THE THERMAL CONDUCTIVITY OF BINARY MIXTURES OF POLAR GASES

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A method is proposed for the calculation of the thermal conductivity of binary mixtures of polar gases and of mixtures containing a polar component. It is demonstrated that the thermal conductivity of the mixtures of the polar gases is an almost linear function of the composition.

In calculating the thermal conductivities of polar-gas mixtures, we have to bear in mind the effect resulting from the resonance exchange of rotational energy and from the energy exchange between the various degrees of freedom (inelastic molecular collisions).

The absence of experimental data on the thermal conductivities of polar-gas mixtures makes it difficult to test existing theoretical concepts.

We have found that the thermal conductivity of polar gases is affected by the resonance exchange of rotational energy, the latter associated with the equalization of molecular rotational-energy levels.

In the case of resonance exchange with a quantum of rotational energy, the lateral cross section for the exchange of intrinsic energy becomes extremely large, because of the presence of dipole forces. The lateral cross section for the exchange of intrinsic energy is associated with the coefficient of diffusion and is a function both of the dipole moment and of the molecular moment of inertia.

In calculating the thermal conductivity of a mixture of polar gases, we must know the correction factor for the resonance energy exchange in order to calculate the diffusion coefficient.

Mason and Monchick [6] assume that for a polar gas the diffusion coefficient is equal to

$$D_{ii_{\text{in}}} = D_{ii}/(1+\delta), \tag{1}$$

where δ is the correction factor for the resonance energy exchange.

For the case of linear dipoles

$$\delta = a\left(\frac{3}{16}\,\frac{\mu h}{\sigma_D kT}\right)^2 \frac{m^{1/2}}{(C_{V_{\text{in}}}/R)\,I^{3/2}}. \tag{2}$$

Here $a = 0.44$ is a dimensionless quantity; σ_D is the characteristic diameter defined from the relationship

$$\sigma_D = \sigma\,(\Omega^{(1,1)*})^{1/2}.$$

For dipoles of virtually spherical gyroscopes characterized by three moments of inertia, the correction factor δ is equal to

$$\delta = \frac{5\pi}{16}\,a\left(\frac{3}{16}\,\frac{\mu h}{\sigma_D kT}\right)^2 \times$$

$$\times\,\frac{R}{C_{V_{\text{in}}}}\,\frac{m^{1/2}}{I_A (I_B)^{1/2}}\left(\frac{5}{4} - \frac{I_B}{4I_A}\right)^{-7/2}. \tag{3}$$

Here $I_B = I_C$.

In the case of the molecules of symmetrical gyroscopes $I_A = I_B = I_C$ we can use relationships (2) or (3), which differ by $5\pi/16$.

When $I_A \neq I_B \neq I_C$,

$$\delta = \frac{5\pi}{16}\,a\left(\frac{3}{16}\,\frac{\mu h}{\sigma_D kT}\right)^2 \times$$

$$\times\,\frac{R}{C_{V\,\text{in}}}\,\frac{m^{1/2}}{I_A (I_B^{1/2} I_C^{1/2})^{1/2}}\left(\frac{5}{4} - \frac{I_B^{1/2} I_C^{1/2}}{4I_A}\right)^{-7/2}.$$

The energy of the dipole-dipole interaction between polar molecules of kinds 1 and 2 in the rotational state J_1 and J_2 is given by the relationship

$$E = -\frac{1}{3}\,\frac{\mu_1^2\mu_2^2}{r^6}\,[(2J_1+1)(2J_2+1)]^{-1} \times$$

$$\times\left[\left(\frac{B_1}{J_1+1} + \frac{B_2}{J_2+1}\right)^{-1} + \right.$$

$$+\left(\frac{B_1}{J_2} - \frac{B_2}{J_1+1}\right)^{-1} -$$

$$\left. -\left(\frac{B_1}{J_2+1} - \frac{B_2}{J_1}\right)^{-1} - \left(\frac{B_1}{J_2} - \frac{B_2}{J_1}\right)^{-1}\right], \tag{4}$$

where B_i is the rotational constant which determines the absolute value of the rotational energy of the molecules.

Brokaw and Baker [7] investigated the thermal conductivity of the H_2O—D_2O mixture as a function of the D_2O concentration at a temperature of 478° K (Fig. 1). The experimental data were compared with the theoretical data derived from (6), with a correction factor for the exchange of energies both between molecules of a single kind and between molecules of various kinds; the experimental data were also compared with the theoretical data obtained from formula (5), with consideration given to the resonance exchange between molecules of one kind; in addition, the comparison was carried out with theoretical data derived from the linear relationship $\lambda = x_1\lambda_1 + x_2\lambda_2$.

The following are the formulas with which the thermal conductivity of the mixture was calculated:

The Hirschfelder-Eucken formula [1]

$$\lambda = \lambda^* + \sum_{i=1}^{2} \frac{\lambda_i - \lambda_i^*}{x_i + \sum\limits_{\substack{j=1\\ i\neq j}}^{2} x_j D_{ii}/D_{ij}} \tag{5}$$

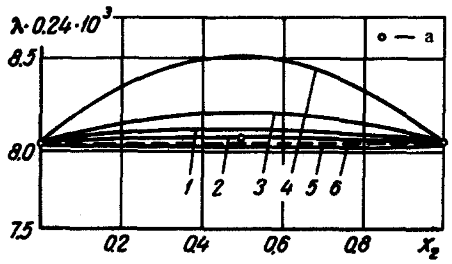

Fig. 1. Thermal conductivity of H_2O—D_2O mixture at a temperature of 478° K [2]. a) Experimental data: 1) data obtained from formula (5), 2) from (6) with account for nonelastic collisions of molecules without correction for resonance energy exchange between molecules of one kind, 3) from (5) with correction for resonance energy exchange between molecules of one kind, 4) the same for formula (6) with account for resonance energy exchange between molecules of different kinds, 6) data obtained from linear relationship

$$\lambda = x_1\lambda_1 + x_2\lambda_2 .$$

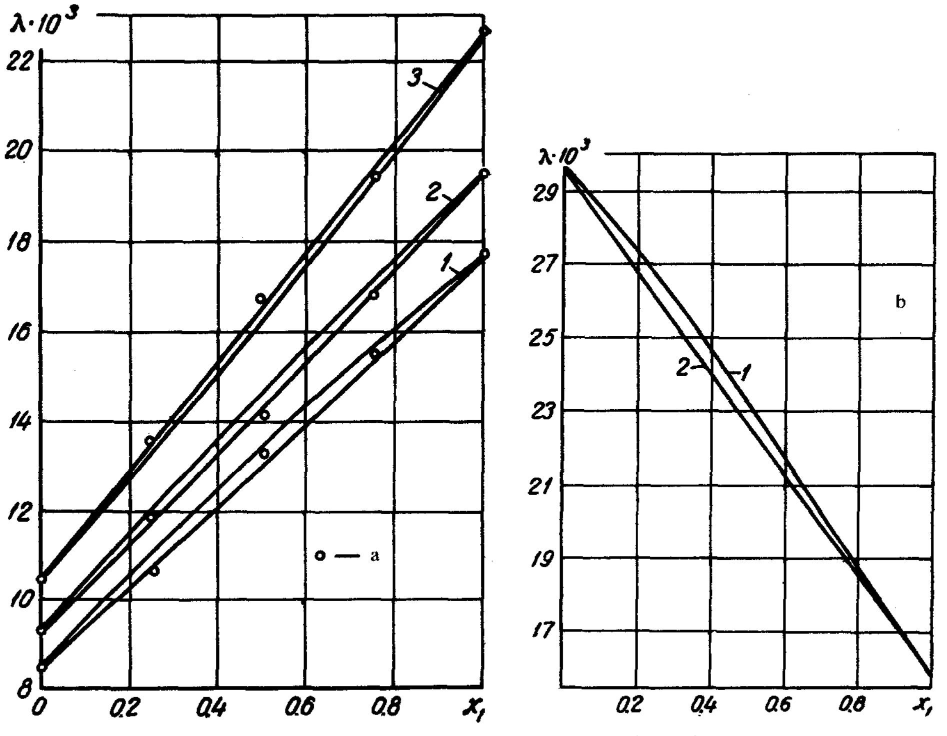

Fig. 2. Comparison of thermal conductivity data for $(C_2H_5)_2O$—$CHCl_3$, calculated from formulas (7) and (8) with data obtained from the linear relationship: a) experimental data 1–3). Data from linear relationship; 1) T = 332.5° K, 2) 347.5, 3) 337.0.

and the formula by means of which we take into consideration the molecular inelastic collisions:

$$\lambda = \lambda^* + \sum_{i=1}^{2} \frac{\lambda_i - \lambda_i^*}{x_i + \sum\limits_{\substack{j=1\\ i\neq j}}^{2} \frac{D_{ii}}{D_{ij}} x_j} +$$

$$+ 4\sum_{i=1}^{2}\Big\{ x_i \sum_{\alpha} \Lambda_{i\alpha} \sum_{\beta} \Lambda_{\alpha\beta}^{10,10} \sum_{\gamma} \Lambda_{\beta\gamma} x_\gamma -$$

$$- 2(x_i/L_{ii}^{01,01}) \sum_{\alpha} L_{i\alpha}^{10,10} \sum_{\beta} \Lambda_{\alpha\beta} x_\beta - \frac{x_i^2}{L_{ii}^{01,01}} \times$$

$$\times \Big[\frac{l_{ii}^{01,01}}{l_{ii}^{10,10}} \frac{\Delta l_{ii}^{10,10}}{l_{ii}^{10,10}} + 2\frac{\Delta l_{ii}^{10,01}}{l_{ii}^{10,10}} +$$

$$+ \frac{\Delta l_{ii}^{01,01}}{l_{ii}^{01,01}} - \frac{\Delta l_{ii}^{01,01}}{L_{ii}^{01,01}} \Big]\Big\}. \tag{6}$$

We calculated the thermal conductivities of various polar-gas mixtures and, where possible, we compared the theoretical and experimental data.

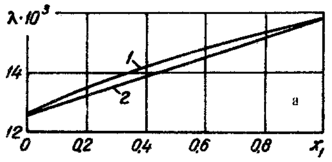

Fig. 3. Thermal conductivity of $(CH_3)_2CO$—HBr mixture (a) and $(CH_3)_2CO$—NH_3 mixture (b) at a temperature of 373.2° K: 1) according to formula (7) and (8), 2) according to the linear relationship.

Because there are no relaxation-time data at hand, the thermal conductivities of the mixtures were calculated from the relationship

$$\lambda = \frac{\lambda_{1\,\mathrm{trans}}}{1 + A_{12}\frac{x_2}{x_1}} + \frac{\lambda_{2\,\mathrm{trans}}}{1 + A_{21}\frac{x_1}{x_2}} +$$

$$+ \frac{\lambda_{1\,\mathrm{in}}}{1 + \frac{D_{11\,\mathrm{in}}}{D_{12}}\,\frac{x_2}{x_1}} + \frac{\lambda_{2\,\mathrm{in}}}{1 + \frac{D_{22\,\mathrm{in}}}{D_{21}}\,\frac{x_1}{x_2}}. \tag{7}$$

The constants A_{ij} in expression (7) were calculated from the relationship

$$A_{ij} = \Big\{0{,}5\Big[1 + \Big(\frac{\delta_{0i}}{\delta_{0ij}}\Big)^{1/3}\Big(\frac{2M_j}{M_i + M_j}\Big)^{1/4} \times$$

$$\times \Big(\frac{\sigma_{ij}}{\sigma_i}\Big)\Big(\frac{\Omega_{ij}^{(2,2)*}(T_{ij}^*)}{\Omega_i^{(2,2)}(T_i^*)}\Big)^{1/2}\Big]\Big\}^2, \tag{8}$$

where δ_{0i}, and σ_i, and ε_i are the power constants of the intermolecular interaction potential (12, 6, 3) [3].

We calculated the thermal conductivities of $(C_2H_5)_2O$—$CHCl_3$ mixtures for various temperatures (the experimental data have been taken from reference [5]); in addition, the calculations were carried out for $(CH_3)_2CO$—HBr and $(CH_3)_2CO$—NH_3 mixtures at a temperature of 373.2° K (there are no experimental data).

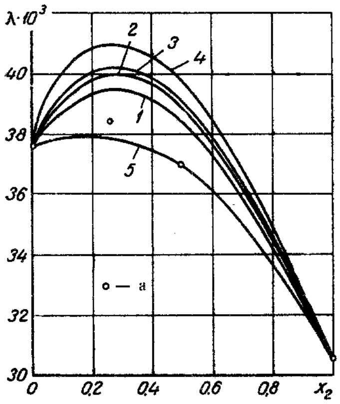

Fig. 4. Thermal conductivity of O_2—H_2O mixture at a temperature of 450° K: a) experimental data [2]; 1) according to formula (5) [2], 2) the same according to (6) [2]; 3 and 4) the same from (5) and (6), respectively, with account for correction for resonance energy exchange [2], 5) according to (9) and (10).

The thermal conductivities of these mixtures as functions of the molar fractions are shown in Figs. 2 and 3.

The thermal conductivities of the $(CH_3)_2CO$—HBr and $(CH_3)_2CO$—NH_3 mixtures were calculated to ascertain the effect of the magnitude of the dipole moments for the molecules of the components of the mixture on the behavior of the relationship between the thermal conductivity of the mixture and the composition of the latter.

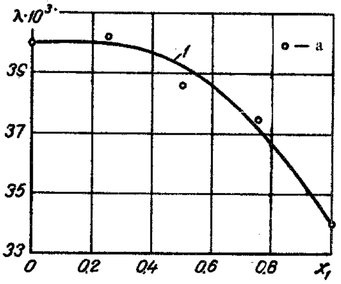

Fig. 5. Thermal conductivity of N_2—NH_3 mixture at a temperature of 425° K: a) experimental data [4]; 1) according to (9) and (10).

As in the above-cited case, in the mixtures in which the molecular dipole moments of the components in the given mixtures were approximately equal, the thermal conductivity of the $(CH_3)_2CO$—HBr and

Basic Parameters of Mixture Components

Mixture	T, °K	$\lambda_i \cdot 10^3$	M_i	μ_i	D_{ii}	ξ_{ii}	δ_{ii}
H_2O	478	33.23	18.0	1.83	0.481	2.3	0.287
D_2O	478	33.4	20.0	1.86	0.456	1.2	0.083
$(CH_3)_2CO$	373	15.8	60.0	2.88	0.074		
HBr	373.2	12.7	81.0	0.8	0.129	3.0	0.095
$(C_2H_5)_2O$	377.2	22.6	74.12	1.14	0.065		
$CHCl_3$	377	10.4	119.4	1.15	0.132		
O_2	450	37.5	32.0	0	0.424	4.0	0
O_2	700	53.7	32.0	0	0.892	7.5	0
H_2O	450	30.6	18.0	1.85	0.409	4.0	0.7
N_2	348	29.3	28.0	0	0.277	4.0	0
NH_3	348	29.5	17.0	1.47	0.244	2.0	0.118

$(CH_3)_2CO—NH_3$ mixtures whose molecules exhibit various dipole moments is close to the linear relationship $\lambda = x_1\lambda_1 + x_2\lambda_2$. This is apparently associated with the fact that the dipole-dipole interaction of the molecules counteracts the thermal motion of the latter (orientational effect).

With increasing temperature, the thermal conductivity of the polar-gas mixtures will deviate from a linear relationship, since the dipole-dipole molecular interaction is weakened with the rise in temperature.

Of particular interest is the interaction of polar and nonpolar molecules. Bennet and Vines [5] undertook an experimental investigation of the thermal conductivity of mixtures containing a polar component. They noticed that if the mixture contains a small amount of a polar gas, such an addition will significantly affect its nonpolar nature. The thermal conductivity of such mixtures is markedly diminished with an increase in the concentration of the polar gas.

We calculated the thermal conductivity of mixtures containing a polar component and we compared our results with those of other authors and with experimental data.

The calculation was carried out with the following formula:

$$\lambda = \frac{\lambda_{1\,\mathrm{trans}}}{1 + A_{12}\dfrac{x_2}{x_1}} + \frac{\lambda_{2\,\mathrm{trans}}}{1 + A_{21}\dfrac{x_1}{x_2}} + \frac{\lambda_{1\,\mathrm{in}}}{1 + \dfrac{D_{11}}{D_{12}}\,\dfrac{x_2}{x_1}} + \frac{\lambda_{2\,\mathrm{in}}}{1 + \dfrac{D_{22\,\mathrm{in}}}{D_{21}}\,\dfrac{x_1}{x_2}}, \tag{9}$$

where $D_{22\,\mathrm{in}}$ pertains to the diffusion coefficient of the polar component.

The constants A_{ij} were determined from the relationship

$$A_{ij} = \left\{0.5\left[1 + \left(\frac{2M_j}{M_i + M_j}\right)^{1/4} \times \left(\frac{\sigma_{ij}}{\sigma_i}\right)\left(\frac{\Omega_{ij}^{(2.2)*}\,(T_{ij}^*)}{\Omega_i^{(2.2)*}\,(T_i^*)}\right)^{1/2}\right]\right\}^2. \tag{10}$$

Figure 4 shows a comparison of the theoretical and experimental data for the thermal conductivity of an $O_2—H_2O$ mixture at a temperature of 450° K, calculated according to formulas (5), (6), (9), and (10).

We then compared the experimental and theoretical thermal-conductivity values (Fig. 5) for an $N_2—NH_3$ mixture at a temperature of 425° K. The experimental data have been taken from reference [4]. The experimental and theoretical data are in good agreement.

The properties of the components in the mixtures are given in the table.

In conclusion, it should be noted that to calculate the thermal conductivities of polar-gas mixtures and of mixtures containing a polar component, we can use approximate theoretical relationships which yield results that are in better agreement with experimental data than in the case of strictly theoretical relationships.

In addition, the strictly theoretical relationships are cumber some and require the knowledge of many parameters which cannot always be determined.

NOTATION

μ_i is the dipole moment of the molecule of the i-th component, D; h is the Planck constant, erg · sec; k is the Boltzmann constant, erg/°K; m is the mass of the molecule, g; $C_{V\mathrm{in}}$ is the thermal conductivity due to the inner degree of freedom, cal/mol · deg; R is the universal gas constant, cal/mol · deg; I is the molecular moment of inertia, g · cm^2; λ_i is the thermal conductivity of the i-th component, W/m · deg; λ_i trans is the thermal conductivity of the i-th component due to the translational degree of freedom, W/m · deg; $\lambda_{i\mathrm{in}}$ is the thermal conductivity of the i-th component due to the inner degree of freedom, W/m · · deg; M_i is the molecular weight, g/mol; D_{ii} is the self-diffusivity cm^2/sec; D_{ij} is the interdiffusion coefficient, cm^2/sec; ξ is the number of collisions required for stabilization of equilibrium between the translational and intrinsic energy of the molecule; x_i is the molar fraction of the i-th component; $T^* = T/(\varepsilon/k)$ is the reduced temperature; $\Omega(l, s)^*(T^*)$ is the collision integral.

REFERENCES

1. G. Hirschfelder, et al., The Molecular Theory of Gases and Liquids [Russian translation], IL, 1961.
2. L. Monchick, A. N. G. Pereira, and E. A. Mason, Journ. Chem. Phys., 42, no. 9, 1963.

3. L. Monchick and E. A. Mason, Journ. Chem. Phys., 35, no. 5, 1961.
4. H. Geier and K. Schafer, Allgemeine Wärmetechnik, 10, no. 4, 1961.
5. L. A. Bennet and R. G. Vines, Journ. Chem. Phys., 23, no. 9, 1955.
6. E. A. Mason and L. Monchick, Journ. Chem. Phys., 36, no. 6, 1962.
7. C. E. Baker and R. S. Brokaw, Journ. Chem. Phys., 43, no. 10, 1965.

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