure supplemented data available in the literature substantially, and extended the range of measurement for krypton and xenon. The approximating dependences

$$\lambda_{He} = 0.02593 + 0.5144 \cdot 10^{-3} T - 0.3165 \cdot 10^{-6} T^2, \qquad T = 90{-}280 \ \text{K}$$

$$\lambda_{Ne} = 0.3740 \cdot 10^{-2} + 0.2057 \cdot 10^{-3} T - 0.1879 \cdot 10^{-6} T^2, \quad T = 90 - 280 \ \text{K}$$

$$\lambda_{Ar} = 0.128 \cdot 10^{-3} + 0.6765 \cdot 10^{-4} T - 0.302 \cdot 10^{-7} T^2, \qquad T = 90 - 280 \text{K}$$

$$\lambda_{Kr} = 0.592 \cdot 10^{-3} + 0.2985 \cdot 10^{-4} T, \qquad\qquad T = 120{-}280 \ \text{K}$$

$$\lambda_{Xe} = 0.6188 \cdot 10^{-3} + 0.1638 \cdot 10^{-4} T, \qquad\qquad T = 165 - 280 \ \text{K}$$

reproduce the data in [1, 2] with an error not exceeding the experimental value (±1.3% for He, Ne, Ar and ±1.5% for Kr, Xe), and are in agreement, within these limits, with the heat conductivity values recommended in [3, 4].

In addition to their practical value (for cryogenic, chemical, and other branches of engineering), these data are of interest for the verification of methods of computing the heat conductivity of monatomic gases, as well as for interaction and force parameter models used in analysis, since the mechanism of heat transfer in gases at low temperatures (especially under conditions of approaching the phase transition domain) has still been studied inadequately.

The analysis of the heat conductivity of inert gases at 90–280°K temperatures in a third approximation of the Chapman–Enskog method [5] by using a number of potential functions and different sets of parameters for each showed (see Fig. 1a) that none of the models used most often for intermolecular interaction permits a correct description for the heat conductivity of all monatomic gases in the low temperature domain, even with a special selection of the force parameters.

It is seen that out of all the inert gas groups, a large spread in the deviations of the theoretical from the measured values holds for helium; as should be expected, the Morse potential with parameters [9] computed from experimental data on viscosity permits obtaining the best agreement with the results of experiment; in this case, the discrepancy does not exceed 1.8% in the temperature range investigated. Satisfactory correspondence (within ±2% limits) between the theoretical and experimental data is observed for neon (with the exception of a computation using the Morse potential); the model (12-6) with parameters determined in [5] from viscosity data yields agreement within the limits of experimental error. As regards the remaining inert gases, a clear tendency (see Fig. 1a) towards growth of the quan-
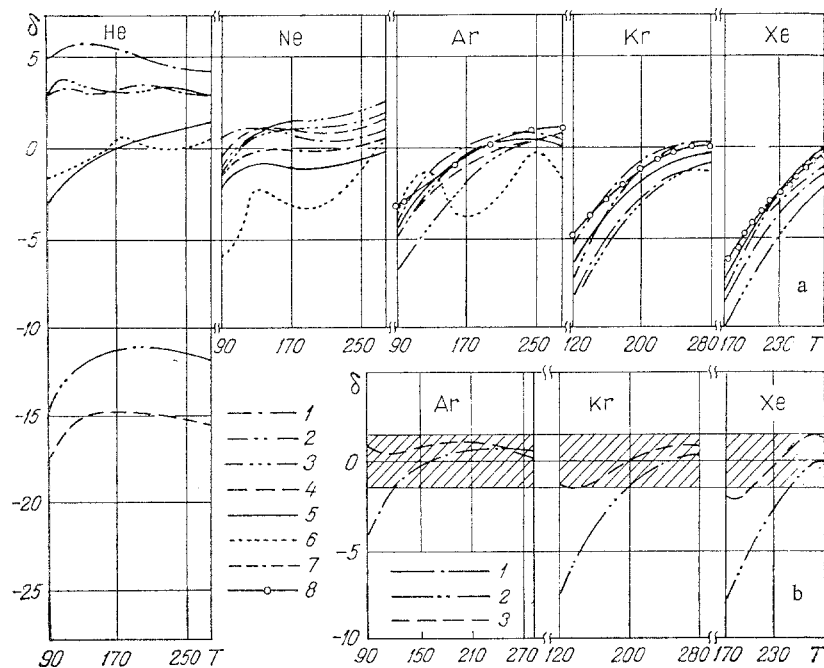
Fig. 1. Deviation of theoretical values of the heat conductivity of inert gases from experimental data [1-2]: a) 1-8) analysis by the Chapman—Enskog method by using different interaction and force parameter models: 1) (12-6) with parameters from [5]; 2) (12-6) with parameters from [6]; 3) (12-6) with parameters from [7]; 4) (exp-6) with parameters from [8]; 5) (exp-6) with parameters from [6]; 6) Morse with parameters from [9]; 7) analysis [10] by the potential (12-7); 8) (m-6-8) with parameters from [11] (a); b) 1-2) the same as in fig. a; 3) analysis by a quasichemical method [12-14] by using the potential (12-6) with parameters indicated in the table; hatched domains indicate limits of error in the experimental data. δ, %; T, °K.

tity $\delta = (\lambda_{theor} - \lambda_{exp})/\lambda_{exp}$, % with the reduction in temperature and the increase in molecular weight is apparent, whose raison d'etre is of indubitable interest for investigation.

It is seen from Fig. 1a that all the models used, with the different parameter variations for each, describe the heat conductivity of argon, krypton, and xenon quite well at the 280°K temperature, and yield reduced values as the temperature diminishes. At the lowest temperatures, the quantity δ reaches 5-8% on the average, and the deviation from these values because of using different models and force parameters does not exceed ±1.5%.

This permits the assumption that the reason for the increase in divergence between the theoretical and experimental data on the heat conductivity of the heavy gases as the temperature is lower is most probably that the Chapman—Enskog theory does not take account of effects due to the appearance of the real gas properties as the temperature diminishes under the isobaric experimental conditions. In this case, the gas density increases as the temperature is lowered, and effects due to three-particle collisions and finite molecule dimensions, which are not taken into account by the Chapman—Enskog theory because of the assumptions implicit in the Boltzmann equation, about binarity of the collisions and smallness of the molecule dimensions in comparison with the average intermolecular spacing, probably start to play a part.

In order to verify this assumption for the computation of the heat conductivity of argon, krypton, and xenon at low temperatures, the quasichemical method developed by Stogryn and Hirschfelder [12-14] for moderately dense gases was used. The crux of this method is the application of representations about the molecular association to a pure gas between whose molecules attractive forces act. Such an approach affords the opportunity of provisionally replacing the examination of multiparticle collisions by binary collisions of associates whose formation is considered as a chemical reaction.

TABLE 1. Comparison of Experimental Data [1, 2] on the Heat Conductivity of Inert Gases at Low Temperatures with the Results of a Computation by the Quasichemical Method [12-14] by Using the Potential (12-6) ($\lambda \cdot 10^3$, $W \cdot m^{-1} \cdot {}^\circ K^{-1}$).

Gas, values of the force parameters	T, K	x_2	λ_0	λ_r	λ_c	λ_Σ	λexp	δ, %
Ar $\varepsilon_1/k = 124$ K, $\sigma_1 = 3,42$ Å	90	0,0262	5,67	0,28	0,08	6,03	5,97	1,0
	100	0,0208	6,34	0,24	0,06	6,64	6,59	0,6
	120	0,0128	7,62	0,17	0,05	7,84	7,81	0,4
	160	0,0061	10,13	0,10	0,03	10,26	10,18	0,8
	200	0,0033	12,49	0,06	0,03	12,58	12,45	1,0
	240	0,0021	14,67	0,05	0,02	14,74	14,62	0,8
	280	0,0014	16,70	0,04	0,02	16,76	16,70	0,4
Kr $\varepsilon_1/k = 193$ K, $\sigma_1 = 3,57$Å	120	0,0294	3,83	0,23	0,06	4,12	4,17	—1,2
	160	0,0135	5,15	0,13	0,03	5,31	5,37	—1,1
	200	0,0076	6,46	0,09	0,02	6,57	6,56	0,2
	240	0,0047	7,74	0,06	0,02	7,82	7,76	0,8
	280	0,0032	8,96	0,05	0,01	9,02	8,95	0,8
Xe $\varepsilon_1/k = 256$ K, $\sigma_1 = 3,92$ Å	170	0,0247	3,13	0,15	0,05	3,33	3,40	—2,1
	180	0,0209	3,32	0,13	0,04	3,49	3,57	—2,2
	200	0,0159	3,70	0,11	0,03	3,84	3,89	—1,3
	240	0,0098	4,46	0,08	0,02	4,56	4,55	0,2
	280	0,0067	5,20	0,06	0,02	5,28	5,21	1,3

According to [12-14], the coefficient of heat conductivity of a moderately dense gas, considered in the form of a mixture of monomers and dimers:

$$\lambda = \lambda_0 + \lambda_r + \lambda_c, \qquad (1)$$

where λ_0 is the coefficient of heat conductivity of the chemically nonreacting well-mixed mixture, and is computed by the Chapman—Enskog method [5] under the conditions $m_2 = 2m_1$ and $x_2 \ll x_1$; $\lambda_r = \dfrac{pD_{12}}{T}\left(\dfrac{\Delta h}{RT}\right)^2 x_2$, contributions to the heat conductivity because of the "reaction"

of dimer formation in the gas $(2A \rightleftarrows A_2)$; $\lambda_c = \dfrac{23}{40}\left[B + T\dfrac{dB}{dT}\right]\dfrac{p}{RT}\lambda_1$, contribution to the heat

conductivity by the pairwise interactions of monomers (transfer by collisions); and $x_2 = 1 + \dfrac{N_A}{2nK_2}\left(1 - \sqrt{1 + \dfrac{4nK_2}{N_A}}\right)$, dimer concentration.

The monomer coefficient of heat conductivity in a mixture λ_1 is computed from the heat conduction formula for a monatomic gas [5]. The quantity nK_2/N_A is determined for each temperature in terms of the components of the second virial coefficient, B_b and B_m, due to the presence of stable and metastable dimers, respectively, in the mixture:

$$\frac{nK_2}{N_A} = -\frac{p}{RT}\,b_0\,[B_b^*(T_{11}^*) + B_m^*(T_{11}^*)].$$

Let us note that the dimerization effect results in the appearance of a new component in the gas at low temperatures; hence, Eq. (1) should, strictly speaking, take account of cross effects.

It is known that if a chemical reaction proceeds in a gas mixture because of the presence of a temperature gradient, whereupon a concentration gradient is formed, then even in the stationary state the diffusion rates and mass fluxes are not zero, and the expression for the heat flux density will contain the contribution of cross effects. In the case of a binary mixture consisting of monomers and dimers:

$$\vec{q} = -\lambda \nabla T + pk_T(\vec{V}_1 - \vec{V}_2) + (H_1\vec{J}_1 + H_2\vec{J}_2), \qquad (2)$$

where $\lambda = \lambda_0 - \dfrac{pD_{12}}{T}\alpha_T k_T$ is the coefficient of heat conductivity of the nonreacting mixture in the stationary state when the thermal diffusion process results in the appearance of an inhomogeneous concentration distribution; H_i, specific enthalpy of the i-th component of the mixture; and $\vec{V}_i = -\dfrac{D_{ij}}{x_i x_j}(\nabla x_i + k_T \nabla \ln T)$, $\vec{J}_i = n_i m_i \vec{V}_i$, $i = 1, 2$.

Since the mass of the gas does not change as a result of the dimerization "reaction," then

$$\vec{q} = -\left[\lambda_0 + \frac{pD_{12}}{T}\,\alpha_{\tau}k_{\tau}\,\frac{dx_1}{dT} + \frac{H_1 - H_2}{T}\,\frac{n^2 m_1 m_2}{\rho}\,D_{12}\left(\frac{dx_1}{dT} + k_{\tau}\right)\right]\nabla T,$$

from which the coefficient of heat conductivity of the mixture with cross effects taken into account is

$$\lambda_{mix} = \lambda_0 + \frac{pD_{12}}{T}\,\alpha_{\tau}\,\frac{dx_1}{dT} - \frac{\Delta h}{RT}\,\frac{pD_{12}}{T}\,\frac{1}{1 + x_2}\left(\frac{dx_1}{dT} + k_{\tau}\right).$$

Determining the quantity dx_1/dT from the expression for the equilibrium constant

$$K_2 = \frac{x_2 N_A}{x_1^2 n}$$

and the isochore equation for the reaction

$$\frac{d\ln K_{\tau}}{dT} = -\frac{\Delta h}{RT^2}\,,\quad K_{\tau} = RTK_2,$$

we obtain

$$\lambda_{mix} = \lambda_0 + \left(\frac{\Delta h}{RT}\right)^2 \frac{pD_{12}}{T}\,\frac{x_1 x_2}{(1 + x_2)^2} - 2\,\frac{pD_{12}}{T}\,\frac{\Delta h}{RT}\,\alpha_{\tau}\,\frac{x_1 x_2}{1 + x_2}\,. \tag{3}$$

Expanding the last two terms in (3) in powers of x_2 and limiting ourselves to terms containing x_2 to the first degree, we find

$$\lambda_{mix} = \lambda_0 + \lambda_{\tau} + \lambda_{ce}, \tag{4}$$

where $\lambda_{ce} = -2\,\dfrac{pD_{12}}{T}\,\dfrac{\Delta h}{RT}\,\alpha_{\tau}x_2$ represents two equal terms corresponding to the thermal diffusion and diffusion heat conductivity contributions.

Taking account of the heat transfer by collisions, we represent the computational formula for the coefficient of heat conductivity in the form

$$\lambda_{\Sigma} = \lambda_0 + \lambda_{\tau} + \lambda_c + \lambda_{ce}. \tag{5}$$

The computation was performed by using the Lennard–Jones potential function (12-6), the pressure was assumed constant and equal to atmospheric pressure in conformity with the conditions of the experiment. The quantities B_b^*, B_m^*, $\dfrac{\Delta h}{RT}$, $\dfrac{23}{40}\left[B^* + T^*\dfrac{dB^*}{dT^*}\right]$ needed for the computation are tabulated in [12–14] as functions of the reduced temperature with dimer and monomer interaction parameters $\varepsilon_{12} = 1.32\varepsilon_1$, $\sigma_{12} = 1.04\sigma_1$.

The tabulated data show that the dimer concentration in inert gases is small at room temperature at atmospheric pressure (tenths of a percent), but the value of x_2 increases with the reduction in temperature, reaching 2.6% in Ar at T = 90°K, 2.9% in Kr at T = 120°K, and 2.5% in Xe at T = 170°K.

The contribution of the terms λ_r and λ_c to the total heat conductivity is quite small at room temperature and grows as it is reduced, increasing the heat conductivity of each of the species by 5-6 and 1.5%, respectively, at the lowest temperatures; i.e., in the case of moderately dense gases, the heat transfer because of the dimerization "reaction" predominates over the collisional transfer. The maximum contribution of the cross effects was 0.05-0.09% at the lowest temperatures and had practically no influence on the magnitude of the heat conductivity of the gases.

It is seen from Fig. 1b that the computation by the quasichemical method yields quite good agreement with experimental data for Ar in the temperature range 90-280°K under consideration (within 0.4-1.0% limits for an experiment error of ±1.3%). The discrepancies between the theoretical and experimental values for Kr in the whole 120-280°K range investigated and for T = 220-280°K for Xe do not exceed the limits of experimental error. As the temperature is reduced for Xe it increases to −2.2% for T = 170-180°K, but is substantially less than for a computation by the Chapman–Enskog method (−7.7% at T = 170°K).

Thus, an investigation of the applicability of the Chapman—Enskog method and the quasi-chemical method for a correct description of the heat conductivity of inert gases in the low temperature range, realized on the basis of experimental material in [1, 2], showed the necessity for taking account of the density correction under conditions of approaching the phase transition region. This apparently refers to not only monatomic but also polyatomic gases and gas mixtures.

NOTATION

T is the temperature, °K; p, pressure, $N \cdot m^{-2}$; λ, coefficient of heat conductivity, $W \cdot m^{-1} \cdot °K^{-1}$; D_{12}, coefficient of mutual diffusion, $m^2 \cdot sec^{-1}$; k_T thermodiffusion ratio; $\alpha_T = \frac{k_T}{x_1 x_2}$; $\Delta h = h_2 - 2h_1$, difference in enthalpy of the final and initial "reaction" products (dimers and monomers), $J \cdot mole^{-1}$; m_i, mass of molecules of the i-th component, kg; x_i, concentration of the i-th component; n, density of the number of particles, m^{-3}; ρ, mass density, $kg \cdot m^{-3}$; $\vec{V_i}$, diffusion velocity of the i-th component, $m \cdot sec^{-1}$; $\vec{q}$, heat flux density, $W \cdot m^{-2}$; B, second virial coefficient, $m^3 \cdot mole^{-1}$; $B^* = B/b_0$; $b_0 = \frac{2}{3} \pi N_A \sigma_1^3$, $m^3 \cdot mole^{-1}$; N_A, Avogadro number, $mole^{-1}$; R, universal gas constant, $J \cdot mole^{-1} K^{-1}$; ε/k and σ_1, parameters of the potential interaction function, °K and Å; k, Boltzmann constant, $J \cdot °K^{-1}$; and $T^* = \frac{T}{\varepsilon/k}$. Subscripts: 1 for monomer and 2 for dimer.

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