ANOMALOUS BEHAVIOR OF THERMAL CONDUCTIVITY OF A MIXTURE OF STRONGLY POLAR AND MONATOMIC GASES IN A CONSTANT ELECTRIC FIELD

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The results of an experimental study of the thermal conductivity of a gas mixture of acetonirile (CH_3CN) and argon in an electric field (E) are presented. The concentration dependences obtained for the thermal conductivity are compared with the theory in which it is assumed that the probabilities of direct and reverse transitions are not equal to one another for molecule—molecule collisions and are equal for molecule—atom collisions.

It is known [1-7] that the transfer coefficients of molecular gases decrease in magnetic (H) and electric (E) fields and depend on the angle between the direction of the field and the gradient of the appropriate macroscopic value, i.e., they are tensors (the Senftleben effect). The effect is connected with the fact that the magnetic (or electric) field causes the reorientation of the rotational moment of the molecules during free travel because of the precession of the molecule in the field. This leads to an increase in the nonspherical-scattering cross section of the molecules in the field averaged over all orientations and consequently to a decrease in the transfer coefficients. The magnitude of the relative change, in the coefficient of thermal conductivity ε ($\varepsilon = \Delta\varkappa/\varkappa_0$), for example, in an electric field is determined by the ratio of the precession frequency ($\Omega \sim dE$) to the collision frequency of the molecules ($\nu \sim p$), i.e., the magnitude of ε is a function of the ratio E/p. The dependence $\varepsilon(E/p)$ is a monotonic function and with an increase in the ratio E/p the value ε approaches the limiting value ε_{sat}.

The anomalous change in the coefficient of thermal conductivity of a number of strongly polar gases in electric and magnetic fields was discovered and studied in [7-10]. It was established that in such gases ε reaches a maximum (ε_{max}) at certain values $(E/p)_{max}$ and changes sign at a certain value of the ratio E/p. The available experimental data [7-10] do not contradict the theory [9, 11, 12] in which collisions of molecules with unequal probabilities of direct (w) and reverse (w') transitions were taken into account. The role of such collisions in transfer phenomena has hardly been studied. Therefore it is of interest to continue the studies of this effect. In particular, in a mixture of strongly polar and nonpolar gases the number of collisions with different probabilities of direct and reverse transitions, and consequently the nature of the effect of the field on the thermal conductivity of the mixture, should depend on the concentration of the polar gas.

TABLE 1

x_2	$\varepsilon_{max}\cdot 10^5$	$(E/p)_{max}$, V/cm · torr	$(E/p)_0$, V/cm · torr	$\psi_+\cdot 10^5$	$\psi_-\cdot 10^5$	$\mathring{\xi}_-/\mathring{\xi}_+$
0	2,0	180	350	2,94	6,05	20,0
0,2	1,0	80	170	1,92	11,9	20,8
0,5	0,16	10	20	1,54	30,3	22,9
0,8	—	—	—	0,50	38,0	23,8
0,9	—	—	—	0,39	19,1	24,0

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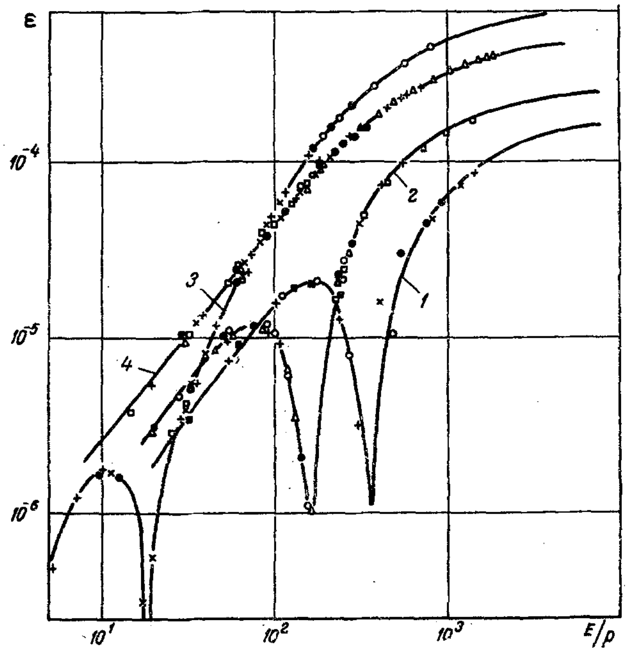

Fig. 1. Dependence of the value ε of a mixture of CH_3CN and Ar on the ratio E/p (V/cm·torr). The dependences 1-4 correspond to argon concentrations $x_2 = 0$, 0.2, 0.5, and 0.9. The solid curves are theoretical functions constructed in accordance with (5); the experimental points in the figure correspond to pressures p = (0.15-2) torr.

In a study published earlier [13] de Groot et al. studied the thermal conductivity of a mixture of CH_3CN and N_2 in the electric field of a cylindrical capacitor. With the experimental geometry used ($\Delta T \parallel E$) the authors were measuring the value $\varepsilon_{\parallel}$. In the present report we present the results of a study of the thermal conductivity of a mixture of strongly polar (CH_3CN) and monatomic (Ar) gases in the constant electric field of a flat capacitor. The gas mixture of CH_3CN and Ar which we selected is a more suitable subject than the mixture of CH_3CN and N_2 for the study of the given effect since the nonspherical nature of the interaction of the different molecules of the mixture is determined entirely by the nonsphericity of the molecules of the polar gas. In contrast to [13], in our experimental geometry the value measured was a combination of the components of the thermal conductivity tensor $[\varepsilon = 1/5\,(3e_{\parallel} + 2\varepsilon_{\perp})]$.

The theory developed in [2, 3, 9, 14] has a semiphenomenological nature. In the examination of effects in external fields the form of the nonspherical-interaction potentials is not made specific, and in the final expressions for the changes in the coefficients of thermal conductivity or viscosity generalized collision-integrals are involved whose values can be found from comparison with experimental data. The nonsphericity of the interaction [i.e., the dependence of the cross section on the direction of the vectors of velocity (**V**) and rotational moment (**M**) of the molecule] results in the dependence of the distribution function in the presence of a temperature gradient on the direction of the vectors **V** and **M**, and therefore the nonequilibrium distribution function can be found in the form of an expansion with respect to the irreducible tensors constructed from the components of the vectors **V** and **M**. A model description in the framework of such a theory consists in the choice of nonzero terms of the expansion which permit the description of the observed change in the coefficient of thermal conductivity in the field. The generalized collision integrals which emerge are frequencies of the relaxation of fluxes of the corresponding tensor values, such as $\langle \mathbf{V}[\mathbf{M}]^2 \rangle$ ($[\;]^2$ is an irreducible tensor of second rank).

According to [9, 14], the presence of collisions with unequal probabilities of the direct and reverse transitions can be taken into account if the perturbation operators $\hat{I}^{(1)}_{ij}$ $[\delta \hat{I}^{(1)}_{ij} = \hat{I}_{ij} - \hat{I}^{(0)}_{ij}$, $\delta \ll 1$, $\hat{I}^{(0)}_{ij}$ is a collision operator which is diagonal in the space of the functions $\psi_n = \Sigma C^{lm}_{l_1 m_1 l_2 m_2} Y_{l_1 m_1}(\mathbf{V}) \times Y_{l_2 m_2}(\mathbf{M})\, \varphi(V^2, M^2)$ where Y_{lm} are spherical tensors describing the nonspherical scatterings of a molecule on a

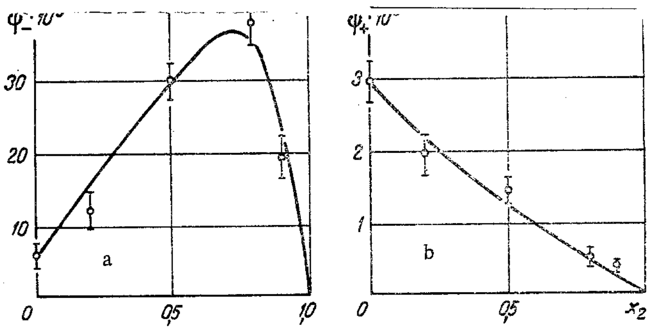

Fig. 2. Dependence of ψ_- (a) and ψ_+ (b) on argon concentration x_2.

molecule and a molecule on an atom] in the kinetic equation is represented in the form

$$\hat{I}_{ij}^{(1)} = \hat{I}_{ij}^{s} + \hat{I}_{ij}^{a}. \tag{1}$$

Here I_{ij}^{s} and I_{ij}^{a} are operators describing collisions for which the scattering probabilities are symmetrical and antisymmetrical relative to interchanging of the sites of the variables **V**, **M**, and σ of the colliding molecules before and after the collision. We note that the partition of (1) corresponds to even and odd terms with respect to M in the expansion of the nonequilibrium-distribution function. The operator $\hat{I}_{ij}^{a}$ is different from zero if the probabilities of the direct and reverse collisions do not differ from one another.

The property of symmetry of the operator $\hat{I}_{ij}^{(1)}$ relative to time reversal and inversion of the coordinates and its scalar nature impose certain restrictions ("selection rules") on the rank of the irreducible tensors, constructed from the components of the vectors **V** and **M**, from which the nonequilibrium-distribution function is decomposed. In the simplest model of the nonspherical scattering of a molecule on a molecule and of a molecule on an atom which permits a description of the anomalous behavior of the coefficient of thermal conductivity of the mixture in a field the matrix elements differ from zero for the operator $\hat{I}_{ij}^{s}$ for transitions from a spherically-symmetrical state in **M** space (the state n_0) to states described by the functions $\chi_{n_1} \sim \Sigma C_{1m_1 2m_2}^{1m} Y_{1m_1}(\mathbf{V})\, Y_{2m_2}(\mathbf{M})$, and for the operator $\hat{I}_{ij}^{a}$ for transitions to states of $\chi_{n_2} \sim \Sigma C_{1m_1 1m_2}^{1m} Y_{1m_1}(\mathbf{V})\, Y_{1m_2}(\mathbf{M})$. We note that the spherical tensors correspond in the Cartesian coordinate system to irreducible tensors constructed from components of the vectors **V** and **M**.

Using the results of [9, 14], one can obtain the following expressions for $\varepsilon_\perp$ and $\varepsilon_\parallel$:

$$\begin{gathered}\varepsilon_\perp = \psi_+ f(\xi_+) - \psi_- [f(\xi_-) + 2f(2\xi_-)],\\ \varepsilon_\parallel = 2[\psi_+ f(\xi_+) - \psi_- f(\xi_-)],\end{gathered} \tag{2}$$

$$\psi_+ = \frac{1}{2}\varphi_+, \quad \psi_- = \frac{3}{10}\varphi_-, \tag{3}$$

where

$$\varphi_+ = \delta^2 \frac{2k^2T}{3m_1\varkappa_0} \sum_{n_0} n^{-2} b_{n_0} (x_1\lambda_{n_0}^{11} + x_2\lambda_{n_0}^{12})^{-1} (x_1\lambda_{n_2}^{11} + x_2\lambda_{n_2}^{12})^{-1} (I^a)_{n_0n_2}^2 \langle A_{11}, \psi_{n_0} \rangle,$$

$$\varphi_- = \delta^2 \frac{2k^2T}{3m_1\varkappa_0} \sum_{n_0} n^{-2} b_{n_0} (x_1\lambda_{n_0}^{11} + x_2\lambda_{n_0}^{12})^{-1} (x_1\lambda_{n_1}^{11} + x_2\lambda_{n_1}^{12})^{-1} (I^c)_{n_0n_1}^2 \langle A_{11}, \psi_{n_0} \rangle.$$

The dependence of $\varepsilon_\parallel$ and $\varepsilon_\perp$ on the ratio E/p in (2) is determined by the function

$$\begin{gathered}f(\xi) = \frac{\xi^2}{1+\xi^2}, \quad \xi_+ = \frac{d\sqrt{kT}}{(x_1\lambda_{n_2}^{11} + x_2\lambda_{n_2}^{12})\sqrt{2I_A}} \cdot \frac{E}{p},\\ \xi_- = \frac{d\sqrt{kT}}{(x_1\lambda_{n_1}^{11} + x_2\lambda_{n_1}^{12})\sqrt{2I_A}} \cdot \frac{E}{p},\end{gathered} \tag{4}$$

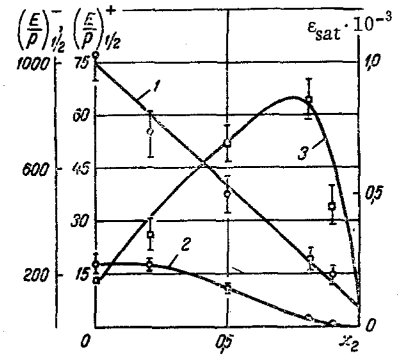

Fig. 3. Dependence of $(E/p)^+_{1/2}$ (curve 1), $(E/p)^-_{1/2}$ (curve 2), and ε_{sat} (curve 3) on the concentration x_2.

where x_i is the concentration of component i in the mixture. The remaining notation in Eqs. (2)-(4) coincides with that introduced in [14].

In accordance with (2)-(4) the equation for the value $\varepsilon = 1/5\,(3\varepsilon_{\parallel} + 2\varepsilon_{\perp})$ in the field of a flat capacitor measured in the present work has the form

$$\varepsilon = \varepsilon_+ + \varepsilon_-,$$

$$\varepsilon_+ = \frac{8}{5}\psi_+ f(\xi_+), \quad \varepsilon_- = -\frac{4}{5}\psi_-\,[2f(\xi_-) + f(2\xi_-)].$$

For an analysis of the theoretical equations obtained and their comparison with experiment it is convenient to introduce the value $\xi_{1/2}$ (the values of ξ at which $\varepsilon = 1/2\,\psi$) and the corresponding value $(E/p)_{1/2}$. Keeping in mind the expressions for ξ_+ and ξ_-, one can show that

$$(E/p)^+_{1/2} = (E/p)'^+_{1/2}\,(x_1 + x_2\gamma^+), \tag{6}$$

$$(E/p)^-_{1/2} = (E/p)'^-_{1/2}\,(x_1 + x_2\gamma^-), \tag{7}$$

where

$$\gamma^+ = \lambda^{12}_{n_2}/\lambda^{11}_{n_2}, \quad \gamma^- = \lambda^{12}_{n_1}/\lambda^{11}_{n_1},$$

$$(E/p)'^+_{1/2} = \frac{\lambda^{11}_{n_2}}{d}\sqrt{\frac{2I_A}{kT}}, \quad (E/p)'^-_{1/2} = \frac{\lambda^{11}_{n_1}}{d}\sqrt{\frac{2I_A}{kT}}. \tag{8}$$

It is seen from (6) and (7) that within the framework of this model of the nonspherical scattering of molecules the values $(E/p)^{\pm}_{1/2}$ must be linear functions of the concentration x_2 of the monatomic gas.

The measurements were conducted on an instrument similar to that described in [7]. The gas pressure was varied in the range of (0.1-2) mm Hg and the electric-field strength in the flat capacitor was E = (0-200) V/cm. The absolute values of ε were obtained through calibration measurements analogous to those conducted in [15], with allowance for the dependence of ε on p. The error in the determination of ε did not exceed 10%. The thermal conductivity of mixtures of CH_3CN and Ar with argon concentrations $x_2 = 0$, 0.2, 0.5, 0.8, and 0.9 was studied in the experiments.

Dependences $\varepsilon = \varphi(E/p)$ obtained at different pressures are presented in Fig. 1. It is seen from the figure that ε depends on the ratio E/p within the limits of the measurement error, with the dependence $\varepsilon = \varphi(E/p)$ having an anomalous nature for the mixtures with argon concentrations $x_2 = 0.2$ and 0.5. The dependence of ε on E/p becomes monotonic with an increase in the Ar concentration ($x_2 = 0.9$). The dependence of ε on E/p for pure CH_3CN ($x_2 = 0$) is shown in the same figure. With an increase in the concentration of the monatomic gas the values $(E/p)_{max}$ and $(E/p)_0$ [the values of E/p at which ε reaches the highest value (ε_{max}) and changes sign ($\varepsilon = 0$)] shift toward smaller E/p and the value of ε decreases. The values of ε_{max} and of $(E/p)_{max}$ and $(E/p)_0$ for the different concentrations are presented in Table 1. The values of ψ_+, ψ_-, and ξ_-/ξ_+ which are obtained from comparison of the experimental data with the theoretical functions constructed in accordance with (5) (the solid curves in Fig. 1) are also presented in the table.

In accordance with (5) the positive (ε_+) and negative (ε_-) parts of the variation of the coefficient of thermal conductivity are characterized by the values ψ_+ and ψ_-.

The dependence $\psi_- = f(x_2)$ is presented in Fig. 2a. It is seen from the figure that ψ_- increases with an increase in x_2, reaching the maximum value at $x_2 = 0.8$ and approaching zero with a further increase in x_2. In accordance with (3) the value ψ_- is determined by the matrix elements of the operator $\hat{I}^S$:

$$\psi_- \sim (1 - x_2)\,(I^S)^2_{n_0 n_1}, \quad (I^S)_{n_0 n_1} = (1 - x_2)\,(I^S_{11})_{n_0 n_1} + x_2\,(I^S_{12})_{n_0 n_1}. \tag{9}$$

The matrix elements $(I^S_{11})_{n_0 n_1}$ and $(I^S_{12})_{n_0 n_1}$ are proportional to the cross sections of the nonspherical interaction of a molecule with a molecule and with an atom. If the concentration of the monatomic gas is equal to unity then obviously $\varepsilon_- = 0$ (the interaction of atoms is spherically symmetrical). The maximum in the dependence of ψ_- on x_2 can be explained if the nonspherical cross section of molecule—atom scattering is greater than the nonspherical molecule—molecule cross section. Actually, with an increase in the concentration of the monatomic gas the number of atom—molecule collisions increases, which leads to an increase in ε_- (ψ_-). However, at small enough concentrations $(1-x_2)$ of the polar gas the number of precessing molecules decreases and therefore ε_- drops. Thus, from the concentration dependence of ψ_- it follows that the matrix elements $(I^S_{12})_{n_0 n_1} > (I^S_{11})_{n_0 n_1}$.

The concentration dependence of ψ_+ on x_2 is monotonic in contrast to the dependence $\psi_- = f(x_2)$ (see Fig. 2b). This result can be explained if one assumes that the matrix elements of the operator $\hat{I}^a_{12}$ describing the nonspherical scattering of a molecule on an atom with $w \neq w'$ are considerably smaller than the matrix elements of the operator $\hat{I}^a_{11}$. Actually, according to (3)

$$\psi_+ \sim (1-x_2)(I^a)^2_{n_0 n_2}, \quad (I^a)_{n_0 n_2} = (1-x_2)(I^a_{11})_{n_0 n_2} + x_2 (I^a_{12})_{n_0 n_2}. \tag{10}$$

From Eqs. (3) and (10) it follows that if $(I^a_{12})_{n_0 n_2} = 0$, the dependence of ψ_+ on the concentration of the monatomic gas will be monotonic.

Such behavior of ψ_+ and ψ_- accounts for the nature of the dependence of ε_{sat} on x_2 (See Fig. 3), since in accordance with (5)

$$\varepsilon_{\text{sat}} = \frac{8}{5}\psi_+ - 3\psi_-. \tag{11}$$

Thus, it follows from the experiments conducted that for the given mixture the probability of the interaction of a molecule with an atom satisfies the principle of detailed equilibrium in the simplest form

$$w_{12} = w'_{12},$$

since the equalities $w^a_{12} = 0$ and $\hat{I}^a_{12} = 0$ occur.

The dependences of the values $(E/p)^{\pm}_{1/2}$ on the argon concentration are presented in Fig. 3. Within the limits of the error the value $(E/p)^-_{1/2}$ is described by a linear dependence relative to x_2. According to (7) the ratio of the values of $(E/p)^-_{1/2}$ for $x_2 = 0$ and 1 is equal to the ratio $\lambda^{11}/\lambda^{12}$. The values λ^{11} and λ^{12} are relaxation frequencies of the polarization tensor flux of the rotational moment of the molecule $\langle \mathbf{V} [\mathbf{M}]^2 \rangle$, produced by molecule—molecule and molecule—atom collisions, respectively. Using the data presented in Fig. 3 we obtain $\lambda^{11}/\lambda^{12} = 12$. This means that the corresponding scattering cross sections for the collision of a molecule on a molecule are an order of magnitude higher than for the collision of a molecule with an atom.

The dependence of $(E/p)^+_{1/2}$ on x_2 differs somewhat from the linear dependence (6). This fact is apparently connected with the imperfect model used to describe the nonspherical collisions of molecules with unequal probabilities of direct and reverse transitions in the given gas mixture. For example, one can show that if in the expansion of the nonequilibrium-distribution function of a polar gas in addition to the terms $\chi_{n_2} \sim \Sigma C^{1m}_{1m_1 1m_2} Y_{1m_1}(\mathbf{V}) Y_{1m_2}(\mathbf{M})$ and $\chi_{n_1} \sim \Sigma C^{1m}_{1m_1 2m_2} Y_{1m_2}(\mathbf{V}) Y_{2m_2}(\mathbf{M})$ one takes into account at least $\chi \sim \Sigma C^{1m}_{3m_1 3m_2} Y_{3m_1}(\mathbf{V}) Y_{3m_2}(\mathbf{M})$ (such a dependence of the distribution function on the velocity and angular moment of the molecule is allowed by the "selection rules" for the operator $\hat{I}^a_{11}$), then in this case the dependence of $(E/p)^+_{1/2}$ on x_2 becomes nonlinear:

$$(E/p)^+_{1/2} = (E/p)'^+_{1/2} f(x_2)(x_1 + x_2\gamma^+). \tag{12}$$

It should be noted, however, that the use of a theory taking χ into account for the description of the results of the experiment is difficult because of the increase in the number of unknown parameters.

The viscosity of a mixture of CH_3CN and Ar in a constant electric field was studied in [16]. It was found that the viscosity coefficient (η) decreases in an electric field ($\Delta\eta/\eta < 0$) and the value $\Delta\eta/\eta$ is a monotonic function of the ratio E/p at any Ar concentration. Such a difference in the behavior of the coefficients of viscosity and thermal conductivity of a mixture of CH_3CN and Ar is apparently connected with the fact that terms even with respect to **M** make the main contribution in the expansion of the nonequilibrium-distribution function in the description of momentum transfer.

NOTATION

$\varepsilon = \Delta\varkappa/\varkappa_0$: relative change in coefficient of thermal conductivity; $\varkappa_0$: coefficient of thermal conductivity in the absence of an electric field ε_{sat}: values of ε as $E/p \to \infty$; $\varepsilon_{\max}$: value of ε at $(E/p)_{\max}$; ∇T: temperature gradient; $\varepsilon_{\parallel}$: value of ε when $\nabla T \parallel \mathbf{E}$; $\varepsilon_{\perp}$: value of ε when $\nabla T \perp \mathbf{E}$; Ω: precession frequency of molecules; ν: collision frequency of molecules; d: dipole moment of molecule; p: gas pressure; **V**:

velocity of molecule; **M**: rotational moment of molecule; **M**: molecule torque; x_i: concentration of i-th component of mixture; $\hat{I}_{ij}$: operator for collision of i-th and j-th molecules; C::: Clebsch-Gordan coefficient; ψ_+, ψ_-, (> 0): limiting values of ε as $E/p \to \infty$; λ^{ij}: relaxation frequency of polarization tensor flux and of rotational moment of molecule; w: scattering probability for molecules; $(E/p)_{max}$: value of E/p for which $\varepsilon = \varepsilon_{max}$; $(E/p)_0$: value of E/p for which $\varepsilon = 0$; $Y_{lm}(x)$: spherical tensor; $\Delta\eta/\eta$: relative change in viscosity coefficient.

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