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CALCULATION OF THE THERMAL CONDUCTIVITY OF DENSE REAL GASES AND THEIR MIXTURES

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A procedure is proposed for calculating the thermal-conductivity coefficients of compressed gases and their mixtures; the real first density correction is introduced into the Enskog equation with allowance for the contribution of the internal degrees of freedom of the molecules.

In the calculation of the thermal conductivities of compressed real gases serious difficulties have been incurred to date by the lack of a rigorous and reliable transport theory for dense systems.

The only theoretically justified mathematical expression is the well-known Enskog equation [1]

$$\lambda/\lambda_0 = \frac{1}{\varkappa} + 1.2\,b\rho + 0{,}7554\,(b\rho)^2\varkappa, \tag{1}$$

which is exceedingly difficult to apply to real gases. The reason for this difficulty lies in certain specifics of the rigid-spheres model on which the Enskog theory is based (only pairwise collisions are taken into account, and forces of mutual attraction are disregarded), as well as in the restrictions and assumptions inherent in that model (the molecular-chaos hypothesis, approximate allowance for "screening" of molecules, etc.).

In addition, Eq. (1) describes only the translational part of the thermal conductivity, i.e., the part associated with translational motion of the molecules. In principle, therefore, it cannot be applied to polyatomic gases, whose thermal conductivity is largely determined by the presence of molecular internal degrees of freedom.

In the present study we attempt to modify the Enskog equation so that it can be used to calculate reliable values of the thermal conductivity of dense real gases and their mixtures. It is reasonable to speculate that to treat the attractive forces ignored by the original model as a perturbation in the system of rigid spherical molecules will result in a substantially more realistic version of the Enskog equation. We note that the attractive forces are felt primarily at moderate densities and to a lesser extent at high densities.

The latter consideration justifies the inclusion of mutual attraction only insofar as it influences the linear term of the expansion of the thermal conductivity in powers of the density:

$$\lambda/\lambda_0 = 1 + \beta\rho + \ldots,$$

where β is the so-called first density correction, which takes into account the contribution of ternary collisions [2].

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TABLE 1. Calculation of λ for CH_4 at t = 43.6°C and p = 239.2 atm

Quantity determined	Calc. per equation	Reference	Value
σ, Å	—	[14]	3,77
ε/k, K	—	[14]	151,0
T^*	—	—	2,098
$\lambda_0\cdot 10^7$, cal/cm·sec·°K	—	[9]	886
$\eta\cdot 10^7$, g/cm·sec	—	[9]	1178
$\lambda_0'\cdot 10^7$, cal/cm·sec·°K	(8)	—	1,62
δ	(8)	—	1,62
ρ, mole/cm³	—	[9]	0,0103
d, Å	(11)	—	3,715
b, cm³/mole		—	64,68
$b\rho$	—	—	0,6662
y	(10)	—	2,0555
z^{rs}	(10)	—	2,0555
$\varkappa$	(9)	—	1,584
b_0, cm³/mole	(12)	—	67,59
β', cm³/mole	(12)	—	80,71
$\lambda\cdot 10^7$, cal/cm·sec·°K	(7)	—	1533
$\lambda^{ex}\cdot 10^7$, cal/cm·sec·°K	—	[9]	1540
Error, %	—	—	0,45

Assuming that the internal degrees of freedom do not depend on the intermolecular distance, we can express the thermal conductivity as the sum of the contributions from translational and internal degrees of freedom [3, 4]:

$$\lambda = \lambda' + \lambda''. \tag{2}$$

In the given case it is practical to calculate λ' according to the Enskog equation, replacing the quantity $\beta = 0.575b$ therein by the real temperature function $\beta'(T)$, which represents the translational part of the first density correction and takes into account the influence of attraction on the thermal conductivity of a moderately dense gas [2]:

$$\lambda' = \lambda_0' \left[\frac{1}{\varkappa} + \beta'(T)\rho + 0{,}625\, b\rho + 0{,}7554\,(b\rho)^2 \varkappa \right]. \tag{3}$$

Here, according to [2, 5], $\beta' = \beta\left[1 + \frac{8}{25} A^* \left(\frac{C_{P_0}}{R} - \frac{5}{2}\right)\right]$, where $A^* = \Omega^{(2,2)*}/\Omega^{(1,1)*}$. The value of λ'' estimated on the basis of notions concerning the diffusion nature of energy transport by the internal degrees of freedom [6] is

$$\lambda'' = \rho D C_V'', \tag{4}$$

where within the framework of the stated assumption $C_V'' = C_V^{0''}$, and the self-diffusion coefficient, according to the Enskog theory, is

$$D = D_0/\varkappa. \tag{5}$$

From (4) and (5) we readily obtain [3, 4]

$$\lambda'' = \lambda_0''/\varkappa = (\lambda_0 - \lambda_0')/\varkappa. \tag{6}$$

Substituting (3) and (6) into (2), we arrive at the following equation for the thermal conductivity:

$$\lambda/\lambda_0' = \frac{\delta}{\varkappa} + (\beta' + 0.625\, b)\rho + 0{,}7554\,(b\rho)^2 \varkappa, \tag{7}$$

where

$$\lambda_0' = \frac{15}{4} \cdot \frac{R}{m} \eta_0, \quad \delta = \lambda_0/\lambda_0'. \tag{8}$$

TABLE 2. Comparison of Calculated and Experimental [9] Values of λ for CH_4 (10^7 cal/cm•sec•°K) at t = 43.6°C

p, atm	Calculated	Experimental	δ, %
11,5	901,1	888	1,5
21,4	914,3	913	0,1
69,1	995,4	1010	—1,4
120,1	1112	1174	—5,3
171,1	1260	1298	—2,9
273,2	1588	1653	—3,9
341,2	1810	1833	—1,3
407,6	1974	1940	1,7
463,7	2133	2072	3,0
518,1	2269	2170	4,6
573,9	2412	2274	6,1

The thermal conductivities of gases are calculated according to Eq. (7) by the following scheme.

The initial data are the thermal conductivities and viscosities of the rarefied gas ($\rho \to 0$) and the density of the compressed gas for the particular state parameters of interest. Relations (8) are used to determine λ_0' and the parameter δ. The value of the radial distribution function at distance d from the center of the individual molecule is calculated in terms of the compressibility of a system of rigid spheres:

$$\varkappa = (z^{\mathrm{rs}} - 1)/b\rho, \quad b = \frac{2}{3}\pi N d^3, \tag{9}$$

which, in turn, can be determined from the simple Carnahan—Starling equation of state [7], which is the one most commonly used today:

$$z^{\mathrm{rs}} = \frac{1 + y + y^2 - y^3}{1 - y^3}, \tag{10}$$

in which $y = {}^1/_6 \pi d^3 \rho = {}^1/_4 b\rho$. The most important aspect of the given procedure (as, of course, in any computations involving the rigid-spheres model) is the correct choice of diameter d of the rigid sphere.

An investigation has shown that the best results are obtained by determining d according to the Barker—Henderson relation [8]

$$d = \int_0^{\sigma} \{1 - \exp[-u(r)/kT]\}\, dr,$$

which is well approximated by the equation [13]

$$d/\sigma = \frac{0.3837 + 1.068\,\dfrac{1}{T^*}}{0.4293 + 1/T^*}. \tag{11}$$

For the determination of $\beta'(T)$ we use the following relation derived in [2]:

$$\lg \beta'^* = 0.47 + 1.59 \lg 1/T^* + 1.26 (\lg 1/T^*)^2 + 0.37 (\lg 1/T^*)^3, \tag{12}$$

in which

$$\beta'^* = \beta'/b_0; \quad b_0 = \frac{2}{3}\pi N \sigma^3; \quad T^* = kT/\varepsilon,$$

and which is valid in the interval $0.35 \le T^* \le 40$. For the calculation of λ in the case of dense binary gas mixtures good results are obtained with effective values $\beta_m' = \Sigma x_i x_j \beta_{ij}'$ and $b_m = \Sigma x_i x_j b_{ij}$. For practical computations we recommend using the temperature-dependent effective potential parameters $\sigma(T)$ and $\varepsilon(T)$, the technique for the determination of which is described in detail in [11, 12].

Moreover, detailed tables of these parameters covering a wide range of temperatures for bulk quantities of substances are given in [14]. The indicated parameters are particularly well suited to calculations of the thermal conductivities of mixtures, because the simple combination rules $\sigma_{ij} = {}^1/_2(\sigma_i + \sigma_j)$ and $\varepsilon_{ij} = (\varepsilon_i \cdot \varepsilon_j)^{1/2}$ [14] used to determine β_m' and b_m

TABLE 3. Comparison of Calculated and Experimental [10] Values of λ for Mixture $3H_2$—N_2 (10^4 W/m•°K) at T = 298.25°K

p, bar	Calculated	Experimental	
6,0	1142	1140	1160
50,7	1165	1170	1180
101,3	1189	1180	1200
202,6	1240	1230	1250
303,9	1289	1280	1290
405,2	1340	1320	1330

can be applied to them with full justification. The procedure described here has been tested on a large array of experimental data on the thermal conductivities of nitrogen, argon, carbon dioxide, steam, methane, hydrogen, propane, isobutane, ethylene, n-octane, ammonia, three nitrogen—hydrogen mixtures, and two hydrogen—ethylene mixtures.

The average error of the calculations is ±3%, and the maximum error does not exceed 7%. Table 1 gives as an illustration the results of a sample calculation of the thermal conductivity of methane gas at a temperature of 43.6°C and pressure of 239.2 atm. The results of the calculations of λ for CH_4 at other pressures on the same isotherm are compared with the experimental data of [9] in Table 2. The calculated and experimental [10] values of λ for a dense gas mixture $3H_2$—N_2 at T = 298.25°K are given in Table 3.

The foregoing results evince good reliability on the part of Eq. (7) for describing the thermal-conductivity coefficients of dense real gases and their binary mixtures over a wide range of state parameters.

NOTATION

λ, thermal conductivity of compressed gas; λ_0, thermal conductivity of rarefied gas; λ', λ'', contributions of translational and internal degrees of freedom to thermal conductivity of the compressed gas; λ_0', λ_0'', contributions of translational and internal degrees of freedom to thermal conductivity of the rarefied gas; η_0, viscosity of rarefied gas; ρ, density; $\varkappa$, value of radial distribution function at distance d from center of molecule; d, diameter of model rigid sphere; D, self-diffusion coefficient; C_V'', internal specific heat; m, molecular mass; b, four times proper volume of molecules; z^{rs}, compressibility coefficient of system of rigid spheres; $\Omega^{(2,2)*}$, $\Omega^{(1,1)*}$, collision integrals used in calculating the thermal conductivities and diffusion coefficients, respectively; u(r), potential energy of molecular interaction; T*, reduced temperature; σ, ε, parameters of Lennard-Jones (12, 6) potential; x_i, mole fraction of i-th component of mixture.

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