SOVIET PHYSICS JETP VOLUME 14, NUMBER 3 MARCH, 1962

TRANSPORT PHENOMENA IN A PARAMAGNETIC GAS

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Submitted to JETP editor April 3, 1961

J. Exptl. Theoret. Phys. (U.S.S.R.) **41**, 842-852 (September, 1961)

A kinetic theory is developed for a paramagnetic gas in an arbitrary magnetic field. A transport equation is derived with account of rotational degrees of freedom, discreteness of the magnetic momentum, and dependence of the scattering cross section on the angle between the direction of the molecular moment and the direction of the relative velocity, which is of decisive importance for the problem under consideration. With the thermal conductivity problem taken as an example, a general method for solving the kinetic equation is developed. An explicit expression for the thermal conductivity tensor in a magnetic field is deduced and comparison is made with the experimental results on the Senftleben effect.

1. INTRODUCTION

As is well known, the thermal conductivity of a paramagnetic gas depends on the magnetic field. This effect was first observed in oxygen by Senftleben,[1] and later in another diatomic gas possessing paramagnetism, namely NO. In the Thirties a whole series of experimental papers was published, devoted to this effect, principally in oxygen.[2] It was found simultaneously that the viscosity coefficient of a paramagnetic gas also depends on the magnetic field.[3]

The experimental researches have shown that both the thermal conductivity and the viscosity decrease in a magnetic field, and this effect has a universal dependence on the ratio H/p at fixed temperature. At low values of H/p a quadratic dependence of this effect on the ratio is observed, and with further increase of H/p saturation sets in. Special experiments were also used to show that the variation of the thermal conductivity depends on the angle between the temperature gradient and the direction of the magnetic field.

A first attempt at a theoretical analysis was made by Laue.[4] Disregarding the nature of the effect, Laue introduced in purely formal fashion the hypothesis that the mean free path depends on the angle between the direction of the molecule velocity and the direction of the magnetic field. Treating subsequently the transport phenomena in terms of the mean free path, he arrived at a phenomenological relation which contained in explicit form only the dependence on the angle between **H** and ∇T.

In another paper, Zernike and Van Lier[5]* correctly related this effect with the nonsphericity of the molecules. They treated the transport phenomena (thermal conductivity) in the mean-free-path approximation.

In the present paper we use the kinetic equation for molecules with rotational degrees of freedom to develop a theory for transport phenomena in a paramagnetic gas situated in a magnetic field; this theory will enable us to establish all the fundamental laws.

2. KINETIC EQUATION FOR A PARAMAGNETIC GAS IN A MAGNETIC FIELD

The effect of the magnetic field on a neutral paramagnetic gas reduces to polarization and precession of the magnetic moments of the molecules. At room temperature and reasonable magnetic fields, the polarization is very weak. Indeed, if $H \lesssim 10^4$ oe, then $\mu_0 H/kT \lesssim 10^{-3}$. The polarization thus plays no role in kinetic processes, and the effect in magnetic fields can be connected only with precession.

In the case of nonspherical molecules, the interaction (scattering cross section) will in general depend on the relative orientation of the molecules. The presence of angular-momentum precession in the magnetic field causes the orientation of the molecule relative to the direction of its velocity to vary continuously if the motion between two collisions is free. Since each orientation can, roughly speaking, be set in correspondence with its own scattering cross section, the precession results in an effective increase of the statistical weight of the larger cross sections. Consequently the kinetic coefficients will in general always decrease in a magnetic field. Obviously, in this case the decisive quantity is not $\mu_0 H/kT$, but the

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*The authors are grateful to A. Sazykin who called their attention to this paper.

ratio of the characteristic precession time to the free path time. The ratio of these times can be made without difficulty either much greater than unity or much less than unity.

It is clear from the foregoing that to describe the kinetic phenomena in a paramagnetic gas it is necessary to examine the kinetic equation for molecules having rotational degrees of freedom. We confine ourselves to an examination of linear (particularly, diatomic) molecules and to a temperature interval in which the rotational motion can be regarded classically and the vibrational degrees of freedom are not yet excited. In this case the kinetic equation can be written in the form

$$\frac{\partial f}{\partial t}+\mathbf{v}\nabla f+\frac{\partial}{\partial \mathbf{M}}(f\dot{\mathbf{M}})=\left[\frac{\partial f}{\partial t}\right]_{\text{col}}. \tag{2.1}$$

The form of the left half of (2.1) is connected with the assumption that the distribution function depends on the rotational degrees of freedom only through the angular momentum **M**. In other words, we assume equiprobable distribution over the angle that characterizes the position of the molecule in a plane perpendicular to **M** (see[6] for details).

For a complete determination of the left half of (2.1) we must determine $\dot{\mathbf{M}}$. As is well known,

$$\dot{\mathbf{M}}=[\boldsymbol{\mu}\mathbf{H}], \tag{2.2}^*$$

where μ is the magnetic moment of the molecule. However, the magnetic moment of paramagnetic molecules is of purely quantum nature, connected with the uncompensated spin or orbital moments of the electron shell. Accordingly, the value of μ must be determined from a quantum-mechanical analysis as the limiting value corresponding to large rotational quantum numbers.

Let the magnetic field be limited in magnitude so that the Zeeman splitting is small compared with the fine structure of the molecular spectrum. Then the magnetic moment can be determined by averaging over the unperturbed state of the molecule. In this case

$$\boldsymbol{\mu}=\hat{\boldsymbol{\mu}}=\gamma\mathbf{M}, \tag{2.3}$$

$$\gamma=\mu_0 g/\hbar. \tag{2.4}$$

Here μ_0 is the Bohr magneton, g the gyromagnetic ratio, and **M** the total momentum of the molecule. In considering large rotational quantum numbers, we shall neglect the difference between the total and rotational momentum of the molecule.

For diatomic and polyatomic linear molecules, the spin-axial interaction energy is always small, at sufficiently high temperatures, compared with the energy of rotational motion (case b considered by Hund[7]). We confine ourselves to this case only. Then, assuming that the spin of the molecule differs from zero, we can show that when $M \gg \hbar$ we have

$$\gamma\cong 2\mu_0\sigma/M, \tag{2.5}$$

where σ runs through $2S+1$ values

$$\sigma=-S,\ -S+1,\ldots,S, \tag{2.6}$$

(S is the spin of the molecule). In (2.5) we have neglected terms of order M^{-2}, and consequently, in particular, the contribution of the orbital momentum drops out.

It is clear that the distribution function in (2.1) should depend on the discrete variable σ. The last term on the left in the kinetic equation (2.1) is now written in the form

$$\gamma(\sigma)\,[\mathbf{MH}]\frac{\partial}{\partial \mathbf{M}}f\,[\mathbf{r},\ t,\ \mathbf{v},\ \mathbf{M},\ \sigma]. \tag{2.7}$$

Assuming that $\lambda/L \ll 1$ and $\tau_{\text{col}}/\tau \ll 1$ (λ and τ_{col} are the mean free path length and time; L and τ are the characteristic length and time for the changes in the macroscopic quantities), we seek a first-approximation solution of the kinetic equation (2.1) in the form

$$f=f^{(0)}[1+\chi], \tag{2.8}$$

where $f^{(0)}$ is the local Maxwellian distribution function

$$f^{(0)}=n\left(\frac{m}{2\pi kT}\right)^{3/2}\frac{1}{4\pi IkT}\exp\left(-\frac{\varepsilon}{kT}\right). \tag{2.9}$$

Here

$$\varepsilon=mu^2/2+M^2/2I,\quad \mathbf{u}=\mathbf{v}-\mathbf{v}_0. \tag{2.10}$$

where $\mathbf{v}_0(\mathbf{r},t)$ is the macroscopic velocity and I the moment of inertia of the linear molecule.

In (2.9) and what follows we neglect the multiplet-splitting energy (coupling of type b!) and the energy of the magnetic interaction ($\mu_0 H/kT \ll 1$). By virtue of this, in particular, $f^{(0)}$ is independent of σ.

The conditions imposed on the total distribution function are

$$\int f\,d\Gamma^*=n,\quad \int f\varepsilon\,d\Gamma^*=\tfrac{5}{2}nkT,$$
$$\int f\mathbf{u}\,d\Gamma^*=0,\quad \int f\mathbf{M}\,d\Gamma^*=0. \tag{2.11}$$

Here

$$\int d\Gamma^*\ldots=\frac{1}{2S+1}\sum_{\sigma}\int d\Gamma\ldots,$$

$$d\Gamma=v^2dv\,MdM\,d\Omega_v\,d\Omega_M. \tag{2.12}$$

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*$[\mu\mathbf{M}]=\mu\times\mathbf{M}$.

(The difference between the phase volume of the momentum and the ordinary volume is connected with the linearity of the molecule).

We note that in (2.11) and (2.10) we have assumed the absence of a macroscopic angular momentum.

Taking (2.9) into consideration, we arrive at the following homogeneous conditions for χ

$$\int f^{(0)}\chi d\Gamma^* = 0, \quad \int f^{(0)}\chi\varepsilon d\Gamma^* = 0,$$
$$\int f^{(0)}\chi\mathbf{u}d\Gamma^* = 0, \quad \int f^{(0)}\chi\mathbf{M}d\Gamma^* = 0. \qquad (2.11')$$

Let us substitute (2.8) in (2.1). Using the conservation laws and retaining the first non-vanishing terms, we obtain

$$f^{(0)}\Big\{\Big(\frac{\varepsilon}{kT}-\frac{7}{2}\Big)\mathbf{u}\nabla\ln T+\frac{m}{2kT}\Big(u_iu_k-\frac{1}{3}\delta_{ik}u^2\Big)$$
$$\times\Big(\frac{\partial v_{0k}}{\partial x_i}+\frac{\partial v_{0i}}{\partial x_k}-\frac{2}{3}\delta_{ik}\frac{\partial v_{0l}}{\partial x_l}\Big)$$
$$+\Big(\frac{mu^2}{3kT}-\frac{2}{5}\frac{\varepsilon}{kT}\Big)\frac{\partial v_{0l}}{\partial x_l}\Big\}$$
$$+\gamma[\mathbf{MH}]\frac{\partial\chi}{\partial\mathbf{M}}f^{(0)}=J_{\text{col}}(\chi),$$

$$J_{\text{col}}(\chi)=\int f^{(0)}f_1^{(0)}(\chi'+\chi_1'-\chi-\chi_1)Wd\Gamma_1^*d\Gamma^{*'}d\Gamma_1^{*'}. \qquad (2.13)$$

(By writing the collision integral in this form we imply that the collision probability W is an even function of the momenta of the colliding molecules.)

The form of the function W is not known in the general case. We start from the assumption that the nonsphericity of the molecules is small, and that it is difficult for the momentum of the molecule to change upon collision. Then the effect of nonsphericity manifests itself principally on the dependence of the cross section of the angle between the momenta of the molecules and the direction of the relative velocity. It is clear that this dependence should not change if **M** is replaced by **−M**, and the approximate expression for W can be written

$$Wd\Gamma'^*d\Gamma_1'^* = wgd\sigma, \qquad (2.14)$$
$$w = 1 + \lambda\,[P_2(\cos\widehat{\mathbf{gM}}) + P_2(\cos\widehat{\mathbf{gM}_1})$$
$$+ P_2(\cos\widehat{\mathbf{g}'\mathbf{M}}) + P_2(\cos\widehat{\mathbf{g}'\mathbf{M}_1})],$$

where **g** and **g′** are the relative velocities before and after collision, dσ—differential cross section of elastic scattering of the molecules neglecting nonsphericity, and P_2 is a Legendre polynomial.

The form of the term in the square brackets is connected with the equality of the probabilities of the direct and reverse transitions, which follows from the principle of detailed balance, and also from the necessary symmetry of W with respect to M and M_1.

In writing out (2.14) we have assumed that the momentum of each molecule remains unchanged in the collision and that the interaction is independent of σ. (In addition, it is assumed that λ does not change with variation of g^2 and M^2.) Such an interaction model is quite satisfactory in investigations of the thermal conductivity, first viscosity, and diffusion as functions of the magnetic field, but needs to be made much more precise for an analysis of second viscosity.

3. THERMAL CONDUCTIVITY OF PARAMAGNETIC GAS. THE SENFTLEBEN EFFECT

1. In the thermal conductivity problem, the expression for χ can be represented in the form

$$\chi = -\sqrt{2kT/m}\,\boldsymbol{\chi}\nabla\ln T. \qquad (3.1)$$

The corresponding kinetic equation is written

$$-u_i(u^2+M^2-{}^7\!/_2)f^{(0)}+\gamma f^{(0)}[\mathbf{MH}]\,\partial\chi_i/\partial\mathbf{M}=J_{\text{col}}(\chi_i) \qquad (3.2)$$

Starting from this expression, we shall take **u** and **M** to mean everywhere dimensionless quantities that differ from the preceding quantities by the factors $\sqrt{m/2kT}$ and $\sqrt{1/2IkT}$, respectively.

We expand the function χ in irreducible tensors made up of **u** and **M**:

$$\chi_i(\mathbf{u},\mathbf{M},\sigma)$$
$$=\sum_{p,q}T^{pq}_{ik_1\ldots k_{p+q}}[u_{k_1}\ldots u_{k_p}][M_{k_{p+1}}\ldots M_{k_{p+q}}], \qquad (3.3)$$

where the square brackets denote the corresponding irreducible tensors. The expansion coefficients (3.3) are functions of u^2, M^2, and of the index σ, and can in turn be expanded in the orthogonal polynomials

$$T^{pq}_{ik_1\ldots k_{p+q}}=\sum_{st}T^{pqst}_{ik_1\ldots k_{p+q}}S^{(s)}_{{}^1\!/_2p+1}(u^2)\,S^{(t)}_{{}^1\!/_2q}(M^2), \qquad (3.3a)$$

where $S_n^{(m)}$ are Sonin polynomials of index n. The coefficients in the expansion (3.3a) depend only on the discrete variable σ.

From the form of (3.2) it follows that χ is an odd function in **u** and an even function in **M**. This means that the only nonvanishing coefficients in (3.3) are those with odd p and even q.

The conditions (2.11′) leads to the single relationship

$$T^{1000}_{ik}=0.$$

Let us write down the equation for the heat flow

$$q_i\equiv-\varkappa_{ik}(\nabla T)_k=kT\sqrt{\frac{2kT}{m}}\int f^{(0)}\chi u_i(u^2+M^2)d\Gamma^*.$$

Using (3.1), (3.3), and (3.3a) we obtain for the thermal conductivity tensor, in the general case,

$$\varkappa_{ik} = k(2kT/m)\left(\tfrac{5}{4}\,\overline{T}^{1010}_{ki} + \tfrac{1}{2}\,\overline{T}^{1001}_{ki}\right),$$

$$\overline{T} = \frac{1}{2S+1}\sum_{\sigma} T(\sigma). \tag{3.4}$$

Thus, the thermal conductivity tensor is determined in terms of two coefficients of the expansion (3.3) averaged over σ.

Let us proceed to find the approximate solution of (3.2). For this purpose we confine ourselves in (3.3) to terms with $p = 1$ and $q \leq 2$, and in (3.3a) we retain the first nonvanishing terms. Then

$$\chi_i = T^1_{ik}\psi^1_k + T^2_{ik}\psi^2_k + T^3_{iklm}\psi^3_{klm}, \tag{3.5}$$

$$\psi^1_k = u_k(u^2 - {}^5/_2), \qquad \psi^2_k = u_k(M^2 - 1),$$

$$\psi^3_{klm} = u_k(M_l M_m - {}^1/_3\delta_{lm} M^2), \tag{3.6}$$

$$T^1 = T^{1010}, \qquad T^2 = T^{1001}, \qquad T^3 = T^{1200}. \tag{3.7}$$

If we substitute (3.3) into (3.2), we can readily verify that the only components of (3.3) contributing to the term containing the magnetic field are those with $q \neq 0$. On the other hand, a detailed analysis shows that an account of the terms with $q > 0$ and $p > 1$ in (3.3) yields for the thermal conductivity corrections that are proportional to the nonsphericity parameter raised to the power $q + 2(p - 1)$. Since the sphericity is assumed from the very outset to be small, the limitation (3.5) concerning p and q is of an obvious character [the approximation (3.5) is actually quadratic in λ]*.

The fact that terms with high values of s and t are discarded in (3.5) is not connected with any explicit smallness parameter. Nonetheless, as is well known, it usually turns out that these terms are numerically small. We shall later on (Sec. 4) refine (3.5), taking account of the terms of next higher order in t for $q = 2$.

2. To find the coefficients in (3.5) we multiply (3.2) by each of the functions (3.6) and integrate over the phase volume (without averaging over the discrete variable σ [see (2.13)]. As a result we arrive at the system

$$\tfrac{5}{4}\, n\delta_{ik} = T^1_{ik}A^{11} + \overline{T}^1_{ik}B^{11} + 2\,(T^3_{illk} - \overline{T}^3_{illk})\,A^{13},$$

$$\tfrac{1}{2}\, n\delta_{ik} = T^2_{ik}A^{22} + 2T^3_{illk}A^{23},$$

$$-\xi T_{iklm}\,H_{lmnp} = (T^1_{il} - \overline{T}^1_{il})\,\Delta_{lknp}\,A^{13}$$

$$+ T^2_{il}\Delta_{lknp}A^{23} + 2T^3_{iknp}A^{33}. \tag{3.8}$$

Here

$$\Delta_{iklm} = -\tfrac{2}{3}\,\delta_{ik}\delta_{lm} + \delta_{il}\delta_{km} + \delta_{im}\delta_{kl},$$

$$H_{iklm} = h_{il}\delta_{km} + h_{im}\delta_{kl} + h_{kl}\delta_{im} + h_{km}\delta_{il},$$

$$h_{ik} = \varepsilon_{ikl}H_l/H,$$

$$\xi(\sigma) = n(\sqrt{\pi}\mu_0/20\sqrt{2kTI})\,H\sigma, \tag{3.9}$$

where ε_{ikl} is a unit antisymmetrical tensor.

In the calculation of the term with the magnetic field in (3.8) we took account of the dependence of the coefficient on the rotational momentum M [see (2.5)]. An explicit expression for $A^{\alpha\beta}$ and $B^{\alpha\beta}$ is given in Appendix A.

3. We present the solutions of (3.8) in the form

$$T^\alpha = X^\alpha + Y^\alpha(\mathbf{H}), \tag{3.10}$$

where X^α is independent of **H** and $Y^\alpha(0) = 0$. We consider first the case $\mathbf{H} = 0$. We seek the tensors X^α in the form

$$X^1_{ik} = X_1\delta_{ik}, \quad X^2_{ik} = X_2\delta_{ik}, \quad X^3_{iklm} = X_3\Delta_{iklm}.$$

(In the absence of a magnetic field, $T^\alpha = X^\alpha$ are independent of the discrete variable.) From (3.8) we obtain

$$X_1 = \frac{5}{4}\,\frac{n}{A^{11} + B^{11}}, \qquad X_2 = \frac{1}{2}\,\frac{n}{A^{22}}\left[1 - \frac{10}{3}\,\frac{(A^{23})^2}{A^{22}A^{33}}\right]^{-1},$$

$$X_3 = -A^{23}X_2/2A^{33}. \tag{3.11}$$

The coefficients X_1 and X_2 determine the thermal-conductivity tensor in the absence of a magnetic field [see (3.4)]:

$$(\varkappa_{ik})_{H=0} = \varkappa_0\delta_{ik}, \qquad \varkappa_0 = nk(2kT/m)\left(\tfrac{5}{4}\,X_1 + \tfrac{1}{2}\,X_2\right). \tag{3.4'}$$

4. Let now the magnetic field differ from zero. Substituting (3.10) into (3.8) we arrive at a system of equations for Y^α:

$$0 = Y^1_{ik}A^{11} + \overline{Y}^1_{ik}B^{11} + 2\,(Y^3_{illk} - \overline{Y}^3_{illk})\,A^{13},$$

$$0 = Y^2_{ik}A^{22} + 2Y^3_{illk}A^{23}. \tag{3.12}$$

As shown in Appendix A, when $\lambda \gtrsim 1$ the nondiagonal elements of the matrix $A^{\alpha\beta}$ are small compared with the diagonal elements. From the first two equations of (3.12) we can conclude that $Y^2_{ik} \sim Y^3_{illk}A^{23}/A^{22}$ and $Y^1_{ik} \sim Y^3_{iilk}A^{13}/A^{11}$. We can certainly then neglect in (3.12) the first two terms on the right side. We obtain thus an equation for Y^3_{iklm} in closed form:

$$Y^3_{iknp}A^{33} + \tfrac{1}{2}\,\xi Y^3_{iklm}\,H_{lmnp} = -\xi X_3 H_{iknp}. \tag{3.13}$$

The thermal-conductivity tensor (3.8) includes the tensors Y^1_{ik} and Y^2_{ik}, averaged over the discrete variable. Averaging the first two equations in (3.12) over σ, we obtain

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*We note that actually the nonsphericity parameter employed is not λ [see (2.14)], but at least $\lambda/5$.

$$\overline{Y}^1_{ik} = 0, \qquad \overline{Y}^2_{ik} = -2A^{23}\overline{Y}^3_{illk}/A^{22}. \tag{3.14}$$

Thus, the thermal conductivity depends only on that part of the tensor $Y^3_{ikl m}$ which is even in σ. Taking this into account, we seek a solution of (3.13) by writing for the tensor Y^3_{iklm}

$$\mathbf{Y}^3 = \mathbf{Y}^+ + \mathbf{Y}^-, \tag{3.15}$$

where $\mathbf{Y}^+$ and $\mathbf{Y}^-$ are respectively even and odd in σ.

Starting with (3.15), we shall use the convenient symbol **L** to denote fourth-rank tensors, and the product of two tensors **LM** will again be taken to be a tensor of fourth rank with components

$$L_{iklm} M_{lmnp}. \tag{3.16}$$

Using this notation, we rewrite (3.13) in the form

$$A^{33}(\mathbf{Y}^+ + \mathbf{Y}^-) + \tfrac{1}{2}\xi(\mathbf{Y}^+ + \mathbf{Y}^-)\mathbf{H} = -\xi X_3\mathbf{H}.$$

This equation separates into two:

$$A^{33}\mathbf{Y}^+ + \tfrac{1}{2}\xi\mathbf{Y}^-\mathbf{H} = 0, \tag{3.17}$$

$$A^{33}\mathbf{Y}^- + \tfrac{1}{2}\xi\mathbf{Y}^+\mathbf{H} = -\xi X_3\mathbf{H}. \tag{3.18}$$

We took account here of the fact that ξ is a linear function of the variable σ [see (3.9)].

Multiplying (3.18) from the right by $\xi\mathbf{H}$ and using (3.17) we obtain an equation for $\mathbf{Y}^+$ in closed form:

$$-(A^{33})^2\mathbf{Y}^+ + \tfrac{1}{4}\xi^2\mathbf{Y}^+\mathbf{H}^2 = -\tfrac{1}{2}\xi^2 X_3\mathbf{H}^2. \tag{3.19}$$

It can be shown (see Appendix B) that

$$\mathbf{H}^6 = -4(5\mathbf{H}^4 + 16\mathbf{H}^2). \tag{3.20}$$

Using this equation to solve (3.19), we get

$$\mathbf{Y}^+ = c_1\mathbf{H}^2 + c_2\mathbf{H}^4, \tag{3.21}$$

$$c_1 = \frac{\eta^2(1+5\eta^2)}{2(1+\eta^2)(1+4\eta^2)} X_3,$$

$$c_2 = \frac{\eta^4}{8(1+\eta^2)(1+4\eta^2)} X_3, \tag{3.22}$$

$$\eta = \xi/A^{33}. \tag{3.23}$$

According to (3.14) we must contract $\mathbf{Y}^+$ about the two internal indices. Using the contractions of the tensors H^2 and H^4, written out in the Appendix B, we can readily obtain

$$Y^+_{illk} = (c_1'\delta_{ik} + c_2' H_i H_k/H^2) X_3, \tag{3.24}$$

$$c_1' = -\frac{3\eta^2(3+4\eta^2)}{(1+\eta^2)(1+4\eta^2)}, \qquad c_2' = \frac{\eta^2(7+4\eta^2)}{(1+\eta^2)(1+4\eta^2)}. \tag{3.25}$$

The expression (3.24) is the solution of our problem. Indeed, substituting (3.24) into (3.14) and using (3.4), (3.7), (3.10), and (3.11) we obtain directly a general expression for the thermal-conductivity tensor. Separating from this tensor only the part dependent on the magnetic field, and taking (3.4′) into account, we get

$$\Delta\varkappa_{ik} = \varkappa_{ik} - (\varkappa_{ik})_{H=0}$$

$$= \varkappa_0 \frac{\psi}{2S+1} \sum_{\sigma} \left(c_1'\delta_{ik} + c_2' \frac{H_i H_k}{H^2} \right), \tag{3.26}$$

$$\psi = \frac{(A^{23})^2}{A^{22}A^{33}} \left\{ 1 + 5\frac{A^{22}}{A^{11}+B^{22}} \left[1 - \frac{10}{3}\frac{(A^{23})^2}{A^{22}A^{33}} \right] \right\}^{-1}. \tag{3.27}$$

The expressions in (3.26), (3.27), and (3.25) describe the Senftleben effect completely.

4. DISCUSSION OF RESULTS

The expressions obtained show that in a paramagnetic gas in the presence of a magnetic field, the coefficient of thermal conductivity becomes anisotropic. This causes the thermal conductivity to have different values when the magnetic field is parallel and perpendicular to the temperature gradient. Moreover, when the angle between the vectors **H** and ∇T differs from 0 to 90°, a heat-flow component exists in a direction perpendicular to the temperature gradient.

The character of the dependence of the tensor $\Delta\kappa_{ik}$ on the magnetic field and on the pressure is completely determined by (3.25), where the value of η is [see (3.22) and (3.9)]

$$\eta = \frac{\sqrt{\pi}}{20} \frac{\mu_0 k n^2 \sqrt{T}}{\sqrt{2kI}\, A^{33}} \frac{H}{p}\sigma. \tag{4.1}$$

It follows from (4.1) that at a fixed temperature the effect depends only on the ratio H/p, which coincides with the main experimental result obtained in[2]. The temperature dependence at fixed H/p is determined in (4.1) by the ratio $n^2\sqrt{T}/A^{33}$.

It is shown in Appendix A that $A^{33} \sim \Omega^{11}n^2$ and consequently the temperature dependence is essentially connected with the form of the molecule scattering cross section. Thus, for the solid-sphere model $\Omega^{11} \sim T^{1/2}$ and (4.1) is completely independent of T. In the case of Maxwellian molecules ($U \sim r^{-4}$), Ω^{11} is independent of the temperature and $\eta \sim T^{1/2}$. The true character of the interaction will lead, as a rule, to an intermediate dependence, that is, $\sim T^n$, where $0 \leq n \leq 1/2$.

The overwhelming majority of the experiments on the determination of the thermal conductivity of a pagamagnetic gas were carried out with oxygen. From the temperature dependence of the ordinary ($H = 0$) kinetic coefficients for O_2 (see, for example,[8]), we can conclude that Ω^{11} is independent of T. Consequently, the character of relative variation of $\Delta\kappa_{ik}$ should depend in practice on the combination $H\sqrt{T}/p$, as was indeed observed experimentally.[2]

Let us examine the variations of the thermal-conductivity coefficients in the case when **H** is parallel and perpendicular to ∇T.

From (3.26) we obtain

$$\frac{\Delta\varkappa_\perp}{\varkappa_0} = \frac{\psi}{2S+1}\sum_\sigma c_1'', \qquad \frac{\Delta\varkappa_\parallel}{\varkappa_0} = \frac{\psi}{2S+1}\sum_\sigma (c_1' + c_2'). \quad (4.2)$$

From (3.27) and (3.25) it follows that at all values of η

$$\Delta\varkappa_\perp/\varkappa_0 < 0, \qquad \Delta\varkappa_\parallel/\varkappa_0 < 0. \quad (4.3)$$

At sufficiently large values saturation sets in, and both quantities attain the following absolute maxima

$$\left(\frac{\Delta\varkappa_\perp}{\varkappa_0}\right)_\infty = -\frac{2S}{2S+1}3\psi,$$

$$\left(\frac{\Delta\varkappa_\parallel}{\varkappa_0}\right)_\infty = -\frac{2S}{2S+1}2\psi. \quad (4.4)$$

Hence

$$(\Delta\varkappa_\parallel/\Delta\varkappa_\perp)_\infty = {}^2/_3, \quad (4.5)$$

which is in splendid agreement with Senftleben's experiments.

From expressions (3.26) and (3.27), and also from formulas (A.5) of Appendix A, it can be concluded that the change in the thermal conductivity in a magnetic field is completely connected with the nonsphericity of the interaction, and that $\Delta\kappa_{ik} \sim \lambda^2$. If we use (4.3), we can readily relate the parameter with the value $(\Delta\kappa/\kappa_0)_\infty$ which is independent of the magnetic field and of the pressure. Comparison with experiments shows that in the case of oxygen λ is close to unity. As already indicated, the actual expansion parameter is a quantity smaller than $\lambda/5$, and all the assumptions made above remain in force.

Let us examine the region of small values of η. Then

$$\left(\frac{\Delta\varkappa_\perp}{\varkappa_0}\right)_{H\to 0} = -\frac{9\psi}{2S+1}\sum_\sigma \eta^2,$$

$$\left(\frac{\Delta\varkappa_\parallel}{\varkappa_0}\right)_{H\to 0} = -\frac{2\psi}{2S+1}\sum_\sigma \eta^2. \quad (4.6)$$

In the case of oxygen S = 1 and (4.6) goes into

$$(\Delta\varkappa_\perp/\varkappa_0)_{H\to 0} = -6\psi\eta_1^2,$$

$$(\Delta\varkappa_\parallel/\varkappa_0)_{H\to 0} = -\frac{4}{3}\psi\eta_1^2, \quad (4.6')$$

where $\eta_1 = (\eta)_{\sigma=1}$.

The dependence of (4.6′) on the magnetic field and on the pressure coincides with the experimentally observed one. Bearing in mind a comparison of the absolute values of the calculated and measured coefficients, we have increased the number of terms in (3.5), taking in (3.3a) the terms of higher order in M^2 with q = 2 (specifically the terms responsible for the effect and connected with the magnetic field). The term with t = 1 [see (3.3a)] introduces a correction which is still noticeable, whereas inclusion of t = 2 changes the results very little. The calculation procedure obviously remains the same, and we shall only give the final results.

Inclusion of the term with t = 1 changes the numerical coefficients in (4.4) by a factor $^4/_3$, and a multiplier 25/36 appears in the coefficients from (4.6). We then have for the ratio $(\Delta\kappa_\perp)_{H\to 0}/(\Delta\kappa_\perp)_\infty$ a value

$$(\Delta\varkappa_\perp)_{H\to 0}/(\Delta\varkappa_\perp)_\infty = 25\eta^2/16 = a^2(H/p)^2.$$

We have calculated a for oxygen, using the well known value $\hbar^2/2Ik = 2.1°$ K and determining Ω^{11} from the value of the self-diffusion coefficient.[8] If H is in gausses and p in mm Hg, we obtain a ≈ 2.5. The corresponding experimental value is close to 1.7. If we recognize that the number of terms included in (3.3a) is small, and if we bear in mind in particular the differential term in (3.2), the agreement of the results should be regarded as satisfactory.

APPENDIX A

Let us determine the coefficients in the right half of the system (3.8). We integrate the collision integral with one of the functions ψ^α (3.6):*

$$-\int d\Gamma\psi_k^\alpha J_{\mathrm{col}}(\chi_i) = -\langle\psi_k^\alpha(\chi_i' + \bar{\chi}_{1i}' - \chi_i - \bar{\chi}_{1i})\rangle. \quad (A.1)$$

We introduce here the symbol $<\Phi>$ for the integral

$$\sqrt{\frac{4kT}{m}}\int d\Gamma d\Gamma_1 f^{(0)} f_1^{(0)} w g d\sigma \Phi, \quad (A.2)$$

where g is a dimensionless relative velocity. In (A.1) we averaged in explicit form over the discrete variable of particle 1. Using the well known symmetry properties of the integrand of (A.2) we can transform the integral of (A.1) to the form

$$\sum_\rho T_{il}^\beta A_{kl}^{\alpha\beta} + \sum_\beta \bar{T}_{il}^\beta B_{kl}^{\alpha\beta}; \quad (A.3)$$

$$A_{kl}^{\alpha\beta} = \frac{1}{2}\langle[(\psi_k^\alpha)' - \psi_k^\alpha][(\psi_l^\beta)' - \psi_l^\beta]\rangle,$$

$$B_{kl}^{\alpha\beta} = \frac{1}{2}\langle[(\psi_k^\alpha)' - \psi_k^\alpha][(\psi_l^\beta)_1' - (\psi_l^\beta)_1]\rangle, \quad (A.4)$$

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*It must be remembered that the function ψ^3 has three indices

$$\psi_{\mathbf{k}}^3 \equiv \psi_{\mathbf{k}_1\mathbf{k}_{23}\mathbf{H}}^3.$$

with

$$A^{\alpha\beta}_{kl} = A^{\beta\alpha}_{lk}, \qquad B^{\alpha\beta}_{kl} = B^{\beta\alpha}_{lk}.$$

The coefficients of (A.4) can be directly calculated for the model of (2.14):

$$A^{11}_{ik} = A^{11}\delta_{ik},$$

$$A^{11} = \tfrac{1}{3}n^2\left(\frac{55}{4}\Omega^{11} - 5\Omega^{12} + \Omega^{13} + 2\Omega^{22}\right),$$

$$B^{11}_{ik} = B^{11}\delta_{ik},$$

$$B^{11} = \tfrac{1}{3}n^2\left(-\frac{55}{4}\Omega^{11} + 5\Omega^{12} - \Omega^{13} + 2\Omega^{22}\right),$$

$$A^{12}_{ik} = B^{12}_{ik} = B^{22}_{ik} = 0, \qquad A^{22}_{ik} = A^{22}\delta_{ik}, \quad A^{22} = \tfrac{4}{3}n^2\Omega^{11};$$

$$A^{13}_{ik_1k_2k_3} = -B^{13}_{ik_1k_2k_3} = A^{13}\Delta_{ik_1k_2k_3},$$

$$A^{13} = \tfrac{1}{25}\lambda n^2\left[\tfrac{4}{3}\left(-\tfrac{5}{2}\Omega^{11} + \Omega^{12}\right) + \left(\tfrac{5}{2}\Omega^{21} - \Omega^{22}\right)\right],$$

$$A^{23}_{ik_1k_2k_3} = A^{23}\Delta_{ik_1k_2k_3}, \qquad A^{23} = \frac{2}{25}\lambda n^2\left(\tfrac{4}{3}\Omega^{11} - \Omega^{21}\right),$$

$$B^{23}_{ik_1k_2k_3} = 0, \qquad A^{33}_{i_1i_2i_3k_1k_2k_3} = A^{33}\left(\delta_{i_1k_1}\Delta_{i_2i_3k_2k_3} + \tfrac{1}{35}\lambda D_{i_1k_1i_2k_2i_3k_3}\right),$$

$$A^{33} = \tfrac{2}{15}A^{22}. \qquad \text{(A.5)}$$

The numerical coefficients in (A.5) are determined in terms of standard integrals of the kinetic theory of monatomic gases (see[8]),

$$\Omega^{(l,s)} = \sqrt{\frac{kT}{\pi m}}\int e^{-g^2}g^{2s+3}(1-\cos^l\theta)\,d\sigma dg. \qquad \text{(A.6)}$$

The tensor Δ_{iklm} has been defined in the text [see (3.9)]. The sixth-rank tensor D_{hiklmn} is symmetrical within the index pairs hi, k*l*, mn, and vanishes upon contraction in any of these pairs.

The tensor $A^{33}{}_{i_1i_2i_3k_1k_2k_3}$ makes the following contribution to (A.3):

$$T^{33}_{il_1l_2l_3}A^{33}_{k_1k_2k_3l_1l_2l_3}$$

$$= 2A^{33}\left\{T^{3}_{ik_1k_2k_3} + \tfrac{1}{35}\lambda\left[-\tfrac{4}{3}T_{ik_1k_2k_3} + T_{ik_3k_2k_1} + T_{ik_2k_3k_1} - \tfrac{4}{3}T_{illk_1}\delta_{k_2k_3} + T_{illk_2}\delta_{k_1k_3} + T_{illk_3}\delta_{k_1k_2}\right]\right\}. \qquad \text{(A.7)}$$

We have neglected in the text terms proportional to λ/35 in (A.7).

APPENDIX B

The powers of the tensor H can be readily calculated with the aid of tensors of the form

$$F^{\alpha\beta}_{iklm} \equiv F(f^{\alpha}_{ik};\ f^{\beta}_{lm}) = f^{\alpha}_{il}f^{\beta}_{km} + f^{\alpha}_{im}f^{\beta}_{kl} + f^{\alpha}_{kl}f^{\beta}_{im} + f^{\alpha}_{km}f^{\beta}_{il},$$

$$\alpha, \beta = 0, 1, 2, \qquad \text{(B.1)}$$

where

$$f^0_{ik} = \delta_{ik}, \quad f^1_{ik} = h_{ik}, \quad f^2_{ik} = h_{il}h_{lk} = -\delta_{ik} + H_iH_k/H^2. \qquad \text{(B.2)}$$

The tensors (B.1) have the symmetry properties

$$F^{\alpha\beta}_{iklm} = F^{\alpha\beta}_{kilm} = F^{\alpha\beta}_{ikml} = F^{\beta\alpha}_{iklm}. \qquad \text{(B.3)}$$

The product of two tensors given by (B.1) is

$$F^{\alpha\beta}_{ikst}F^{\gamma\delta}_{stlm} = 2\left[F(f^{\alpha}_{is}f^{\gamma}_{sk};\ f^{\beta}_{lt}f^{\delta}_{tm}) + F(f^{\alpha}_{is}f^{\delta}_{sk};\ f^{\beta}_{lt}f^{\gamma}_{tm})\right]. \qquad \text{(B.4)}$$

Using (B.4), we obtain

$$\mathbf{H} = \mathbf{F}^{01}, \qquad \mathbf{H}^2 = 2(\mathbf{F}^{02} + \mathbf{F}^{11}),$$

$$\mathbf{H}^4 = -4\mathbf{H}^2 + 24(\mathbf{F}^{22} - \mathbf{F}^{11}),$$

$$\mathbf{H}^6 = -4(5\mathbf{H}^4 + 16\mathbf{H}^2). \qquad \text{(B.5)}$$

The thermal-conductivity tensor includes the tensors $\mathbf{H}^2$ and $\mathbf{H}^4$, contracted in the internal indices

$$(\mathbf{H}^2)_{illk} = 2(-9\delta_{ik} + 7H_iH_k/H^2),$$

$$(\mathbf{H}^4)_{illk} = 8(33\delta_{ik} - 31H_iH_k/H^2). \qquad \text{(B.6)}$$

In calculations with more terms than in (3.5), it is best to use instead of powers of the tensor **H** the tensors

$$\mathbf{G}_1 = \mathbf{F}^{02} + \mathbf{F}^{22}, \qquad \mathbf{G}_2 = \tfrac{1}{4}(\mathbf{F}^{11} - \mathbf{F}^{22}),$$

which are the eigenfunctions of the operator $\mathbf{H}^2$:

$$\tfrac{1}{4}\mathbf{G}_1\mathbf{H}^2 = -\mathbf{G}_1, \quad \tfrac{1}{4}\mathbf{G}_2\mathbf{H}^2 = -4\mathbf{G}_2.$$

The tensor $\mathbf{H}^2$ is connected with these tensors by the relation

$$\mathbf{H}^2 = \mathbf{G}_1 + 4\mathbf{G}_2.$$

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Translated by J. G. Adashko
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