REVIEWS

HEAT AND MASS TRANSPORT IN GASES AND THEIR MIXTURES

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The theory of transport phenomena in rarefied gases consisting of structureless molecules is developed in [1, 2]. The Chapman–Enskog theory is, strictly speaking, applicable only to monatomic gases. Inelastic collisions are possible between molecules possessing internal degrees of freedom. In such collisions kinetic energy is no longer conserved. The thermal conductivity depends significantly on the presence of internal degrees of freedom since energy transport includes internal energy as well as translatory. Simple molecular-kinetic theory yields for the thermal conductivity the relationship $\lambda m/\eta = fc_v$, which is experimentally obeyed by monatomic gases. It has been shown experimentally [4] that for all monatomic gases the factor f equals 2.5 ± 0.05.

To take the internal degrees of freedom into account Eucken effectively postulated that $f = f_{Eu} = 1/4\,(9\gamma-5)$, assuming that there is no interaction between the translatory and internal degrees of freedom.

Ubbelohde [3] treated the molecules of a gas with excited internal energy states as the components of a chemically reacting mixture and regarded the flow of internal energy as the energy transported by the diffusion of these excited states, setting $f_{int} = \rho D_{int}/\eta$ and

$$\frac{\lambda m}{\eta}=\frac{5}{2}c_{trans}+\frac{\rho D_{int}}{\eta}c_{vint} \tag{1}$$

for

$$\frac{\lambda m}{\eta}=f_g c_v.$$

The factor f_g is defined by

$$f_g=\frac{\rho D_{int}}{\eta}+\frac{3}{2}\frac{k}{c_v}\left(\frac{5}{2}-\frac{\rho D_{int}}{\eta}\right). \tag{2}$$

Experimental data on the thermal conductivity of gases show that the factor f lies between f_{Eu} and f_g.

Exchange of energy between the translatory and internal degrees of freedom was taken into account by Wang-Chang and Uhlenbeck, who obtained the following relationship for the thermal conductivity

$$\lambda=\frac{25kTc_{v\,int}}{4a_{tt}m}\left[1-\frac{6}{5}\frac{c_{v\,int}}{c_{v\,trans}}\frac{a_{it}}{a_{ii}}+\frac{9}{25}\left(\frac{c_{v\,int}}{c_{v.trans}}\right)^2\frac{a_{tt}}{a_{ii}}\right]\left(1-\frac{a_{it}^2}{a_{ii}a_{tt}}\right)^{-1}.$$

In the limit of a very slow exchange of energy between the translatory and internal degrees of freedom, relationship (3) goes over into Eucken's formula.

Expression (3) was used by Mason and Monchick [6] to describe the properties of polyatomic gases. They considered the limiting case of a very long relaxation time τ. In effect this corresponds to an expansion of the thermal conductivity as a series in τ_c/τ, where τ_c is the time between two collisions. The zeroth approximation, used by Mason and Monchick, corresponds to the case $1/Z = \tau_c/\tau = 0$ for $\tau \to \infty$ and gives:

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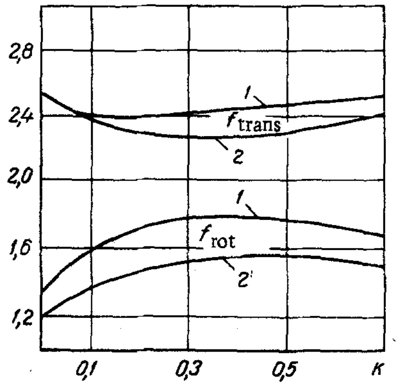

Fig. 1

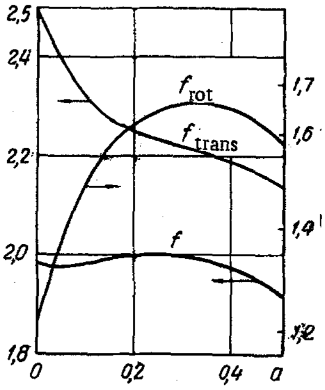

Fig. 2

Fig. 1. Eucken factor versus dimensionless parameter κ (rough spheres). 1) The Kagan–Afanas'ev approximation; 2) Pidduck's approximation.

Fig. 2. Eucken factor versus dimensionless parameter *a* (loaded spheres).

$$f_{\text{м}} = \frac{\rho D_{\text{int}}}{\eta} a_{it} + \frac{3}{2}\left(\frac{5}{2} a_{tt} - \frac{\rho D_{\text{int}}}{\eta} a_{it}\right)\frac{k}{c_v},$$

where

$$a_{tt} = \frac{5}{2}\frac{kT}{\eta} + \frac{25}{12}\frac{c_{v\text{int}}}{nk\tau}; \quad a_{it} = \frac{5}{4}\frac{c_{v\text{int}}}{nk\tau}. \tag{4}$$

Allowing for energy exchange between the translatory and internal degrees of freedom has the effect of decreasing f_{trans} and increasing f_{int}.

Starting from intuitive considerations Saxena et al. [7] obtained a modified Eucken factor of the form

$$f_g = \frac{\rho D}{\eta} + \frac{3}{2}\left(\frac{5}{2} - \frac{\rho D}{\eta}\right)\frac{k}{c_v} - \frac{3}{2}\frac{k}{c_v}\left(\frac{5}{2}c_v - \frac{\rho D}{\eta}\right)\left(1 - \frac{3k}{2c_v}\right)$$

$$\times\left\{1 - \exp\left(-\frac{1}{Z}\frac{2c_v}{3k}\right)\right\} = f_g - \frac{3k}{2c_v}\left(\frac{5}{2} - \frac{\rho D}{\eta}\right)\left(1 - \frac{3k}{2c_v}\right)\left\{1 - \exp\left(-\frac{1}{Z}\frac{2c_v}{3k}\right)\right\}. \tag{5}$$

For large Z only two terms need be retained in the series expansion of $(-(1/Z)(2c_v/3k))$. This gives $f_g = f_g - 1/Z(5/2 - \rho D/\eta)c_{v\,\text{trans}}/c_v$. It should be noted that the theories of Eucken, Mason–Monchick, and Saxena et al. were developed without specifying any real model for the molecules of a polyatomic gas. The relationships obtained in these theories for calculating the thermal conductivities of gases are valid for any polyatomic gas.

We shall now consider certain specific molecular models and the associated theoretical concepts.

1. Rough Spherical Molecules. In this case the molecule has the form of a rough sphere of diameter σ, mass m, and moment of inertial I. The distribution function for a gas of rough-sphere molecules has the form $f = f(\vec{r}, \vec{v}, \vec{\omega}, t)$. The equilibrium distribution function has the form

$$f^{(0)} = n(m/2\pi kT)^{3/2}(I/2\pi kT)^{3/2}\exp[-(mv^2 + I\omega^2)/2kT].$$

Boltzmann's equation for a gas of rough spheres can be written

$$\frac{\partial f_i}{\partial t} + \vec{v}_i\frac{\partial f_i}{\partial \vec{r}} + \frac{\vec{X}}{m}\frac{\partial f_i}{\partial \vec{v}_i} = \sigma^2\iiint (f'_i f'_j - f_i f_j)\,\gamma(\vec{k}\cdot\vec{v}_{ji})\,d\vec{k}\,d\vec{v}_j d\vec{\omega}_j.$$

The thermal conductivity of such a gas can be expressed as

$$\lambda = \frac{k^2T}{16m}\left(-10a_1^{100} - 6a_1^{010} + 2a_2^{000} - 5a_2^{100} - 5a_2^{010}\right).$$

Retaining only a_1^{100} and a_1^{010} leads to Pidduck's approximation [8]

$$\lambda = \frac{9}{16\sigma^2}\left(\frac{k^3T}{\pi m}\right)^{1/2}\frac{(\kappa+1)^2(50\kappa^2+151\kappa+37)}{102\kappa^3+101\kappa^2+75\kappa+12}.$$

Kagan and Afanas'ev took the three terms a_1^{100}, a_1^{010} and a_2^{000} into account and obtained

$$\lambda = \frac{3}{16\sigma^3}\left(\frac{k^3T}{\pi m}\right)^{1/2}\frac{(\kappa+1)^2(2000\kappa^4+9490\kappa^3+13449\kappa^2+7336\kappa+1121)}{1360\kappa^5+3626\kappa^4+3973\kappa^3+2560\kappa^2+969\kappa+116},$$

where κ is a dimensionless parameter, $\kappa = 4I/m\sigma^2$.

Figure 1 shows the Eucken factor f plotted as a function of κ.

2. Loaded Spheres. A loaded sphere is a sphere whose mass-center does not coincide with the center of geometrical symmetry.

Suppose the system consists of n loaded-sphere molecules. The mass of the i-th molecule is m_i; the mass-center is spaced from the geometrical center by a distance ξ; the moment of inertia relative to a coordinate system fixed in space is I_i; $\vec{r}_i$ is the radius vector of the mass-center of molecule i; $\vec{\alpha}_i = (\alpha_i, \beta_i, \gamma_i)$ are angles characterizing the orientation of the molecule relative to the coordinate system; and $\vec{\omega}_i$ is the angular velocity of molecule i. Boltzmann's equation for loaded spheres has the form

$$\frac{\partial f_i}{\partial t} + \vec{v}_1\frac{\partial f_i}{\partial \vec{r}} + \frac{\vec{X}}{m_i}\frac{\partial f_i}{\partial \vec{v}_1} + \frac{\partial(\dot{a}_1 f_i)}{\partial \vec{\alpha}_1} + \dot{N}_{1f}\frac{\partial f_i}{\partial N_1}$$
$$= \sum_j \sigma_{ij}^2 \int_{(\vec{k}\cdot\vec{g}_{21}>0)}\cdots\int \vec{k}\cdot\vec{g}_{21}\,[f_i(\vec{v}_1', \vec{\alpha}_1, N_1', t)\, f_j(\vec{v}_2', \vec{\alpha}_2, N_2', t)$$
$$- f_i(\vec{v}_1, \vec{\alpha}_1, N_1, t)\, f_j(\vec{v}_2, \vec{\alpha}_2, N_2, t)]\, d\vec{k}\, d\vec{v}_2 d\vec{\alpha}_2 dN_2,$$

where

$$N_i = \vec{r}_i\cdot\vec{\omega}_i.$$

The thermal conductivity can be expressed in terms of the quantity $a = m\xi^2/2I$. The Eucken factor is plotted as a function of a in Fig. 2.

3. Spherocylinders. A spherocylinder is a smooth right cylinder of length l with hemispheres of radius σ fixed to its ends. The mass of a spherocylinder molecule is distributed symmetrically about the axis of the cylinder, so that the mass-center and the geometrical center coincide. Boltzmann's equation for a gas of spherocylinders has the form [9]

$$\frac{\partial f_i}{\partial t} + \vec{v}_i\frac{\partial f_i}{\partial \vec{r}} + \dot{\vec{v}}_i\frac{\partial f_i}{\partial \vec{v}_i} + \frac{\partial}{\partial \Omega}(\dot{\Omega} f_i) = \sum_j \int\ldots\int = (f_i' f_j' - f_i f_j)\, W d\vec{v}_i d\vec{v}_j' d\vec{v}_i'\, dI_1 dI_2 dI_1'.$$

The thermal conductivity of a gas of spherocylinders can be written

$$\lambda \approx 1{,}6k\left(\frac{kT}{\pi m}\right)^{1/2}\frac{1}{l^2}\,\frac{1}{\beta^2+\beta+0.12},$$

where $\beta = (l/2)\sigma$. The Eucken factor is plotted versus β and $\Delta = ml^2/4I$ in Fig. 3.

The experimental and theoretical temperature dependence of the Eucken factor is shown in Fig. 4 for nitrogen and oxygen.

Kinetic theory for molecules possessing internal degrees of freedom has been developed both from the classical and the quantum-mechanical points of view. A classical formulation of the theory for gases consisting of rigid nonspherical molecules is developed in [12-15, 17]. A more general form of this theory was discussed by Taxman [18]. The presence of the internal degrees of freedom leads to the appearance of an additional collisional invariant, connected with the angular velocity. This additional invariant gives rise to an additional variable, the "spin" angular momentum of the molecules, and the perturbation function should incorporate terms which couple these two vectors.

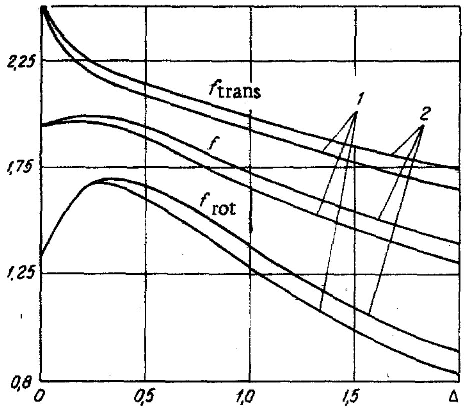

Fig. 3. Eucken factor versus dimensionless parameters β and Δ (spherocylinders). 1) $\beta = 0$; 2) $\beta = 1$.

Curtiss et al. did not allow for this effect. Dahler [15, 19] considered the influence of this effect on transport properties in a gas of rough spheres [20] and spherocylinders, and showed that this effect is small.

A quantum-mechanical treatment for molecules with internal degrees of freedom was given by Wang-Chang and Uhlenbek [21] and by Wang-Chang, Uhlenbeck, and de Boer [22]. They obtained expressions for the transport coefficients in terms of integrals dependent upon the differential scattering cross sections. Their theory assumes the cross sections to be asymptotic, which is true only when the states in which the molecules are found are degenerate.

A more rigorous derivation of the quantum-mechanical Boltzmann equation for a gas of molecules with internal degrees of freedom was given by Waldmann [23] and later by Snider [24]. The Wang-Chang method was used by Monchick, Munn, and Mason [25] to investigate thermal diffusion in mixtures of polyatomic gases. The quantum-mechanical theory of Wang-Chang, Uhlenbeck, and do Boer leads to the following expression for the thermal diffusion factor of mixtures

$$\alpha_{\text{T}} = \frac{1}{5k} \frac{\mu_{ij}(6C^*_{ij} - 5)}{nD_{ij}} \left(\frac{\lambda_{ji}}{x_j m_j} - \frac{\lambda_{ij}}{x_i m_i} \right). \tag{6}$$

As is well known, the Wang-Chang theory does not involve any specific molecular model. Assumption of a particular model requires the evaluation of a term denoted $\tilde{Q}_{ij}^{00.01}$. According to the Wang-Chang theory, $\tilde{Q}^{00.01} \to 0$ and $\lambda_{ij} = \lambda_{i\,\text{trans}}$. For loaded-sphere molecules $\tilde{Q}_{ij}^{00.01} \neq 0$ and makes a significant contribution to the thermal diffusion factor α_T. For this model we have

$$\alpha_{\text{T}} = \frac{(6C^*_{ij} - 5)\mu_{ij}}{5nkD_{ij}} \left(\frac{\lambda_{j\,\text{trans}}}{x_j m_j} - \frac{\lambda_{i\,\text{trans}}}{x_i m_i} \right) + \frac{1}{5nkD_{ij}} \left[\frac{(6\tilde{C}_{ij} - 5)\lambda_{j\,\text{int}}}{x_j} - \frac{(6\tilde{C}_{ij} - 5)\lambda_{i\,\text{int}}}{x_i} \right]. \tag{7}$$

It should be noted that the quantity $\tilde{C}_{ij}$ is not analogous to the quantity C^*_{ij} and is not symmetric with respect to an interchange of indices. The quantity $\tilde{C}_{ij}$ is essentially dependent on inelastic collisions, and reduces to zero if the molecules of the j-th component of the mixture have no internal degrees of freedom.

The mechanism by means of which gaseous mixtures are separated into their constituents is closely linked with the rotational degrees of freedom of the molecules. The thermal diffusion factor is sensitive to the cross section for inelastic collisions. For loaded spheres, the larger ξ the greater the probability of inelastic collisions.

Generally, for nonisotopic mixtures, the second term in (7) is much smaller than the first, which depends essentially on the mass of the molecules and their dimensions. This is indeed why the expression for α_T obtained for a mixture of monatomic gases [25] can generally also be applied to a mixture of polyatomic gases. The second term of (7) becomes important if the masses and dimensions of the molecules are very similar (isotopic mixtures), as effects associated with nonsphericity of the molecules (which this term allows for) are then significant.

An experimental determination of the thermal diffusion of isotopic mixtures of CO (containing the molecules C^{12}, C^{14}, O^{16}, O^{18}) is discussed in [26]. The influence of a magnetic field on the thermal diffusion factor was studied experimentally by de Vries et al. [27] using mixtures of krypton and oxygen. It was shown that an electromagnetic field changes the thermal diffusion factor by not more than 0.4%.

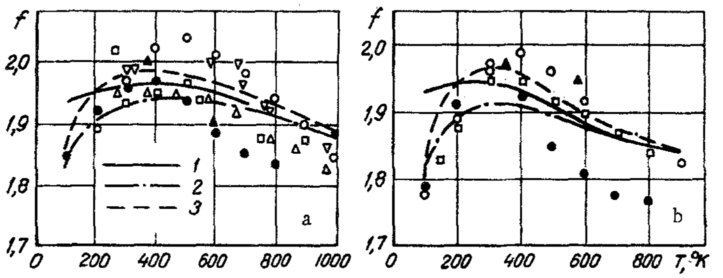

Fig. 4. Dependence of Eucken factor on temperature [108] for (a) nitrogen, and (b) oxygen. Curves correspond to: 1) nonlinearized Mason–Monchick relation; 2) linearized relation; 3) linearized relation and $D_{int}/D = 1 + 0.27/Z + \ldots$.

The quantum-mechanical Boltzmann equation obtained in [23, 24] was used by McCourt and Snider [28] to derive a quantum-mechanical expression for the thermal conductivity of a gas whose molecules possess rotational degrees of freedom. This expression contains terms which are the quantum analogs of the combined linear and angular momenta of the molecule. For the particular case when the "spin" density equals zero, the expression coincides with Wang-Chang's result. Expressions for other transport coefficients are derived in [29]. The results obtained in [28, 29] were later used in [30, 31] to derive exact expressions for the transport coefficients of a gas of loaded-sphere molecules.

We shall now dwell for a moment on the theory of transport phenomena in a dense gas of structureless molecules. Application of Liouville's theorem for an ensemble of distribution functions leads to equations of higher order for the distribution function. A generalized Boltzmann equation can be obtained with the aid of these equations [32]. Bogolyubov's results are used in [33] to derive expressions for the transport coefficients in the form of series expansions in the density. The results are discussed in [34-36]. The effect of triple collisions on the first correction for the density is discussed in [37-39]. Numerical estimation of these corrections in [37, 39] leads to results in satisfactory accord with experimental data at high temperatures, where the influence of forces of attraction is small. Corrections to the quantum-mechanical Boltzmann equation which allows for the finite dimensions of the molecules but ignores the effects of many-molecule collisions are discussed in [40]. A more general treatment of the quantum-mechanical Boltzmann equation is given in [41-48].

In another approach to the theory of transport phenomena in moderately dense gases the transport coefficients are expressed in terms of correlation functions. Expressions for the transport coefficients are obtained in [49-50]. The two approaches to the study of transport processes in dense gases are discussed in [51, 52].

Ernst [53] evaluated his own relationships [54] for the case of a gas of rigid spheres and obtained results identical to those of [1, 2, 55]. Sengers [56, 57] allowed for triple collisions in a gas of rigid spheres and obtained results deviating from [1, 2, 55]. He found a correction to the Enskog relation but it was not estimated numerically. Sengers considers that Enskog neglected certain types of collisions and cyclical collisions.

Expressions for the transport coefficients were derived in [58-60] with the aid of series expansions in the density, and it was shown that the term containing the square of the density and characterizing the collision of four molecules, diverges. It was shown [58, 60, 61] that the logarithm of the density appears in the relations for the transport coefficients. The divergence is discussed in [63, 67].

Sengers [57, 68, 69] used the distribution function to evaluate the logarithmic term for a gas of rigid disks. Identical results were obtained in [70] using the correlation functions method.

The Bogolyubov–Born–Green equation is studied in [71, 72] along with the problem of obtaining a collision integral to the Boltzmann equation. The contemporary state of the theory of transport phenomena in dense gases is reviewed in [73]. The modern theory of transport phenomena in liquids is discussed in [74-82]. Transport phenomena in mixtures of dense gases are studied in [83-85]. In [86] a modified version of Enskog's theory [1, 2, 55] for a dense gas of rigid spheres is used to study transport phenomena in a dense gas of rough spheres.

The thermal conductivity of chemically reacting gases is investigated in [5, 10, 11]. Heat transport in chemically reacting gases will be much greater than in nonreacting gaseous mixtures. A considerable amount of heat can be transported on account of the chemical enthalpy of the molecules, which diffuse under the action of concentration gradients. These gradients exist because the composition of the gas varies depending on the temperature. In chemical equilibrium, irrespective of the geometry of the device for determining the thermal conductivity, the equilibrium thermal conductivity can be written in the form

$$\lambda_e = \lambda_f + \lambda_r,$$

where λ_f is the thermal conductivity in the absence of chemical reactions, and λ_r is the thermal conductivity on account of chemical reactions. The heat-flow equation has the form

$$q = -\lambda_f r^a \frac{dT}{\vec{dr}} + \sum_{i=1}^{v} r^a W_i H_i = -\lambda^* \left(\Delta T \Big/ \int_{r_1}^{r_2} r^{-a} dr \right). \tag{8}$$

The coefficient a characterizes the geometry of the device for determining the thermal conductivity: for parallel plates $a = 0$, for coaxial cylinders $a = 1$, and for concentric spheres $a = 2$. The quantity ΔT is the temperature difference between the walls of the device. Equation (8) serves to define the "thermal conductivity" of a reacting gas. It is well known that λ^* coincides neither with λ_f nor with the thermal conductivity at chemical equilibrium, and depends on the geometry of the device used to determine the thermal conductivity.

Mishina [87] constructed a closed system of differential equations and boundary conditions for heat and mass transport in the reacting (with finite rates) mixture $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$, located in a heat-conducting space of cylindrical geometry bounded by surfaces of arbitrary catalytic activity. On the assumption that the composition does not deviate much from the equilibrium composition and that the temperature drop across the space is small, analytic expressions were obtained for the off-equilibrium composition and for the mean (over the space) and the local "thermal conductivity" of the mixtures $N_2O_4 \rightleftharpoons 2NO_2$ and $2NO_2 \rightleftharpoons 2NO + O_2$.

The thermal conductivity of a nonequilibrium partially ionized gas is discussed in [88]. The properties of an ionized monatomic gas are studied in [89]. It was shown that higher-order approximations should be used to calculate the thermal conductivity. The properties of an ionized polyatomic gas are examined in [90]. A relationship is given by means of which the thermal conductivity of such a gas can be calculated. A number of papers have been devoted to the properties of equilibrium nitrogen plasma. In particular, experimental and theoretical results on the thermal conductivity are compared by Penski [91]. The thermal conductivity is calculated at various pressures with and without charge exchange taken into account. The thermal conductivity of a gas due to thermal diffusion in the presence of chemical reactions and ionization is given by [92, 93]

$$\lambda_{D^{\mathrm{T}}} = \sum_i I_i \left[\frac{1}{T} \frac{D_i^{\mathrm{T}}}{M_i} - \frac{p}{RT} \frac{\sum_j M_j D_{ij} (\partial x_j / \partial T)_p}{\sum_i x_i M_i} \right]$$
$$+ RT \sum_i \frac{D_i^{\mathrm{T}}}{M_i} \left[\left(\frac{\partial \ln x_i}{\partial T} \right)_p - \frac{R}{p} \left\{ \sum_j \frac{1}{D_{ij}} \left(\frac{D_j^{\mathrm{T}}}{M_j} - \frac{x_j}{x_i} \frac{D_i^{\mathrm{T}}}{M_i} \right) \right\}^{-1} \right].$$

The influence of thermal diffusion on the experimental determination of the thermal conductivity of gaseous mixtures is considered in [109]. The results obtained in this paper characterize the maximum correction for thermal diffusion in the nonstationary state.

According to the data of [109], the correction for thermal diffusion, $\lambda_{D}T/\lambda_{\mathrm{exp}}$, for a concentration of the heavy component of $x_2 = 0.1$ equals for the mixtures: He–Xe (T = 302.15°K) approximately 12%; Kr–Xe (T = 302.15°K), ~3%; H_2–CO_2 (T = 298.15°K), ~7.9%; H_2–O_2 (T = 295.15°K), ~7%.

Transport properties in gases and their mixtures at low temperatures are discussed in [94–100, 107]. The influence of quantum effects on the thermal conductivity of a gaseous mixture is investigated in [96].

The concentration dependence of the thermal conductivity of mixtures on nonreacting gases is studied in [93].

We shall dwell for a moment on the thermal conductivity of water vapor. Geier and Schafer [101] measured the thermal conductivity of water vapor, nitrogen, and other gases in the temperature range

100-1000°C. Their experimental data for water vapor at high temperatures are almost 10% less than the smoothed values of Vargaftik and Zimina [102], which form the basis of the standard tables on the thermal conductivity of water vapor at low pressures. Geier and Schafer did not measure the thermal conductivity of argon, so that direct correction of their values for the thermal conductivity of water vapor is not possible. Vargaftik and Zimina [103] measured the thermal conductivity of argon in the temperature range 0-1000°C; their results are in good accord with theoretical calculations using an (exp-6) potential. Further, Vargaftik and Zimina measured the thermal conductivity of nitrogen, so that the experimental data of Geier and Shafer could be corrected:

$$\lambda_{H_2O\ \text{corrected}} = \lambda_{H_2O,\,G\text{-}S}\ \frac{\lambda_{N_2,\,V\text{-}Z}}{\lambda_{N_2,\,G\text{-}S}}\ \frac{\lambda_{Ar,\,exp-6}}{\lambda_{Ar,\,V\text{-}Z}}.$$

Vargaftik and Zimina noted [104] that Geier and Schafer did not correct for the temperature step. In order to find this correction one must know the geometry and dimensions of the device for determining the thermal conductivity, the gas pressure, and accommodation coefficients of the surfaces. When this correction is made we then have

$$\lambda_{\text{corrected}} = \lambda_{\text{exp}}\,(1+\alpha).$$

For a device of cylindrical geometry

$$\alpha = \frac{2-a}{a}\ \frac{(2\pi MRT)^{1/2}}{r_1 \ln(r_2/r_1)}\ \frac{\lambda}{(2c_p - R)\,p},$$

where a is the accommodation coefficient of the inner cylinder, and r_1 and r_2 are the radii of the inner and outer cylinders respectively. The lower limit of α for the experimental data of Geier and Schafer can be calculated on setting $a = 1$, p = 20 mm Hg.

Theoretical results for the thermal conductivity of water vapor can be obtained for the formula

$$\lambda = \frac{\eta R}{M}\left[\frac{15}{4} + \frac{\rho D_{\text{int}}}{\eta}\,\frac{c_{v\text{int}}}{R} - \frac{\dfrac{3}{\pi Z_{\text{int}}}\left(\dfrac{5}{2} - \dfrac{\rho D_{\text{rot}}}{\eta}\right)^2}{1 + \dfrac{2}{\pi Z_{\text{rot}}}\left(\dfrac{5}{2} + \dfrac{\rho D_{\text{int}}}{\eta}\right)}\right].$$

The dimensionless ratio $\rho D_{\text{int}}/\eta$ can be expressed in the form

$$\frac{\rho D_{\text{int}}}{\eta} = \frac{1{,}2\Omega^{(2,2)*}/\Omega^{(1,1)*}}{1+\delta}.$$

The ratio $\Omega^{(2,2)*}/\Omega^{(1,1)*} \approx 1.1$, and δ is given by

$$\delta = \pi^{3/2} < a_4 > \left(\frac{3}{16}\,\frac{\mu h}{kT}\right)^2 \frac{\Omega^{(2,2)*}}{\Omega^{(1,1)*}}\,\frac{\eta}{\sqrt{kT}}\,\frac{R/c_{v\text{int}}}{I_A (I_B I_C)^{1/4}}\left[\frac{5}{4} - \frac{(I_B I_C)^{1/2}}{4 I_A}\right]^{-7/2},$$

where $< a_4 > = 0.44$.

The equilibrium composition and thermal conductivity of water vapor in the temperature range 600-5000°K was calculated by Svehla [105]. The thermal conductivity of water vapor at temperatures 100-6000°K and pressures 0.1-100 bars was calculated by Kessel'man and Blank [106].

The thermal conductivity of water vapor in the critical region can be calculated using the formula [44]

$$\lambda = \lambda_f + \lambda_r,$$

where λ_r characterizes the contribution to the thermal conductivity from diffusion and dissociation of groups of molecules,

$$\lambda_r = \rho D\,\frac{D_{1n}}{D}\,c_{pr}.$$

The quantity D_{1n}/D can be found from the relationship

$$\frac{D_{1n}}{D} = \left(\frac{2}{1 + 2.1 n^{1/4}}\right)^2 \left[\frac{1}{2}\left(1 + \frac{1}{n}\right)\right]^{1/2}.$$

In conclusion we shall say a few words on energy exchange in collisions of molecules with a rigid wall. The exchange of energy and momentum between the molecules of a gas and a hard wall depends on the properties of the impinging molecules (energy, velocity distribution), the model taken to describe the interaction, and on the properties and structure of the wall. The accommodation coefficients for a trajectory at a fixed position of a gas molecule are obtained by averaging over the velocities of this molecule, which has a Maxwellian distribution. The first attempt to calculate the accommodation coefficient was made by Baule [64] with the aid of the rigid-spheres model, a model which is not, however, suitable for the case of a rigid surface. The energy exchange coefficients were calculated by Barantsev [65], who considered the interaction with a surface of gas molecules having an energy 5-10 eV and a relative mass $\mu = M/m < 1$. The energy accommodation coefficients are calculated in [62] as a function of the collision parameters. In the various models used to date to represent the interaction of a rarefied gas with a rigid wall, the wall is assumed to be clean (i.e., there are no adsorbed atoms). A second assumption made in interaction models is that the wall is smooth. Which theoretical model is to be adopted will depend on the results of an experimental check of the theoretical suppositions.

NOTATION

T	is the temperature;
λ	is the thermal conductivity;
η	is the viscosity;
c_v	is the specific heat at constant volume;
$c_{v\,trans}$, $c_{v\,int}$	are the specific heat due to translatory and internal degrees of freedom respectively;
f	is the Eucken factor;
ρ	is the density;
p	is the pressure;
D	is the coefficient of diffusion;
$\gamma = c_p/c_v$;	
k	is the Boltzmann's constant;
Z	is the number of collisions of molecules required to establish equilibrium between the energies of the translatory and internal degrees of freedom;
μ_{ij}	is the reduced mass of molecules;
x	is the molar fraction of component of a mixture;
C_{ij}	is the ratio of collision integrals;
W_i	is the molar heat flux of i-th component;
H_i	is the enthalpy per molecule.

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