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INVESTIGATION OF THE THERMAL CONDUCTIVITY OF POLAR GASES IN AN ELECTRIC FIELD

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Results of an experimental investigation of the thermal conductivity of the polar gases ChCl$_3$, C$_2$H$_5$Cl, C$_6$H$_5$Cl, C$_6$H$_5$Br, C$_5$H$_5$N, C$_5$H$_{10}$Br$_2$, C$_6$H$_{11}$Cl, and CH$_3$CN in an electric field are presented. It is shown that in all the gases investigated the variation of the thermal conductivity coefficient $\epsilon = \Delta\mathcal{K}/\mathcal{K}$ depends on the field strength E and pressure p via the ratio E/p. The experimental data are compared with the theory and on this basis the parameters characterizing nonspherical scattering of molecules are evaluated. In the gas CH$_3$CN the value ϵ changes sign for E/p = 350 v/cm-mm Hg and with growth of E/p it approaches the value $\epsilon_{\text{sat}} = -4.7 \times 10^{-3}$. The experimental data for CH$_3$CN are compared with those predicted by the theory in which collisions in the gas which do not obey the principle of detailed balance are taken into account.

In 1965, Senftleben,[1] and somewhat later and independently Gorelik and Sinitsyn,[2] observed that the thermal conductivity of certain polar gases, such as CHCl$_3$, C$_2$H$_5$Cl, and NF$_3$ decreases in an electric field (the "electric" Senftleben effect). Subsequently, Gallinaro, Meneghetti, and Scoles[3] obtained a similar result for viscosity. Experimental investigations of the observed effect were continued in [4,5]. In [1-5] it was shown, as a result of the investigations, that at a given temperature this effect is a unique function of the ratio of the electric field E to the gas pressure p and when the ratio E/p increases the relative change of the thermal conductivity coefficient $\epsilon = \Delta\mathcal{K}/\mathcal{K}$ tends to a limiting value ϵ_{sat}. The aforementioned effect is analogous to the previously known effect of the decrease of the coefficients of gas transport in a magnetic field (the "magnetic" Senftleben effect[1)], see, for example, [6-10]). However, Senftleben,[11] and later de Groot et al.,[4] established that, unlike other gases CH$_3$CN, C$_2$H$_5$CN, and C$_6$H$_5$CN increase their thermal conductivity in an electric field.

The theory of the effect for polar gases with molecules of the symmetric-top type is given in [10-12]. Mikhaĭlova and Maksimov[11] solved the kinetic equation for a gas with rotational degrees of freedom by a perturbation-theory method, in which the small parameter was the degree of deviation of the total collision operator from the "ideal" operator describing collisions with a spherically symmetrical potential.[10] The relative changes of the thermal conductivity coefficient in a field, in directions parallel ($\epsilon_{\parallel}$) and perpendicular ($\epsilon_{\perp}$) to the temperature gradient, are described in accordance with [11] for a polar gas with molecules of the symmetric-top type, by the expressions

$$\varepsilon_{\parallel} = -{}^{3}/_{10}\psi f_1(\xi), \qquad \varepsilon_{\perp} = -\psi[{}^{3}/_{20}f_1(\xi) + {}^{3}/_{10}f_2(\xi)]; \tag{1}$$

$$f_1(\xi) = \frac{1}{\sqrt{\pi}}\int_0^\infty dM \int_0^1 \frac{4\xi^2\sigma^2M^4\sqrt{I_A/I_C}}{1+\sigma^2\xi^2/M^2}\exp\left\{-M^2\left[1+\sigma^2\left(\frac{I_A}{I_C}-1\right)\right]\right\}d\sigma,$$

$$f_2(\xi) = f_1(2\xi), \qquad \xi = \frac{d\sqrt{kT}}{\sqrt{I_A}\,\beta_{10}}\frac{E}{p}.$$

Here $I_A = I_B \neq I_C$ are the moments of inertia of the molecules about the principal axes A, B, and C, d is the dipole moment, M is the angular momentum, and $\sigma = \cos(\widehat{dM})$. The dependence of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ on the field and on the pressure is determined by the parameter ξ, which represents the ratio of the average precession frequency $\omega = Ed/\sqrt{kTI_A}$ of the polar molecules to the relaxation frequency $n\beta_{10}$ (n—density, β_{10}—eigenvalue of the "ideal" collision operator). The limiting values to which $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ tend with increasing ξ are determined by the quantity ψ, which is proportional to the square of the matrix element of the perturbed collision operator $\hat{I}^{(1)}_{nn'}$, which describes the nonspherical scattering of the molecules.

For polar gases with molecules of the symmetric-top type and nearly equal moments of inertia ($I_A = I_B \approx I_C$), we obtained the values of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ by solving the kinetic equation by a variational method, in analogy with the procedure used by Kaganov and Maksimov[9] for a paramagnetic gas with linear molecules in a magnetic field:

$$\varepsilon_{\perp} = \psi c_1, \qquad \varepsilon_{\parallel} = \psi(c_1 + c_2); \tag{2}$$

$$c_1 = -3 + \xi^{-1}(\operatorname{arctg}\xi + \operatorname{arctg}2\xi),$$

$$c_2 = 1 + \xi^{-1}(\operatorname{arctg}\xi - \operatorname{arctg}2\xi),$$

$$\xi = \frac{3}{8}\frac{d\sqrt{kT}}{\sqrt{2I_A}\,\Omega^{(11)}}\frac{E}{p}$$

($\Omega^{(11)}$ is the standard integral of the kinetic theory of gases[13]). Bearing in mind the comparison of the theoretical and experimental curves for the quantity ϵ

[1)] In some recent papers this effect is also called the Senftleben-Beenakker effect. For a number of reasons, we assume this designation unjustified. In particular, we note that the presence of the Senftleben effect in N$_2$, first described in 1962 in a note by Beenakker et al. [7], corresponds to the conclusion that the Senftleben effect in paramagnetic gases can be extended to other gases, a conclusion that can definitely be made on the basis of the theory of Kagan and Maksimov of 1961, which unfortunately is not mentioned in the paper of Beenakker et al. The use of the aforementioned double name for the effect in the case of electric fields is certainly not justified.

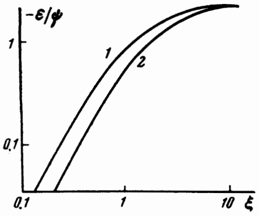

FIG. 1. Plots of $\epsilon(\xi)$ calculated: 1 – from formulas (1) in the case $I_A = I_B = I_C$; 2 – from formulas (2).

$= (\epsilon_{\parallel} + \epsilon_{\perp})/2 = \varphi(E/p)$ measured in the experiments described below, it is of interest to compare relations (1) and (2). Figure 1 shows plots of $\epsilon/\psi = f(\xi)$, constructed on the basis of formulas (1) and (2). The course of the calculated curves coincides with good accuracy, but they are shifted relative to each other along the abscissa axis, this being due to the different definitions of the quantities $\Omega^{(11)}$ and β_{10}. It follows therefore that different methods of solving the kinetic equation—the method of perturbation theory and the variational method, which does not require a small parameter, give for the given effect identical relations. A comparison of the experimental curves with the theoretical ones based on formulas (1) and (2) makes it possible to obtain the values of β_{10} and $\Omega^{(11)}$, and also the parameters characterizing the nonspherical scattering of molecules.

We present below the results of our experimental investigations of the thermal conductivity of a number of polar gases in a constant electric field. We used for the investigations an experimental procedure analogous to that employed in [2,5,8]. The pickup was made of two communicating glass chambers (inside diameter 38 mm) placed in a thermally insulating jacket. Platinum filaments of 50 μ diameter were stretched along the chamber axis. They served as the arms of a measuring bridge. The bridge detector was a photooptical microvoltmeter type F116/1; its maximum sensitivity was 0.02 μV/division. We used in the measurements the homogeneous electric field of a parallel-plate capacitor whose plates were located inside[2)] one of the chambers, parallel to the filament. The voltages applied to the plates were of equal magnitude and opposite polarity relative to the filament potential. The measured quantity in such a geometry is

$$\varepsilon = (\varepsilon_{\parallel} + \varepsilon_{\perp}) / 2.$$

The experiments were performed at room temperature in the pressure range 0.13–2 mm Hg and in fields up to 1 kV/cm; the temperature of the platinum filaments was maintained equal to 130° C. The value of ϵ can be judged from the change of the unbalance Δu of the bridge, occurring when the field is turned on. The measurements were performed using the "procedure of three readings": three readings were made at equal time intervals ($\sim$10 sec)—before turning on, before turning off, and after turning off the field, after which the change of bridge unbalance was determined from the difference between the second reading and the average of the first and third readings. This eliminated the systematic errors connected with thermal null drift of the measuring circuit (uniform null drift). The random errors connected with the non-uniform null drift were eliminated by averaging the results of a series of groups of three readings. The threshold sensitivity attained in the measurements of the changes of the bridge unbalance due to the change of the thermal conductivity was $\sim$0.05 μV. It is easy to show that in our experiments, when the filament voltage was $\sim$1 V, such a change in voltage corresponds to a change of $\sim 2 \times 10^{-5}$ deg in the filament temperature.

By using the heat-balance equation, we obtain the following formula for ϵ:

$$\varepsilon = f(i) \frac{\Delta T}{\Delta T - S} \frac{\Delta u}{u}, \qquad (3)$$

where f(i) is a function of the current i through the filament, ΔT is the difference of the temperatures between the filament and the wall in the chamber, S is the temperature jump between the filament and the gas, u is the filament voltage, and Δu is the change of the voltage in the measuring diagonal bridge when the field is turned on. We note that f(i) is a slowly-varying function of the order of unity. The threshold sensitivity $\epsilon_{\min}$ attained in the measurements of ϵ can be easily estimated in the following manner. We consider the threshold sensitivity in the worst case, namely at the lowest working pressure 0.13 mm Hg, when the temperature jump is maximal. In this case $\Delta T - S \approx 5 \times 10^{-2} \Delta T$ (see, for example, [6]). In accordance with the foregoing data, we obtain

$$\varepsilon_{\min} \approx 20 (\Delta u)_{\min} / u \approx 1 \cdot 10^{-6}.$$

It is obvious that $\epsilon_{\min}$ will decrease with increasing pressure.

The procedure for determining ϵ can be greatly simplified by resorting to calibration of the experimental setup against some standard gas. If we use a standard gas whose pressure is chosen such that the voltage on the measuring filament and the current through it are the same as in the case of the investigated gas at the specified pressure, then we can obtain, on the basis of the heat-balance equation and formula (3), the following simple formula for the calculation of ϵ:

$$\varepsilon = \varepsilon_{\text{st}} \frac{\Delta u}{(\Delta u)_{\text{st}}} \frac{\varkappa}{\varkappa_{\text{st}}}, \qquad (4)$$

where $\epsilon_{\text{st}}(\Delta u)_{\text{st}}$, and $\mathcal{K}_{\text{st}}$ are the values of ϵ, Δu, and $\mathcal{K}$ for the standard gas. We note that at low pressures, when the dependence of the heat transfer on the pressure is strong, it is easy to ensure the aforementioned conditions for the applicability of formula (4).

The standard gas used in the described experiments was NF_3, for which the dependence of ϵ on E/p is known from [5].[3)] The relative error in the determination of ϵ_{sat} amounts to $\sim$15%. It consists of the systematic error due to the calibration, which does not exceed 10%, and a random error, which amounts to not more than 5%. It should be noted that under conditions indicated above, no side effects, particularly discharges, were observed in the described measuring chambers.

[2)] Unlike the pickups used in [2,5], where the plates were located outside the chamber.

[3)] A similar procedure of calibrating the apparatus against the effect in oxygen, with a magnetic field turned on, is used in [5] to determine ϵ for NF_3.

Other systematic errors are likewise eliminated, particularly those due to the Knudsen effect.[4)]

Figures 2–5 show the experimental plots of ϵ against E/p for the gases investigated by us. The solid curves in these figures are theoretical, constructed on the basis of formulas (1). It is seen from the figures that within the limits of the measurement errors ($\Delta\epsilon/\epsilon < 15\%$), the dependence of ϵ on E/p agrees with the theoretical one for all the investigated gases. According to Mikhaĭlova and Maksimov,[11] such a dependence on E and p is characteristic only of gases with molecules of the symmetric-top type, such as $CHCl_3$. On the other hand, the molecules C_2H_5Cl, C_6H_5Cl, and C_5H_5N are asymmetrical tops.[15] There are no published data on the moments of inertia of the molecules of the other investigated gases, but it can be assumed that most of these molecules are also described by the asymmetric-top model.

The applicability of the theory of Mikhaĭlova and Maksimov for the aforementioned models of the asymmetric-top type can be explained in the following manner. The character of the field dependence of the transport coefficients of gases with molecules of the asymmetric-top type is determined by the relation between the splitting δ of the rotational levels, due to the asymmetry parameter (b_p),

$$\delta = (C - B)\,(b_p/8)^{K-1}(J + K)!\{2(J - K)![(K - 1)!]^2\}^{-1} \quad (5)$$

(K is the quantum number of the projection of the angular momentum J, corresponding to the limiting case of a degenerate top[15]), and the interaction between the dipole moment and the field. When $\delta \ll Ed$ we can neglect the splitting of the rotational levels and assume the description of the rotation of the molecules by the symmetric-top model to be sufficiently accurate. In this case $\epsilon = \varphi(E/p)$. On the other hand, if $\delta \gg Ed$, then $\epsilon = \varphi(E^2/p)$. In the intermediate case, the dependence of ϵ on the field and on the pressure turns out to be more complicated. For molecules with rotational constants $\sim 10^3$ MHz and an asymmetry parameter $b_p \sim 10^{-2}$, the values of the splittings of the rotational levels for the mean values $\bar{J} = 15$ and the mean values $\bar{K} = 6$ amount to $\delta \sim 10^{-25}$ erg. Therefore, in field $E \gtrsim 10^{-2}$ V/cm, the relation $Ed \gg \delta$ is satisfied, and the change of the thermal-conductivity coefficient should depend on the ratio E/p, and this causes the experimentally observed relationships.

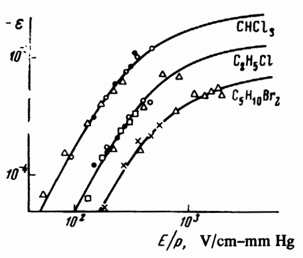

FIG. 2.

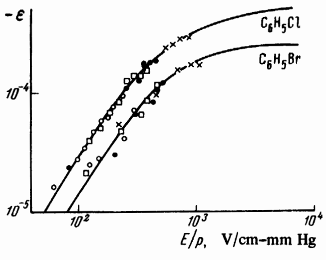

FIG. 3.

FIG. 2. Dependence of $\epsilon(\xi)$ for $CHCl_3$: ○ – p = 0.53; ● – p = 0.67, △ – p = 1.13; for C_2H_5Cl: △ – p = 0.33, ○ – p = 0.67, □ – p = 1.0, ● – p = 1.33; for $C_5H_{10}Br_2$: △ – p = 0.13, X – p = 0.27. The pressure p here and in Figs. 3 – 6 below is in millimeters mercury.

FIG. 3. Dependence of $\epsilon(\xi)$ for C_6H_5Cl: X – p = 0.27, ● – p = 0.61, □ – p = 0.8, ○ – p = 1.25; for C_6H_5Br: X – p = 0.27, ● – p = 0.61, □ – p = 0.87, ○ – p = 1.25.

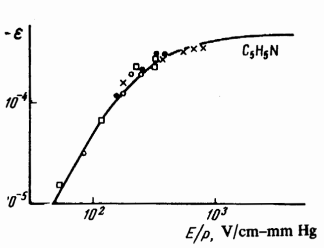

FIG. 4

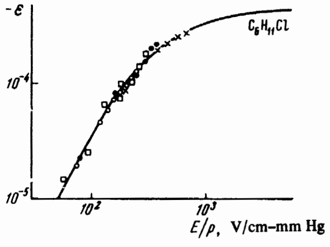

FIG. 5

FIG. 4. Plot of $\epsilon(\xi)$ for C_5H_5N: X – p = 0.27, ● – p = 0.61, □ – p = = 0.87, ○ – p = 1.25.

FIG. 5. Plot of $\epsilon(\xi)$ for $C_6H_{11}Cl$: X – p = 0.27, ● – p = 0.61, □ – p = = 0.87, ○ – p = 1.25.

Some measurement results are listed in the table. The values of ϵ_{sat} indicated in the table ("saturation effect") were determined by extrapolating the experimental data in accordance with the theoretical curve. The largest value of ϵ_{sat} is observed for $CHCl_3$ (-2.68×10^{-3}), and the smallest in C_6H_5Br (-2.9×10^{-4}). Attention is called to the fact that the values of ϵ_{sat} for the investigated gases ($\lesssim 10^{-3}$) are small compared with the values of ϵ_{sat} for simple gases (O_2N_2, NO, CO, CO_3, etc.), obtained in a magnetic field (for example, for N_2 the value of $(\epsilon_\perp)_{sat} = -1.05 \times 10^{-2}$ [8]). As noted above, the value of ϵ_{sat} is proportional to the square of the matrix elements of the collision operator describing nonspherical scattering of molecules. It follows therefore that whereas in a number of cases the deviation of the interaction potentials from spherically-symmetrical ones must be taken into account in calculations of the transport coefficient of simple gases in the absence of a field, for the gases investigated here the potentials of both elastic and inelastic collisions are closer to spherical, and their deviations from spherically-symmetrical ones can be neglected.

It should be noted that $CHCl_3$ and C_2H_5Cl were investigated earlier in [1,4] The authors of these references measured $\epsilon_\parallel$ in an inhomogeneous electric field of a cylindrical capacitor. As already indicated in [5], the values of $(\epsilon_\parallel)_{sat}$ given by de Groot et al.[4] are too low by a factor of approximately 3, whereby the decrease by a factor of 1.5 is due to the fact that the extension of the theory for diamagnetic gases to the case of polar gases,

Gas	Chemical formula	d, dB	$-10^4\epsilon_{sat}$	$(E/p)^{1/3}$ V/cm / mm Hg	β_{10} cm³/sec	$\beta_{10}\sqrt{I_A}$
Chloroform	$CHCl_3$	1.013	26.8	500		$8.8 \cdot 10^{-29}$
Ethyl chloride	C_2H_5Cl	2.03	11.7	425	$2.1 \cdot 10^{-9}$	
Dibromopentane	$C_5H_{10}Br_2$	2.43	6.15	1200		$3.9 \cdot 10^{-28}$
Chlorobenzene	C_6H_5Cl	1.57	6.15	650	$0.9 \cdot 10^{-9}$	
Chlorocyclohexane	$C_6H_{11}Cl$	2.3	4.8	425		$2.0 \cdot 10^{-28}$
Pyridine	C_5H_5N	2.2	3.9	230	$1.2 \cdot 10^{-9}$	
Bromobenzene	C_6H_5Br	1.6	2.9	455		$1.65 \cdot 10^{-28}$

[4)] That is, as shown in [8,14], the experimental difficulties and errors, whose possible existence is indicated in [1,4], are eliminated.

employed by the authors, is not valid, while the remaining discrepancy, by a factor of 2, can be attributed to incorrect measurements of $\Delta T/T$ in the cited paper. That errors could occur in these measurements is indicated by a comparison between the experimental data of [4] and the data of [11], for the latter turned out to be approximately twice as large. A comparison of the results obtained by us in $CHCl_3$ and C_2H_5Cl with the data of [1,4] confirms these conclusions. From a comparison of the values of ϵ_{sat} obtained by us (see the table) with the values of $(\epsilon_{\parallel})_{sat}$ obtained on the basis of extrapolation of the data of Senftleben[11] on the theoretical curve for polar gases in a cylindrical field (-0.24×10^{-2} for $CHCl_3$ and -0.82×10^{-3} for C_2H_5Cl), it follows that $(\epsilon/\epsilon_{\parallel})_{sat} = 1.1$ for $CHCl_3$ and $(\epsilon/\epsilon_{\parallel})_{sat} = 1.4$ for C_2H_5Cl. These relations coincide, within the limits of experimental errors ($\lesssim 15\%$) with the theoretical value 1.25 that follows from (1). Thus, the obtained results do not contradict the model of nonspherical scattering used by Mikhaĭlova and Maksimov[11] in the derivation of (1).

Let us now examine the other data listed in the table. In this table $(E/p)_{1/2}$ is the value of E/p at which $\epsilon = \epsilon_{sat}/2$, and β_{10} is the eigenvalue of the "ideal" collision operator describing spherically symmetrical scattering of the molecules. For gases whose moments of inertia are unknown, we determined the values $\beta_{10}\sqrt{I}$. It was assumed in the expression for $\epsilon = \varphi(E/p)$ that $I_A = I_B = I_C$. A comparison of the theoretical $\epsilon = \varphi(E/p)$ curve calculated from formulas (2) with the experimental data makes it possible to determine the value of $\Omega^{(11)}$. For the gases $CHCl_3$ and C_2H_5Cl, the obtained values are equal to 2.2×10^{-10} cm³/sec and 5.8×10^{-10} cm³/sec (for the $CHCl_3$ molecules we have $I_B = 2.32 \times 10^{-38}$ g-cm² [15]). In [16] the viscosity data were used to calculate the parameters of the elastic Stockmayer potential, and consequently also $\Omega^{(11)}$ for $CHCl_3$ and C_2H_5Cl, namely, 0.97×10^{-10} cm³/sec and 0.83×10^{-10} cm³/sec. A comparison of these quantities shows that the collision frequencies which enter in the expression for ξ (see (1), (2)) are larger than the elastic-collision frequencies. It is therefore impossible to confine oneself only to elastic collisions in the collision operator describing spherically symmetrical scattering in polar gases.

An anomalous behavior of ϵ, compared with the data of de Groot et al.[4] was observed by us in CH_3CN gas. As seen from Fig. 6, at small E/p the value of ϵ is positive and goes through a maximum when this ratio increases ($\epsilon_{max} = +0.5 \times 10^{-3}$ at $E/p = 180$ V/cm-mm Hg. At $E/p = 350$ V/cm-mm Hg, ϵ reverses sign. Experiments performed by us in an inhomogeneous cylindrical field at pressures $p = 0.2-1.4$ mm Hg have shown that the character of the dependence of $\Delta T/T$ on V/p (here ΔT is the change of the temperature of the platinum filament, V is the voltage between the filament and the body of the chamber) is analogous to that observed in a homogeneous field: the plot of $\Delta T/T = f(V/p)$ has a maximum at $V/p \approx 130$ V/mm Hg, and $\Delta T/T = 0$ at $V/p \approx 370$ V/mm Hg. We note that de Groot et al.[4] investigated the thermal conductivity of CH_3CN in an inhomogeneous cylindrical field with the aid of a measuring chamber having an analogous geometry, at pressures from 16.5 to 32.5 mm Hg. Under these conditions, they succeeded in obtaining only the initial section of the $\Delta T/T = f(V/p)$ curve to its maximum. Therefore the plot of the curve obtained by us for CH_3CN clearly indicates that the value $(\epsilon_{\parallel})_{sat} = 0.134 \times 10^{-3}$, given by de Groot et al., is in error (even if we disregard the systematic errors of their measurements).

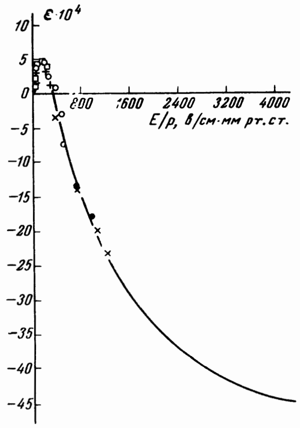

FIG. 6. Plots of $\epsilon(\xi)$ for CH_3CN: × – p = 0.13, ● – p = 0.20, ○ – p = 0.53, + – p = 0.66, □ – p = 1.4.

A theory explaining the increase of the transport coefficients of polar gases in an electric field was developed by Levi, McCourt, and Tip.[12,17] In solving the quantum kinetic equation for a gas with rotating molecules in an external field, these authors considered both the self-adjoint[10] and non-self-adjoint collision operators. The latter describes collisions which have no inverses; in other words, collisions for which the detailed balancing principle is not satisfied. The presence of such collisions in a gas leads, as shown by a solution of the kinetic equation,[17] to the possibility of increasing the transport coefficient (thermal conductivity and viscosity) in an external field. The total change of the coefficient of thermal conductivity is given by the following expression:[12,17]

$$\varepsilon_\perp = \psi_+ c_1 - \psi_- c_2, \qquad \varepsilon_\parallel = 2\psi_+ c_1 - \psi_-(c_2 + c_3); \tag{6}$$

$$c_1 = \frac{\xi'^2}{1+\xi'^2}, \quad c_2 = \frac{\xi^2}{1+\xi^2} + \frac{8\xi^2}{1+4\xi^2}, \quad c_3 = \frac{\xi^2}{1+\xi^2} - \frac{8\xi^2}{1+4\xi^2},$$

$$\xi' = \Omega/\omega', \quad \xi = \Omega/\omega,$$

where Ω is the average precession frequency; ω, ω' — collision frequencies described respectively by the self-adjoint and non-self-adjoint operators. The quantities ψ_+ and ψ_- (> 0) determine the limiting values of the positive and negative change of the thermal conductivity coefficient.

It is seen from Fig. 6 that within the limits of the experimental errors the course of the theoretical curve $\epsilon = \varphi(E/p)$, calculated from formulas (6), agrees with the experimental data. From a comparison of the theoretical and experimental curves it follows that the known parameters in formulas (6) for CH_3CN have the following values: $\psi_+ = 0.68 \times 10^{-3}$, $\psi_- = 2.3 \times 10^{-3}$, and $\omega/\omega' = 20$. Using these values of ψ_+ and ψ_-, we can readily obtain from (6)

$$(\varepsilon)_{sat} = -4{,}7\cdot 10^{-3}, \quad (\varepsilon_\parallel)_{sat} = -3.2\cdot 10^{-3}, \quad (\varepsilon_\perp/\varepsilon_\parallel)_{sat} = 1{,}9.$$

Levi and McCourt[17] conclude that the "positive effect" is inherent in all polar gases, since the collisions of the rotating molecules with dipole–dipole interaction are described by non-self-adjoint operators. In addition, it is indicated in [17] that in the case of saturation in polar gases the effect decreases in absolute magnitude with increasing dipole moment of the molecules. As seen from the table, the experimental data obtained by us contradict the last statement. Apparently this is connected with the possible existence of different ratios of the nonspherical collisions described by the self-adjoint and non-self-adjoint operators, and consequently also the ratios ψ_+/ψ_- for different gases at close frequencies ω and ω'.

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