Investigation of the thermomagnetic effect in a Knudsen gas at low temperatures

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Results are presented of an investigation of the thermomagnetic effect in the gases N_2 and CO interacting with the surface of platinum at temperatures 77–320 K. The dependence of the effect on the gas pressure was studied. The effect was investigated also under conditions of simultaneous physical adsorption of N_2 and Xe molecules. A change in the sign of the effect was observed at a definite Xe concentration on the surface.

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I. INTRODUCTION

The thermomagnetic effect (TME) consists in the change in a magnetic field, of the heat flux through a Knudsen ($Kn \gg 1$; $Kn = \lambda/L$, where λ is the molecule mean free path and L is a characteristic dimension) gas located in a gap between two plane-parallel plates with different temperatures.[1] This effect is due to the nonspherical character of the inelastic interaction of the molecules with the surface of the solid, which leads to the appearance of nonequilibrium polarization in the space of the velocities (**v**) and angular momenta (**M**) of the molecules. When the magnetic field is turned on, the precession of the molecules causes a partial destruction of this polarization, namely, averaging of the orientations of the vector (**M**) in a plane perpendicular to the field direction. This leads to a change of the nonequilibrium distribution function $f(\mathbf{v}, \mathbf{M})$ in the field, and consequently to a change of the heat flux Q through the gas. The value of ΔQ is determined by the dimensionless parameter $\omega\tau$ ($\omega = \gamma H$ is the precession frequency, $\tau = L/\bar{v}$ is the average time of travel of the molecule between the walls).

The TME was investigated in a number of gases (N_2, O_2, CO, CO_2) interacting with the gold and platinum surfaces at room temperatures.[2,3] The damped oscillations of the heat flux, theoretically predicted by the theory of the effect, were observed. For all the investigated gas-surface systems, the heat flux decreased in the field. The authors of Ref. 4 have previously observed an anomalous sign of the effect ($\Delta Q > 0$) in the N_2-Au system at a surface temperature $T \approx 100$ K. The causes of the reversal of the sign of the effect on going to low temperatures are not clear. Interest in further investigations of the TME at low temperatures is due to the possibility of explaining the differences between the molecule-surface interaction mechanisms that cause the molecules to be polarized in a gas at temperatures $T \approx 300$ and ≈ 100 K.

At temperatures close to the boiling point of the gas and at sufficiently high pressures, a layer of physically adsorbed molecules is produced on the surface. The polarization of the gas molecules scattered by such a layer (and consequently also the dependence of $\Delta Q/Q$ on H) can change in comparison with the polarization observed at $T > T_{\text{boil}}$, when the physical adsorption can be neglected.[2] Likewise, when the temperature of the wall is lowered, the average lifetime of the molecules in the adsorbed state increases substantially (e.g., at $T = 77$ K, for adsorption of nitrogen on platinum, t_{lt} 10^{-3}–10^{-4} sec). At such long lifetimes of the molecules on the wall, they can diffuse over the surface in the two-dimensional adsorption layer[5] and the polarization of the molecules that are emitted from such a layer is obviously connected with the directional anisotropy of the angular momentum of the molecules in the adsorbed layer.

We present below the results of an investigation of the TME in nitrogen and in carbon monoxide interacting with the surface of platinum in the temperature range 77–320 K. In particular, the dependence of the magnitude of the effect on the gas pressure in the gap were studied and investigations were performed under conditions of simultaneous adsorption of different molecules (Xe, N_2) on the surface.

II. RESULTS OF EXPERIMENTAL INVESTIGATION

The experiments were performed with a setup similar to that described earlier in Refs. 2 and 4. In the experiments we measured the change, in a field, of the heat flux through a gas located in a gap between two plane-parallel plates (gap $L = 2$ mm) with different temperatures. The "hot" plate was made of thin mica (thickness 5×10^{-3} mm) on both sides of which U-shaped layers of platinum were sputtered. The current flowing through the sputtered layer heated the plate to a temperature $T_{\text{hot}} = 95$–320 K as determined from the resistance of this layer. The "cold" plates, between which the hot plate was placed symmetrically, was made of brass (5 mm thick). The inner surfaces of the plates were polished and were also coated with a sputtered layer of platinum. The cold plates were clamped between two copper plates to which copper tubes were brazed. The temperature T_{cold} was determined with a platinum resistance thermometer secured between the brass and copper plates. Experiments have shown that when liquid nitrogen circulated through the tubes, the readings of the resistance thermometer differed from 77.3 K by 1–2° (depending on T_{hot}). The plate surfaces were treated before the experiments at a temperature 500 K in an oxygen atmosphere.

Figure 1 shows plots of the relative change of the heat flux $\Delta Q/Q$ in the nitrogen vs the magnetic field

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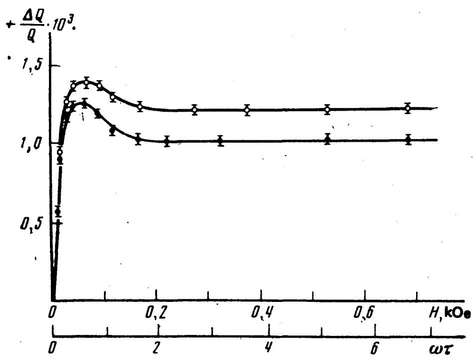

FIG. 1. $T_{\rm cold}\approx 77$ K, $T_{\rm hot}=198$ K, $p=1\times 10^{-3}$ Torr, Kn ≈ 12, k is the vector normal to the surface, H⊥k (●), H∥k (○).

intensity H for the cases H⊥k and H∥k. It is seen from the figure that when H is increased $\Delta Q/Q$ reaches a maximum value $(\Delta Q/Q)_{\rm max}$ and tends next to a limiting value $(\Delta Q/Q)_{\rm sat}$.

In contrast to the results obtained at $T_{\rm cold}\approx 300$ K (see Ref. 2), the following distinguishing features of the effect were observed. The sign of the effect became positive, i.e., when the magnetic field was turned on the heat flux increased. The anisotropy of the effect $(\Delta Q^{\perp}/\Delta Q^{\parallel})_{\rm sat}$ decreased from ≈ 2.2 to ≈ 0.9. We note also that at $T_{\rm cold}\approx 300$ K the change of the heat flux (in absolute value) reached a maximum at $(\omega\tau)^{\perp}_{\rm max}\approx 2$ at H⊥k and $(\omega\tau)^{\parallel}_{\rm max}\approx 3$ at H∥k, while at low temperatures at the maximum was reached $\omega\tau\approx 0.7$, with $(\omega\tau)^{\perp}_{\rm max}\approx(\omega\tau)^{\parallel}_{\rm max}$. The relative change of the heat flux also decreased. For example, in a field H⊥k we obtained $|(\Delta Q/Q)_{\rm sat}|=(3.8\pm 0.2)\times 10^{-3}$ at $T_{\rm cold}\approx 300$ K and $|(\Delta Q/Q)|_{\rm sat}=(1.0\pm 0.1)\times 10^{-3}$ at $T_{\rm cold}\approx 77$ K. The foregoing features were observed also for carbon monoxide. Plots of $\Delta Q^{\perp}/(QH)$ and $\Delta Q^{\parallel}/Q(H)$ for CO are shown in Fig. 2.

The Senftleben effect was also investigated earlier at low temperatures. In Ref. 6 was investigated the change of the thermal conductivity coefficient of nitrogen in a magnetic field at $T=85$ K. It turned out that the effect, just as at room temperature, is negative (when the field is turned on the heat flux decreases). It was therefore of interest to investigate the dependence of the change of the heat flux in a field at various pressures. Plots of $\Delta Q/Q(H)$ for N_2 at different pressures are shown in Fig. 3. At a pressure $p=1.5\times 10^{-3}$ Torr (Kn ≈ 8) the heat-transfer was nearly free-molecular and therefore the plot of $\Delta Q/Q(H)$ is similar to that shown in Fig. 1. With increasing pressure, the number of molecules colliding with one another on moving from wall to wall increases. In the heat-transfer transition regime ($p=3\times 10^{-3}$ Torr, Kn ≈ 4), the dependence of $\Delta Q/Q$ on H becomes alternating in sign. The presence of a maximum of $\Delta Q/Q$ at $H\approx 70$ Oe, together with the negative value $(\Delta Q/Q)_{\rm sat}\approx -1.35\times 10^{-4}$, points to the existence of two contributions to the effect. These contributions are connected with energy transported by the molecules that move from wall to wall without colliding with one another, and by the molecules that experience collisions. On going to a continuous medium, the effect becomes negative in the entire range of the magnetic field (see curves 3 and 4 of Fig. 3), and at $p=1$ Torr (Kn ≈ 0.01) the plots of $\Delta Q/Q(H)$ assume the shape typical of the Senftleben effect in nitrogen at low temperatures.[6] The results indicate that the positive sign of the effect is due to the scattering of the gas molecules by the wall.

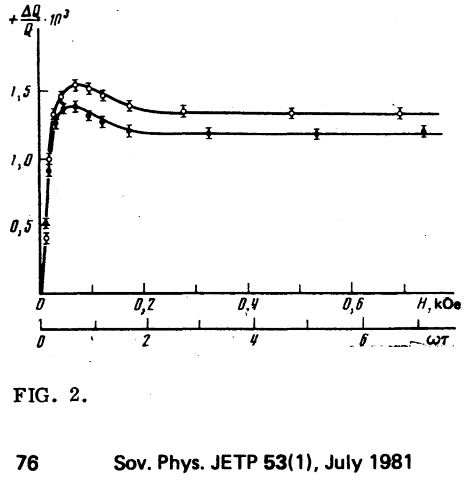

FIG. 2.

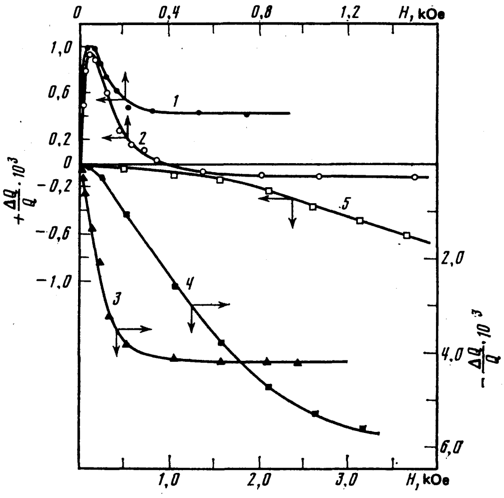

FIG. 3.

We ascertain now the degree ϑ of filling of the surface by the physically adsorbed molecules under the conditions of the performed experiment. The value of ϑ can be estimated from the relation[7] from the relation[7]

$$\vartheta=\alpha\xi(1+\alpha\xi)^{-1};\quad \xi=n\bar{v}r_0^2t,\quad t=t_0\exp(-E_a/T),\tag{1}$$

where α is the molecule adhesion coefficient, n is the gas molecule-number density, $\bar{v}$ is their average velocity, r_0 is the effective radius of the intermolecular forces, and t is the average adsorption time. In the case of physical adsorption of nitrogen by a platinum surface, $E_a=3.38$ kcal/mol[8] and in accordance with (1) we have $\vartheta\sim 1$ at $p=1\times 10^{-3}$ Torr, a temperature $T=77$ K, and $r_0^2\sim 10^{-15}$ cm². It is seen from (1) that the value of ϑ can be changed by several orders of magnitude by varying the temperature. Taking into account the strong dependence of the degree of filling on T, we can expect a change in the character of the nonspherical scattering of the molecules from the surface when the

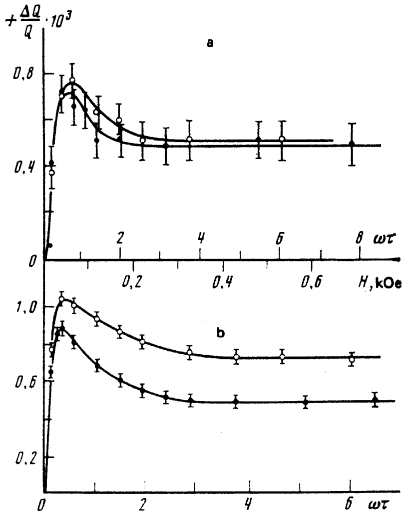

FIG. 4.

surface temperature is changed, and consequently changes in the $\Delta Q/Q(H)$ dependences.

We have performed in this connection experiments in which the temperature of the cold surfaces was maintained constant, and the temperature T_{hot} was varied in the range 95–320 K. It follows from Fig. 4 that although the plots of $\Delta Q/Q$ against H for nitrogen are similar at $T_{hot} = 95$ K and $T_{hot} = 292$ K, the anisotropy of the effect differs substantially. Thus, at $T_{hot} = 95$ K this quantity amounts to $(\Delta Q^{\parallel}/\Delta Q^{\perp})_{sat} \approx 1$, and $T_{hot} = 292$ K it increases to 1.5.

It was also observed as a result of the experiments that the parameters of the TME are greatly changed in the presence of physically adsorbed molecules of another kind on the surface. This was established in an investigation of the TME under conditions of simultaneous physical adsorption of nitrogen and xenon molecules. Xenon was chosen for the following reasons. At $T = 77$ K the saturated vapor pressure of Xe is $p_0 \approx 2 \times 10^{-3}$ Torr, i.e., low enough to ensure nearly monolayer coatings at small partial pressures of the xenon in the mixture ($p_{Xe}/p_{N_2} \ll 1$). This in turn makes it possible to realize in the gap close to free-molecular heat-transfer. Being a monatomic gas, xenon does not contribute to the TME, i.e., the presence of the Xe molecules in the gap at Kn ≫ 1 does not influence the $\Delta Q/Q(H)$ dependence for N_2.

The required degrees of filling the surface with Xe atoms were obtained by the following procedure. We measured the volumes of the pickup chambers and the areas of the walls (including the area of the cold plates of the pickup) having a temperature $T \approx 77$ K. Estimates have shown that to produce a nearly monolayer coating on the surfaces of the hot plates it is necessary to admit the xenon into the pickup chambers at a pressure $p \approx 2 \times 10^{-3}$ Torr (provided that all the Xe molecules are adsorbed on the cold walls when the chamber is subsequently cooled). By varying the partial pressure of the Xe in the admitted $N_2 + Xe$ mixture we were able to vary the degree of filling of the cold surface with Xe molecules.

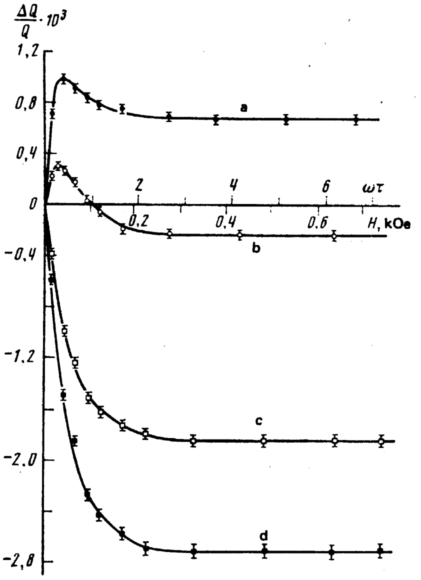

FIG. 5.

Figure 5 shows plots of $\Delta Q^{\perp}/Q(H)$ for different compositions of the $N_2 + Xe$ mixture entering the pickup chamber. At a monolayer-filling degree $\vartheta_{Xe} \approx 0.1$ (Fig. 5a), we obtained the dependence typical of TME at low temperatures (cf. Fig. 1). At the mixture composition corresponding to $\vartheta_{Xe} \approx 0.25$ (Fig. 5b), the quantity $\Delta Q^{\perp}/Q(H)$ was an alternating-sign function of H. With further increase of the partial pressure of Xe in the mixture ($\vartheta_{Xe} \approx 1$ — Fig. 5c, $\vartheta_{Xe} > 1$ — Fig. 5d) the effect becomes negative at any value of the field. We note also that in this case the dependence of $\Delta Q^{\perp}/Q$ on H is monotonic, i.e., the maximum of $\Delta Q/Q$ at $H \approx 70$ Oe vanishes.

We note that according to the estimates made, the adsorption of the nitrogen molecules from the $N_2 + Xe$ mixture by the surface can be neglected.

Thus, the experimental results indicate that the parameters of the TME in the $N_2 + Xe$ gas mixture differ substantially (to the extent that the sign of the effect is reversed) from the case of pure N_2 gas. Taking into account the fact that in monotonic gases there is no TME, and that in all the cases shown in Fig. 5 the Knudsen number was Kn ≫ 1, we can conclude that the observed features of the effect [negative sign and monotonic $\Delta Q/Q(H)$ dependence] are directly connected with the scattering of the N_2 molecules by the physically adsorbed Xe atoms.

III. DISCUSSION OF RESULTS

We consider the states of the surfaces under the conditions of the experiments. At low temperature, the lifetime t of the molecule in the physically adsorbed state can exceed by many orders of magnitude the time of impact on the surface (10^{-11} sec). Thus, for N_2 molecules on platinum (adsorption energy $E_a = 3.4$ kcal/mol) at $T \approx 77$ K, the time is $t \sim 10^{-3}$ sec. In accordance with (1), at this temperature we have $\vartheta \sim 1$. It can therefore be assumed that in the described experiments the cold surface was coated with a layer of physically adsorbed molecules. Since the flux of the molecules emitted from the adsorption layer $N=r_0^{-2}\,t^{-1}$ is in this case of the same order as the total gas flux $n\bar{v}\sim 10^{17}$ m/cm$^2\cdot$sec, the TME can be due to the nonspherical emission (capture) and to nonspherical scattering by the physically adsorbed molecules. The situation is different on the hot surface. At $T \gtrsim 95$ K the molecule lifetime on the surface is $t \lesssim 10^{-5}$ sec, and we have $\xi \lesssim 10^{-2}$ and $\vartheta \lesssim 10^{-2}$. The nonspherical scattering by the physically adsorbed molecules on the hot surface can therefore be neglected in the treatment of the effect.

The presented results of the investigation of the TME at low temperatures offer evidence of a substantial difference between the orientational interaction of the nitrogen molecules with a surface covered by physically adsorbed N_2 molecules, compared with scattering at room temperatures, when the physical adsorption of the nitrogen is small ($\vartheta_{N_2}\sim 10^{-7}$ at $T\approx 350$ K). This difference can be attributed to the increase of the time of interaction of the molecules with the surface (the lifetime in the adsorbed state) and to the ensuing change of the scattering mechanism. Thus, e.g., at a temperature $T_{\rm cold}\approx 77$ K, the values of the parameter $\omega\tau$ at which $\Delta Q^{\parallel}$ and $\Delta Q^{\perp}$ reach a maximum are much lower $[(\omega\tau)^{\parallel}_{\max}\approx(\omega\tau)^{\perp}_{\max}\approx 0.7]$ than the analogous values at $T_{\rm cold}\approx 300$ K $[(\omega\tau)^{\parallel}_{\max}\approx 3,\ (\omega\tau)^{\perp}_{\max}\approx 2]$. In accordance with the precession mechanism of the effect, this means that at low temperatures the dependence of the emission probability on the orientation of the angular momentum, represented in the form of an expansion in spherical tensors,[2] should contain tensors not only of rank $l=2$ (these terms of the expansion correspond to geometric symmetry of the molecule), but also of rank $l>2$. At the same time, from a comparison of the theory with the experimental data obtained for the N_2–Pt system at a temperature $T_{\rm cold}=293$ K, it was found that $l\leqslant 2$ (Ref. 9). We note that if the dependence of the probability on the angle φ_M contains harmonics with a minimum period $2\pi/l$, then the maximum change of the heat flux will be reached in a field such that the angular momentum of the molecules moving with the most probable velocity is rotated through an angle $2\pi/l$, as a result of the precession, during the time of travel between the surfaces. The reason of this dependence ($l>2$) of the nonspherical probability is apparently the corresponding geometrical symmetry of the potential field of the surface in which the physically adsorbed molecule is located. We note also that the nonspherical scattering processes described by this probability should take place on both surfaces.

Thus, our analysis shows that a theoretical description of the TME under conditions of physical adsorption of a gas on a surface should take into account the corresponding processes of interaction between the molecules and the surface. In addition, to describe the obtained data it is necessary to solve the problem at arbitrary surface temperatures ($\Delta T\sim T$) and take into account the temperature dependences of the various interaction processes.

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