SOVIET PHYSICS JETP VOLUME 23, NUMBER 3 SEPTEMBER, 1966

TRANSFER PHENOMENA IN A POLAR GAS

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Submitted to JETP editor October 27, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) **50**, 821-826 (March, 1966)

Transfer phenomena in polar gases in an electric field are considered. A solution of the kinetic equation for polar gases with linear molecules in an electric field is presented in an approximation quadratic with respect to the interaction nonsphericity parameter. An expression for the thermal conductivity tensor of such gases is derived and it is shown that variation of the thermal conductivity coefficient depends on the field and pressure via E^2/P.

1. INTRODUCTION

It has been shown in several papers[1-4] that the coefficients of viscosity and thermal conductivity of gases with nonspherical molecules depend on the magnetic field. Gorter[5] and Zernike and von Lier[6] relate this effect in a paramagnetic gas to the dependence of the collision cross section on the angle between the relative velocity of the nonspherical molecule and its axis of rotation. In a magnetic field, as a result of precession, additional averaging of the nonspherical molecule collision cross section occurs. Therefore the probability of collisions in the field increases, and the transport coefficient decreases. An analysis of the dependence of the thermal conductivity coefficient of a paramagnetic gas on the magnetic field, based on a magnetic equation that takes into account the rotational degrees of freedom of the molecules[7], was made by Kagan and Maksimov[8].

Attempts to observe a similar change in the viscosity coefficient of nonspherical polar molecules in an electric field by experimental means have been made in[9,10]. Amme[9] established the variation of the viscosity of the gas COS (linear molecules with dipole moment $\mu = 0.71$ Debye), which is equal to $-\Delta\eta/\eta = (0.47 \pm 0.16)\%$ when the ratio of the electric field intensity to the pressure is $E/P = 52$ kV/cm-atm. For ethyl chloride (symmetrical-top molecule with dipole moment $\mu = 2.03$ Debye) the value obtained for the change in viscosity was $-\Delta\eta/\eta = (0.46 \pm 0.16)\%$ with a ratio of the electric field to the pressure $E/P = 32$ kV/cm-atm. In the polar gas NO_2 ($\mu = 0.17$ Debye) the effect was not observed. Amme used in his experiments an alternating electric field (40—100 cps) perpendicular to the gas flow in a glass capillary. He proposes that the arguments which explain the Senftleben effect are applicable to the given case too. However, the dependence of the viscosity coefficient on the electric field and on the pressure was not determined by him.

Cioara[10] measured the viscosity coefficient of a mixture of methane with ethyl alcohol vapor in a constant electric field. He observed that the change in viscosity is $\Delta\eta/\eta \sim E^2$, and that $-\Delta\eta/\eta = 0.2\%$ for $E = 35$ kV/cm. The causes for the change of the viscosity coefficient were not discussed by him.

In this paper we obtain, on the basis of a kinetic equation proposed by Kagan and Afanas'ev[7], an expression for the thermal conductivity tensor of polar gases with linear molecules in an electric field.

2. TRANSPORT COEFFICIENTS OF POLAR GASES IN AN ELECTRIC FIELD

The cause of the precession that increases the average collision cross section of nonspherical molecules may be the interaction between the dipole moment and the electric field. There exists a direct connection between the change of the transport coefficient of polar gases in an electric field and the Stark effect in rotational spectra of molecules. The physical meaning of this connection lies in the fact that the energy of the Stark splitting of the rotational levels is, speaking in the language of classical mechanics, the energy of the precession of a polar molecule about the direction of the electric field. The change in the transport coefficient of the gas in the electric field is determined by the nonsphericity of the molecule and depends on the ratio of the precession frequency to the collision frequency. Inasmuch as the precession frequency is proportional to the energy of the

Stark broadening, we expect for molecules with different degrees of symmetry, for which the Stark effect is linear or quadratic, a corresponding field dependence of the variation of the transport coefficient. Thus, for example, inasmuch as the energy of the Stark splitting is proportional to E^2 for linear molecules, the change in the transport coefficient for molecules of this type will depend on E^2/P. Similarly, for molecule of the symmetrical-top type we can expect a dependence on E/P1).

The change in the transport coefficients should reach a saturation value, as is the case in a magnetic field when the electric field intensity is high and the precession frequency is much larger than the collision frequency. Since this saturation depends only on the nonsphericity of the molecule, the saturation effect in the same polar gas should be the same in electric and magnetic fields.

3. THERMAL CONDUCTIVITY OF POLAR GASES WITH LINEAR MOLECULES IN AN ELECTRIC FIELD

As shown in [8], the kinetic equation for linear molecules, taking into account their rotation, is2)

$$\frac{\partial f}{\partial t}+\mathbf{v}\nabla f+\dot{\mathbf{M}}\frac{\partial f}{\partial \mathbf{M}}=\left(\frac{\partial f}{\partial t}\right)_{\text{col}}.$$

Here $\dot{M}$ is determined by the interaction of the dipole moment with the electric field. However, the dipole moment of a linear molecule is equal to zero, since the states of the molecule are nondegenerate [11], and therefore the field should initially induce a dipole moment and polarize the molecule.

We consider a gas in the temperature interval where high rotational states of the molecules are excited and the vibrational degrees of freedom can still be disregarded. In this case $\dot{M}$ can be obtained from classical considerations. We write down the equation for rotation of a polar linear molecule with momentum M and moment of inertia I in an electric field in the form

$$d\mathbf{M}/dt=[\mu\mathbf{E}_{\parallel}]+[\mu\mathbf{E}_{\perp}], \qquad (1)^*$$

where $E_{\parallel}$ and $E_{\perp}$ are the projections of the field parallel and perpendicular to the moment $\mathbf{M}_0$ of the molecule in the absence of the field. We seek a solution of (1) of first order in the ratio of the dipole-field interaction energy to the rotational energy, in the form

$$\mathbf{M}=\mathbf{M}_0+\mathbf{M}_{\parallel}+\mathbf{M}_{\perp}.$$

Substituting **M** in (1) and resolving this equation in terms of the chosen projections, we have

$$d\mathbf{M}_{\parallel}/dt=[\mu\mathbf{E}_{\perp}], \quad d\mathbf{M}_{\perp}/dt=[\mu\mathbf{E}_{\parallel}].$$

The solution of the last equations can be readily obtained by recognizing that the dipole moment rotates with velocity $\Omega_0 = M_0/I$:

$$M_{\perp}=M_0\frac{\mu E_{\parallel}}{I\Omega_0^2}, \quad M_{\parallel}=M_0\frac{\mu E_{\perp}}{I\Omega_0^2}\sin\Omega_0 t;$$

$\mathbf{M}_{\perp}$ corresponds to nutation of the momentum **M** around the direction of $\mathbf{M}_0$ with velocity Ω_0, and the small addition $\mathbf{M}_{\parallel}$ denotes that a small periodic component is added to the constant rotation velocity Ω_0. The mutation and the nonuniform rotation of the molecules lead to the occurrence of nonzero projections with dipole moment μ on the direction M_0 and on a direction opposite to $E_{\perp}$. The mean values of these projections will be

$$\langle\mu_{\parallel}\rangle=\mu\mu E_{\parallel}/I\Omega_0^2, \qquad \langle\mu_{\perp}\rangle=-{}^1\!/_4\mu\mu E_{\perp}/I\Omega_0^2.$$

The interaction of the projections of the dipole moment with the field causes the molecule to precess around the direction of E. The precession energy is equal to the energy of the quadratic Stark splitting, and the moment of the force causing the precession is

$$\mathbf{M}=\frac{5}{4}\frac{\mu^2 I}{M^4}(\mathbf{ME})[\mathbf{ME}]. \qquad (2)$$

We shall seek the distribution function in first approximation in the form

$$f=f^{(0)}(1+\varphi), \qquad (3)$$

where $f^{(0)}$ is the equilibrium distribution function [7]. In the case of the heat-conduction problem, we can represent φ by

$$\varphi=-\sqrt{2kT/m}\mathbf{A}\nabla\ln T. \qquad (4)$$

The unknown function **A** satisfies in this case the equation

$$-(m/2kT)^{1/2}f^{(0)}C_i\left(\frac{M^2}{2IkT}+\frac{mC^2}{2kT}-\frac{7}{2}\right)+\frac{5}{4}\frac{\mu^2 I}{M^4}(\mathbf{ME})[\mathbf{ME}]$$
$$\times f^{(0)}\frac{\partial A_i}{\partial\mathbf{M}}=\int f^{(0)}f_1^{(0)}(A_i'+A_{1i}'-A_i-A_{1i})gw\,d\sigma\,d\Gamma_1, \qquad (5)$$

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1)An interesting exception are the molecules of the ammonia type. For them the Stark effect will be quadratic[12], for owing to the inversion motion of the N atom relative to the plane of the three hydrogen atoms the mean value of the projection of the dipole moment of the molecule in any direction is equal to zero. Therefore the variation of the transport coefficient in an elastic field should depend on E^2/P for molecules of similar type.

2)The rotational motion of the molecule is described by the moment of rotation **M** and the angle that determines the position of the molecule axis in a plane perpendicular to **M**, the distribution of the molecules with respect to this angle being of equal probability[7].

*$[\mu\mathbf{E}] \equiv \mu\times\mathbf{E}$.

where $d\sigma$ is the differential cross section of the elastic collisions of the molecule without account of the nonsphericity and $d\Gamma$ is the phase volume:

$$d\Gamma = MdMd\Omega_M C^2 dC d\Omega_C.$$

The model of the collision is assumed to be the same as in the paper of Kagan and Maksimov[8], that is, in the right side of (5)

$$w = 1 + \beta[P_2(\cos\widehat{\mathbf{gM}}) + P_2(\cos\widehat{\mathbf{gM}_1})$$
$$+ P_2(\cos\widehat{\mathbf{g'M}} + P_2(\cos\widehat{\mathbf{g'M}_1})].$$

Here β is a parameter which takes into account the small nonsphericity of the molecules, P_2 is a Legendre polynomial, and **g** and **g′** are the relative velocities of the molecule before and after the collision.

Equation (5) differs from the equation for a paramagnetic gas in a magnetic field[8] in the second term in the left side. In accordance with this, the expansion of the function **A** in terms of the irreducible tensors made up of the components of the vectors **C** and **M** should contain terms that are odd in **C**, and terms that are both even and odd in **M**. We seek an approximate solution of (5) in the form[3)]

$$A_i = A_{ik}{}^1\varphi_k{}^1 + A_{ik}{}^2\varphi_k{}^2 + \overset{3}{A}_{ikl}\varphi_{kl}{}^3 + \overset{4}{A}_{iklm}\overset{4}{\varphi}_{klm}, \tag{6}$$

where

$$A_{ik}{}^1,\ A_{ik}{}^2,\ \overset{3}{A}_{ikl},\ \overset{4}{A}_{iklm} \tag{7}$$

are unknown coefficients,

$$\varphi_k{}^1 = C_k(C^2 - {}^5/_2),\quad \varphi_k{}^2 = C_k(M^2 - 1),\quad \varphi_{kl}{}^3 = C_k M_l,$$
$$\overset{4}{\varphi}_{klm} = C_k(M_2 M_m - {}^1/_3 M^2\delta_{lm}). \tag{8}$$

Here and throughout in the text **M** and **C** are the dimensionless moment and proper velocity of the molecule, which differ from the earlier quantities respectively by the factors $(1/2IkT)^{1/2}$ and $(m/2kT)^{1/2}$.

We multiply (5) by each of the functions (8) and integrate over the entire phase space. We then obtain the following system of equations for the unknown coefficients (7):

$$\begin{gathered}{}^5/_4 n\delta_{ij} = T^{11}A_{ij}{}^1,\quad {}^1/_2 n\delta_{ij} = T^{22}A_{ij}{}^2 + \overset{4}{A}_{iklm}\Delta_{lmkj}T^{24},\\ -\gamma\overset{4}{A}_{ijlm}E_{lms} = T^{33}\overset{3}{A}_{ijs} + \overset{3}{A}_{ikl}T^{33}(\beta)\Delta_{kjls},\\ -2\gamma\overset{3}{A}_{ijl}E_{stl} = T^{42}A_{ik}{}^2\Delta_{kjst} + T^{44}\overset{4}{A}_{iklm}\delta_{kj}\Delta_{lmst}\\ +\overset{4}{A}_{iklm}T^{44}(\beta)D_{kjlmst}.\end{gathered} \tag{9}$$

Here

$$\Delta_{ijlm} = -{}^2/_3\delta_{ij}\delta_{lm} + \delta_{il}\delta_{jm} + \delta_{im}\delta_{jl},$$
$$E_{lms} = E^{-2}(\varepsilon_{lsq}E_qE_m + \varepsilon_{msq}E_qE_l)$$

(ϵ_{ikl}—unit antisymmetrical tensor),

$$\gamma = {}^1/_{48}\mu^2E^2In\,/\,(2IkT)^{-3/2},$$
$$T^{33} = {}^4/_9 n^2\Omega^{(1,1)},\quad T^{33}(\beta) = {}^2/_{25}\beta n^2[{}^4/_3\Omega^{(1,1)} - \Omega^{(1,2)}]$$

($\Omega^{(l,s)}$ are the standard integrals of the kinetic theory of monatomic gases[13]). The remaining coefficients and the tensor D_{kjlmst} are calculated in terms of $\Omega^{(l,s)}$ in[8].

We seek the solution of the system (9) in the form

$$A_{ij}{}^1 = A_1\delta_{ij} + Y_{ij}{}^1,\quad A_{ij}{}^2 = A_2\delta_{ij} + Y_{ij}{}^2,\quad \overset{3}{A}_{ijl} = \overset{3}{Y}_{ijl},$$
$$\overset{4}{A}_{ijlm} = A_4\Delta_{ijlm} + \overset{4}{Y}_{ijlm}. \tag{10}$$

Here A_α does not depend on **E**, and $Y^\alpha = 0$ when $\mathbf{E} = 0$.

For the case $\mathbf{E} = 0$ we get from (9)

$$A_1 = \frac{5}{4}\frac{n}{T^{11}},\quad A_2 = \frac{n}{2T^{22}}\left[1 - \frac{10}{3}\frac{(T^{24})^2}{T^{22}T^{44}}\right]^{-1}, \tag{11}$$

$$A_4 = -\frac{T^{24}}{2T^{44}}A_2.$$

When the field differs from zero, we obtain from (9) and (10) for Y^α the system of equations

$$\begin{gathered}0 = Y_{ij}{}^1T^{11},\quad 0 = Y_{ij}{}^2T^{22} + \overset{4}{Y}_{iklm}\Delta_{lmkj}T^{24},\\ -\gamma A_4\Delta_{ijlm}E_{lms} - \gamma\overset{4}{Y}_{ijlm}E_{lms} = \overset{3}{Y}_{ijs}T^3 + \overset{3}{Y}_{ikl}T^{33}(\beta)\Delta_{kjls},\\ -2\gamma\overset{3}{Y}_{ijl}E_{stl} = Y_{ik}{}^2\Delta_{kjst}T^{24} + \overset{4}{Y}_{ijlm}\Delta_{lmst}T^4\\ + \overset{4}{Y}_{iklm}T^{44}(\beta)D_{kjlmst}.\end{gathered} \tag{12}$$

If the nonsphericity parameter β is small, then the off-diagonal coefficients T^{pq} and the coefficients $T^{33}(\beta)$ and $T^{44}(\beta)$ are small compared with the diagonal ones. Since the thermal conductivity tensor contains Y^1 and Y^2[8], and since it follows from the second equation of the system (12) that $Y^2 \sim Y^4T^{24}/T^{22}$, we can neglect the last term in the third equation on the right side, and the first and third terms in the fourth equation. Substituting Y_{ijl} from the third system (12) into the fourth, we get

$$\overset{4}{Y}_{ijlm} = \alpha A_4 E_{ijlm}, \tag{13}$$

where

$$E_{ijlm} = 4E^{-4}E_iE_jE_lE_m - E^{-2}(\delta_{il}E_jE_m + \delta_{jl}E_iE_m$$
$$+ \delta_{im}E_jE_l + \delta_{jm}E_iE_l),$$
$$\alpha = 2\gamma^2\,/\,(T^{44}T^{33} + 2\gamma^2). \tag{14}$$

From the second equation of the system (12) it follows that

[3)] This form of the solution will satisfy the condition for the conservation of the number of molecules, the momentum, and angular momentum and the energy.

$$Y_{ij}{}^2 = \frac{2A_4T^{24}}{T^{22}}\alpha\left(\delta_{ij} + \frac{E_iE_j}{E^2}\right). \tag{15}$$

Using expressions (11), (14), and (15) we can obtain the coefficient of thermal conductivity in the absence of an electric field and the part that depends on the field:

$$(\lambda_{ik})_{E=0} = \lambda_0\delta_{ik}, \qquad \lambda_0 = kn(2kT\,/\,m)\,({}^5\!/_4A_1 + {}^1\!/_2A_2), \tag{16}$$

$$\frac{\Delta\lambda_{ik}}{\lambda_0} = -\psi\alpha\left(\delta_{ik} + \frac{E_iE_k}{E^2}\right), \tag{17}$$

$$\psi = \frac{(T^{24})^2}{T^{22}T^{44}}\left\{1 + \frac{25}{4}\frac{T^{22}}{T^{11}}\left[1 - \frac{10}{3}\frac{(T^{24})^2}{T^{22}T^{44}}\right]\right\}^{-1}. \tag{18}$$

Expressions (17) and (18)[4] show that the coefficient of thermal conductivity of a polar gas in an electric field decreases and becomes anisotropic. The dependence of λ_{ik} on the value of the electric field and on the pressure is determined by the coefficient α (14), in which γ is equal to

$$\gamma = \frac{1}{96}\frac{\mu^2n^2}{(2IkT)^{1/2}}\frac{E^2}{P}. \tag{19}$$

It follows from (19) that at a fixed temperature the change in the thermal conductivity should depend on the electric field and the pressure only in terms of the ratio E^2/P as expected from the qualitative consideration when the analogy was made with the Stark effect.

In the region of small values of the electric field the relative change in the thermal conductivity coefficient depends on γ in the following manner:

$$\left(\frac{\Delta\lambda_{ik}}{\lambda_0}\right)_{E\to 0} = -\psi\frac{2}{T^4T^3}\gamma^2\left(\delta_{ik} + \frac{E_iE_k}{E^2}\right). \tag{20}$$

From (17) we can readily find the relative changes of thermal conductivity in cases when the electric field is parallel and perpendicular to the temperature gradient:

$$\frac{\Delta\lambda_\perp}{\lambda_0} = -\psi\alpha, \qquad \frac{\Delta\lambda_\parallel}{\lambda_0} = -2\psi\alpha. \tag{21}$$

Thus, for arbitrary fixed values of the field, temperature and pressure we have

$$\Delta\lambda_\parallel\,/\,\Delta\lambda_\perp = 2. \tag{22}$$

At sufficiently large values of the ratio E^2/P the effect reaches saturation

$$\left(\frac{\Delta\lambda_\perp}{\lambda_0}\right)_{\gamma\to\infty} = -\psi, \qquad \left(\frac{\Delta\lambda_\parallel}{\lambda_0}\right)_{\gamma\to\infty} = -2\psi. \tag{23}$$

It follows from (23) that the magnitude of the effect in the saturation is determined by the nonsphericity of the molecule β.

The authors thank A. A. Sazykin and N. A. Kolokol'tsov for interest in the work and useful advice.

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Translated by J. G Adashko
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[4] In the corresponding expression of[8], the second term in the curly brackets has a factor 5 in lieu of 25/4. This is apparently a misprint.