Investigation of the temperature dependence of the thermomagnetic effect in oxygen interacting with a platinum surface

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A temperature dependence was observed in the relative change of heat flux in free-molecular ($K_H > 10$) oxygen gas interacting with a platinum surface at $T = 310$–550 K. The observed dependence can be explained if it is recognized that the oxygen can be chemosorbed on the platinum surface in the form of atoms and molecules, the fraction of the chemosorbed molecules varying in the investigated temperature interval, and if it is also assumed that the nonspherical inelastic scattering of the gas molecules by the adsorbed molecules and by the absorbed atoms is different.

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The effect of a magnetic field on the heat flux in a Knudsen molecular gas—the thermomagnetic effect (TME)—is due, as shown earlier [1-3] to the dependence of the probability of elastic scattering of the molecules by the surface on their orientation. In this interaction with the surface of a body, the molecules become polarized—their distribution velocity depends on the directions of the velocity and angular momentum-vectors **v** and **M**. The precession of the molecules in the field **H** leads to averaging of the orientation of the vector **M** in a plane perpendicular to the field, and hence to a change in the contribution made by the polarized molecules to the energy transport. The dependence of the change ΔQ of the heat flux on the product $\omega\tau$ ($\omega = \gamma H$ is the precession frequency, γ is the gyromagnetic ratio, L is the distance between the cold and hot surfaces, and $\tau = L/\bar{v}$) takes the form of damped oscillations caused by the periodic variation of the orientations of the molecule when it precesses. As $\omega\tau \to \infty$ the value of ΔQ tends to a limit $\Delta Q_{\rm sat}$ and depends also on the field orientation.

The TME was previously investigated at ~340 K in N_2, CO, and CO_2 gases interacting with a gold surface,[2] as well as in O_2 interacting with gold and platinum surfaces,[3] and the dependences of the probability of nonspherical scattering of these molecules on the orientation of the vectors **v** and **M** were obtained. It was established [3] that for the O_2-Pt system the ratio is $\Delta Q^{\parallel}_{\rm sat}/\Delta Q_{\rm sat}$ ($\Delta Q^{\parallel}_{\rm sat}$ and $Q^{\perp}_{\rm sat}$ are the values of $\Delta Q_{\rm sat}$ in fields $\mathbf{H}\parallel\mathbf{k}$ and $\mathbf{H}\perp\mathbf{k}$, respectively, where **k** is the normal to the surface) is anomalously small (≈ 0.1) compared with the analogous value for the gases N_2, CO, and CO_2 ($\Delta Q^{\parallel}_{\rm sat}/\Delta Q^{\perp}_{\rm sat} = 0.46$– 0.62).

This paper describes an investigation of the TME in the O_2-Pt system, where it was observed that when the temperature varies from 320 to 430 K the values of $\Delta Q^{\parallel}_{\rm sat}/Q$, $\Delta Q^{\perp}_{\rm sat}/Q$ and $\Delta Q^{\parallel}_{\rm sat}/\Delta Q^{\perp}_{\rm sat}$ increase. Further change of the temperature to 520 K does not change these values.

It turned out to be possible to explain the observed change of $\Delta Q^{\parallel}_{\rm sat}/Q$ and $\Delta Q^{\perp}_{\rm sat}/Q$ by taking into account the fact that oxygen can be chemosorbed on a platinum surface in the form of atoms and molecules, and that the number of chemosorbed O_2 molecules changes with temperature, as well as by assuming different nonspherical scattering of molecules from surfaces of Pt coated with adsorbed molecules and atoms. To describe the temperature dependences of $\Delta Q^{\parallel}_{\rm sat}/Q$ and $\Delta Q^{\perp}_{\rm sat}/Q$, boundary conditions were formulated for the distribution function of the gas, with account taken of the nonspherical interaction between the gas molecule and the layer of the adsorbed molecules. The comparison of the experimental data with the theory of the effect has made it possible to determine the degree of filling of the surface by oxygen molecule and to determine the nonspherical scattering probabilities of O_2 molecules from Pt surfaces coated by chemosorbed oxygen atoms and molecules.

1. The experiments were performed with a previously described setup.[3] The influence of the field on the heat flux was investigated in hydrogen located in a gap ($L = 1.6$ mm) between "hot" and "cold" surfaces coated with a sputtered layer of platinum. The change of the heat flux was determined by measuring the resistance of a sputtered platinum layer ($R \approx 50\ \Omega$) on the surface of a thin mica plate ($46 \times 60 \times 0.005$ mm) which served as the hot surface. The gas pressure was chosen to be $p \lesssim 3 \cdot 10^{-3}$ Torr. In this case the heat-transfer is close to the free-molecular regime $K_H \geqslant 10$ and $\Delta Q/Q$ is independent of pressure. The cold-surface temperature was maintained at $T_c = 238$ K and the hot one T_h ranged from 320 to 520 K. Prior to the measurements the surfaces were outgassed and conditioned in an oxygen atomsphere. The relative error in the measurements of ΔQ was < 7%. The magnetic field was produced by Helmholtz coils and a solenoid (to measure $\Delta Q^{\perp}$). Besides ΔQ, we measured the total heat flux, to be able to monitor the diffuse-reflection coefficient (α). The measurement procedure and the setup are described in greater detail elsewhere.[2,3]

The measurement results at the temperature $T_h = 353$ K and $T_h = 483$ K are shown in Figs. 1 and 2. It is seen from the figures that $\Delta Q^{\perp}$ and $\Delta Q^{\parallel}$ are negative in this

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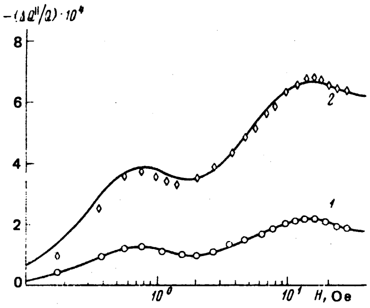

FIG. 1. Plot of $\Delta Q^{\parallel}/Q = \varphi_1(H)$ at $T_h = 353$ K (1) and $T_h = 483$ K (2); $p = 3\cdot 10^{-3}$ Torr.

temperature interval and the functions $\Delta Q^{\parallel}Q = \varphi_1(H)$, $\Delta Q^{\perp}Q = \varphi_2(H)$ have each two characteristic maxima. These maxima correspond to the contributions made to the effect by molecules with spin projections $\sigma = \pm 1$ and $\sigma = 0$, respectively (the ground state of the O_2 molecules is $^3\Sigma$). Since the ratio of the magnetic moments of the O_2 molecules in the states with $\sigma = \pm 1$ and $\sigma = 0$ is equal to $\bar{J}$ ($\bar{J} \sim 15$ at $T = 350$ K), it follows that the field intensitites at which contributions of these molecules in these states to the change in the heat flux differ by a factor $\bar{J}$ (for details see [3]). With increasing temperature, the values of the fields corresponding to the maxima of the functions $\Delta Q^{\parallel}/Q = \varphi_1(H)$ and $\Delta Q^{\perp}/Q = \varphi_2(H)$, remain constant within the limits of error ($\lesssim 5\%$), and the quantities $\Delta Q^{\parallel}_{\rm sat}/Q|$ and $|Q^{\perp}_{\rm sat}/Q|$ increase.

Plots of the values of $\Delta Q^{\parallel}_{\rm sat}/Q$ and $\Delta Q^{\perp}_{\rm sat}/Q$ against the temperature of the hot surface are shown in Fig. 3. It is seen that $\Delta Q^{\parallel}_{\rm sat}/Q$ and $\Delta Q^{\perp}_{\rm sat}/Q$ increase monotically with increasing T_h but become independent of temperature starting with $T_h = 430$ K. The ratio $\Delta Q^{\parallel}_{\rm sat}/\Delta Q^{\perp}_{\rm sat}$ (see Fig. 4) varies in such a way that its value also becomes independent of T_h at temperatures higher than 430 K.

Under conditions when rapid precession ($\omega\tau \gg 1$) causes all the directions of the angular momentum in the plane perpendicular to H to be equally probable, and further increase of the field does not change the nonequilibrium distribution function, the values of $\Delta Q^{\parallel,\perp}_{\rm sat}/Q$ are determined by the nonspherical interaction of the molecules with the surface and by the diffuse-reflection coefficient α. Measurements of the total flux have shown that α does not change with changing temperature T_h, within the limits of the experimental error, and remains equal to $\alpha = 0.92 \pm 0.05$. As already shown,[2] the change of α within the limits of this error leads to a change of $\lesssim 5\%$ in the values of $\Delta Q^{\parallel,\perp}_{\rm sat}/Q$. The observed change of $\Delta Q^{\parallel,\perp}_{\rm sat}/Q$ and $\Delta Q^{\parallel}_{\rm sat}/\Delta Q^{\perp}_{\rm sat}$ in the temperature region < 430 K is therefore evidence of a change in the nonspherical interaction of the O_2 molecules with the platinum surface.

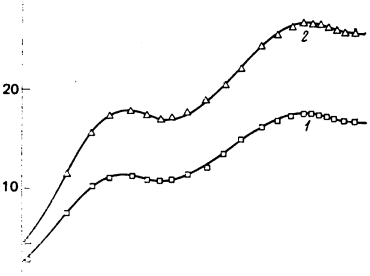

FIG. 2. Plot of $\Delta Q^{\perp}/Q = \varphi_2(H)$ at $T_h = 353$ K (1) and $T_h = 483$ K (2); $p = 3\cdot 10^{-3}$ Torr.

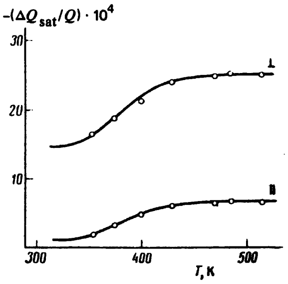

FIG. 3. Plots of $\Delta Q^{\perp}_{\rm sat}/Q$ and $\Delta Q^{\parallel}_{\rm sat}/Q$ vs. temperature.

2. Let us discuss the possible cause of the change of the nonspherical interaction. Investigations of oxygen adsorption on a platinum surface, by the method of thermosorption and x-ray photoelectronic spectroscopy,[4] have shown that oxygen can be chemosorbed in the form of atoms and molecules. The adsorption heat E_m of O_2 molecules was determined in [5] from the temperature dependence of the rate of the catalytic reaction of the oxidation of carbon monoxide in a temperature region where the reaction rate is limited by the rate of the O_2-molecule desorption. According to the data in that reference, $E_m = 8.5 \times 10^3$ K, whereas the heat of dissociative adsorption is, according to various sources,[6] $E_a = (25 - 35) \times 10^3$ K.

Using the presented values of the adsorption heats E_m and E_a we can estimate the lifetimes of the oxygen molecules ($t_m = t_0 \exp(E_m/T)$, $t_0 \approx 10^{-13}$ sec) and of the atoms ($t_a = t_0 \exp(E_a/T)$ on a platinum surface. At $T = 300$ K and $T = 450$ K we have $t_m = (10^{-1} - 10^{-5})$ sec and $t_a = (10^{23} - 10^{11})$ sec. We note that in the investigated temperature interval the lifetime of the oxygen atoms exceeds by many orders of magnitude the duration of the experiment. Since there are at present no data on the structure of the chemsorbed layer of O_2 molecules on a platninum surface, and no theory has been developed for adsorbed matter,[7] we shall assume for the description of the TME temperature dependence that the platinum surface is coated by an invariant layer of oxygen atoms that occupy all the adsorption centers of the atomic oxygen. The number of chemosorbed oxygen molecules (n_{O_2}) on such a surface can be obtained by solving the adsorption equation

$$\frac{dn_{O_2}}{dt} = -t_m^{-1} n_{O_2} + \alpha\left(1 - \frac{n_{O_2}}{N}\right) n\bar{v}, \qquad (1)$$

where N is the number of independent adsorption centers of O_2 molecules per cm^2, α is the adhesion coefficient, and n and $\bar{v}$ are the density and average velocity of the gas molecules.

In accordance with (1), the degree of occupation ($\vartheta = n_{O_2}/N$ of the surface by the O_2 molecules in a stationary state is

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

where $r_0^2 = N^{-1}$ is the surface area occupied by one adsorbed molecule. Under the experimental conditions, at a pressure $p = 10^{-3}$ Torr and a temperature $T = 320$ K we have $\xi \geqslant 10$ and the degree of occupation of the surface by oxygen molecules is $\vartheta \sim 1$, and at $T = 430$ we have $\xi \lesssim 10^{-2}$ and $\vartheta \lesssim 10^{-2}$.

The interaction of rotating gas molecules with a surface is described by the scattering probability averaged over the states of the surface of the solid:

$$W(\mathbf{v}'\mathbf{M}' \to \mathbf{vMk}) = \sum_{\alpha'\alpha} \rho_{\alpha'} w(\alpha'\mathbf{v}'\mathbf{M}' \to \alpha\mathbf{vMk}). \tag{3}$$

Here $w(\alpha'\mathbf{v}'\mathbf{M}' \to \alpha\mathbf{vMK})$ is the scattering probability when the surface states before (α') and after (α) the intraction are fixed, ρ_α is the probability of surface state α, and $\mathbf{k}$ is the normal to the surface.

In the general case of a nonequilibrium gas + solid surface system, ρ_α depends on the gas-molecule flux, and hence on the distribution function of the gas, and the determination of ρ_α is a complicated problem. The situation is much simpler, however, if it is assumed that the deviation from the equilibrium state of the system is small. In this case it can be assumed in the zeroth approximation that ρ_α is the equilibrium distribution. If the oxygen-molecule adsorption centers are independent and have only two states, free and occupied, then, assuming the energy of the free adsorption state equal to zero, and taking into account the condition for the equilibrium of the gas + surface system, we can transform (3) into

$$W=\vartheta w_m+(1-\vartheta)w_a, \tag{4}$$

where the probability w_a describes the scattering of the gas molecules by a surface coated with chemosorbed atoms, as well as the capture of the O_2 molecules by the free centers, while the probability w_m describes the scattering of the gas molecule by the chemosorbed molecules and the emission of the O_2 molecules from the surface. It follows from (2) and (4) that the temperature dependence of the probability of scattering of the gas molecule by a surface coated with chemosorbed molecules is determined by the parameter ξ introduced above.

Using (4), we can write down the boundary conditions that connect the distribution functions of the molecules incident on the cold ($v_z^+ > 0, f^+(v^+, M^+)$) and hot ($v_z^- < 0, f^-(v^-, M^-)$) surfaces:

$$v_z{}^+f^+ = \int d\Gamma^- v_z{}^- W_x f^-, \quad v_z{}^-f^- = \int d\Gamma^+ v_z{}^+ W_r f^+, \quad d\Gamma=d\mathbf{v}\,d\mathbf{M}. \tag{5}$$

Following our preceding paper,[2] we separate in the expression for the scattering probability the part that describes the dependence of the scattering on the molecule orientation

$$W=W^{(0)}+\varepsilon W^{(1)}. \tag{6}$$

Here $W^{(0)}$ is the scattering probability and describes specular elastic reflection and diffuse scattering in which the emitted molecules have a temperature equal to the surface temperature, and ϵ is the nonsphericity parameter ($\epsilon \ll 1$). The experiments have shown that the diffuse-reflection coefficient remains constant in the employed temperature interval, within the limits of the measurement error, and we therefore assume that the coefficient α is the same for the cold and hot surfaces. Taking the foregoing estimates of ξ and ϑ into account, we have for the probabilities of nonspherical scattering by the hot ($0 < \vartheta < 1$) and cold ($\vartheta \approx 1$) surfaces

$$W_c^{(1)} = w_m^{(1)}, \quad W_h^{(1)} = \vartheta w_m^{(1)} + (1-\vartheta) w_a^{(1)}. \tag{7}$$

An earlier investigation of the TME in oxygen at $T_c = 297$ K and $T_h = 393$ K has shown that the nonspherical interaction of O_2 molecules with a platinum surface can be described by the expression[1)]

$$\begin{gathered} W^{(1)}=\alpha_1X_1+\alpha_2X_2, \\ X_1=[1+c_1(2/3-\sigma^2)]\cos\vartheta_m, \\ X_2=[1+c_1(2/3-\sigma^2)]\sin2\vartheta_m\sin2\vartheta_v\cos(\varphi_v-\varphi_m). \end{gathered} \tag{8}$$

The coefficients α_1 and α_2 depend on v'^2 and M'^2; the angles ϑ and φ are the spherical orientation angles of the vectors $\mathbf{v}$ and $\mathbf{M}$ of the reflected molecules. The dependence of $W^{(1)}$ on σ turned out to be necessary for the description of the different contributions made to the effect by the O_2 molecules with $\sigma = \pm 1$ and $\sigma = 0$ ($c_1 = 2^{-5/2}$).

In accord with (8), we assume that

$$\begin{gathered} w_m^{(1)}=\alpha_1X_1+\alpha_2X_2, \quad w_a^{(1)}=\beta_1X_1+\beta_2X_2, \\ \beta_i=\beta_i(v'^2, M'^2). \end{gathered} \tag{9}$$

The choice of the models for the scattering probabilities $w^{(1)}$ and $w_a^{(1)}$ in the form (9) is dictated by the fact, revealed by our experiments, that $\Delta Q^{\parallel}/\Delta Q^{\parallel}_{\text{sat}} = \varphi_1(H)$ and $\Delta Q^{\perp}/\Delta Q^{\perp}_{\text{sat}} = \varphi_2(H)$, and consequently the dependence of the nonspherical scattering probability on the orientation of the vectors $\mathbf{v}$ and $\mathbf{M}$ remains unchanged in the investigated temperature interval.

The solution of the Boltzmann equation with boundary conditions (5), (7), and (9) leads to the following expressions for the variation of the heat flux in the field:

$$\begin{gathered} \frac{\Delta Q^{\parallel}}{Q} = -[A_1\vartheta + A_2(1-\vartheta)]\{I_1(\omega_{\pm1}\tau)+I_1(\omega_0\tau)\}, \\ \frac{\Delta Q^{\perp}}{Q} = -[B_1\vartheta + B_2(1-\vartheta)]\{I_2(\omega_{\pm1}\tau)+I_2(\omega_0\tau)\} - \\ -[A_1\vartheta + A_2(1-\vartheta)]\{I_1(\omega_{\pm1}\tau)+I_1(2\omega_{\pm1}\tau)+I_1(\omega_0\tau)+I_1(2\omega_0\tau)\}, \end{gathered} \tag{10}$$

where A_1, A_2, B_1, B_2 are quantities defined as integrals of the functions α_2^2, $\alpha_2\beta_2$, α_1^2, $\alpha_1\beta_1$, respectively. The dependences of $\Delta Q^{\parallel}/Q$ and $\Delta Q^{\perp}/Q$ on the field are described by the functions I_i:

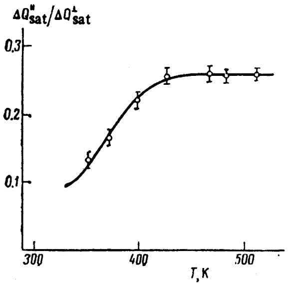

FIG. 4. Temperature dependence of the ratio $\Delta Q^{\parallel}_{sat}/\Delta Q^{\perp}_{sat}$.

$$I_i(\omega_\sigma\tau)=J_i(\omega_\sigma\tau)-J_i(0), \tag{11}$$

where

$$J_1(\omega_\sigma\tau)=\int_0^\infty dx\,dy\,x^3y^5e^{-x^2-y^2}\psi(\omega_\sigma\tau),$$

$$J_2(\omega_\sigma\tau)=\int_0^\infty dx\,dy\,xy^3e^{-x^2-y^2}\psi(\omega_\sigma\tau),$$

$$\psi(\omega_\sigma\tau)=\frac{(1-\alpha)^3-\alpha(2-\alpha)\cos(\omega_\sigma\tau)-(1-\alpha)\cos(2\omega_\sigma\tau)}{1-2(1-\alpha)^2\cos(2\omega_\sigma\tau)+(1-\alpha)^4}$$

$$\omega_{\pm1}\tau=\frac{2\mu_0HL}{\hbar}\frac{(m/2T)^{1/2}}{(\bar{J}(\bar{J}+1))^{1/2}}(xy)^{-1},\quad \omega_0\tau=\frac{2\mu_0HL}{\hbar}$$
$$\times\frac{(m/2T)^{1/2}}{[\bar{J}(\bar{J}+1)]^{1/2}}(xy^2)^{-1},$$
$$x=v_z(m/2T)^{1/2},\quad y=M(2IT)^{1/2}.$$

The parameters A_1, A_2, B_1, B_2 in (10) can be chosen such that the experimental data obtained at various temperatures T_h and two field orientations are satisfactorily described by the theoretical relations (10) and (11) (Figs. 1 and 2).

In accordance with (10), the dependence of the change of the heat flux on the temperature is determined by the parameter ϑ — the fraction of the occupied adsorption centers of the O_2 molecules. From (12) and (13) we have for $\Delta Q^{\perp}_{sat}/Q$ and $\Delta Q^{\perp}_{sat}/Q$ the expressions

$$\begin{gathered}\Delta Q_{sat}/Q=-0.57[A_1\vartheta+A_2(1-\vartheta)],\\ \Delta Q_{sat}/Q=-1.14[A_1\vartheta+A_2(1-\vartheta)]-0.84[B_1\vartheta+B_2(1-\vartheta)]\end{gathered} \tag{12}$$

Plots of $\Delta Q^{\parallel}_{sat}/Q$, $\Delta Q^{\perp}_{sat}/Q$ and $\Delta Q^{\parallel}_{sat}/\Delta Q^{\perp}_{sat}$ against the temperature T_h, corresponding to formulas (2) and (12), are shown in Figs. 3 and 4 ($r_0^2\approx10^{-14}$ cm^2, $E_m=8.5\times10^3$ K). It is seen that the theoretical relations describe the experimental results within the limits of experimental error.

Since the parallel effect is small at $T_h=320$ K ($\Delta Q^{\parallel}_{sat}\approx0.1\Delta Q_{sat}$), it follows from (12) that $A_1\approx0.2B_1$, so that the expression for the probability of nonspherical scattering at this temperature can be approximated by

$$W_h^{(1)}=w_m^{(1)}\approx\alpha_1\cos\vartheta_{mr} \tag{13}$$

It follows from (13) that under conditions when the adsorption centers of the O_2 molecules are occupied, the molecules emitted after nonspherical scattering are isotropically distributed in velocity, with a most probable molecule-axis orientation perpendicular to the normal k. At high temperatures, a correlation appears between the direction of the velocity and the angular momentum of the emitted molecules.

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1) In our paper[3] we mistakenly wrote in expression (8) for the probability $W^{(1)}$ the second term in the form $\{(l_1'1)l_1', (02)2, l_3\}$, $l_1'+l_3=$odd, $l_1'\neq0$ in place of $\{(22)1, (02)2, 2\}$ (in the notation of [3], l stands for the ranks of the spherical tensors in which the probability $W^{(1)}$ is expanded).

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