where $\tan \theta$ is the gradient of the straight-line portion of relation $\Delta T(t^{1/2})$ near the origin.

Since expression (2) for w_E contains easily measured quantities, it is also possible to obtain the numerical value of the coefficient $B(r, \mu^*)$, whose value is required for determination of the degree of degeneracy of the gas, the current carriers, and their scattering mechanism.

Thus, we have shown that measurements of the Ettingshausen galvanomagnetic effect is a varying magnetic field can be used to obtain (in addition to determination of the GTM effects themselves) additional information about the thermophysical properties of the investigated materials.

NOTATION

b, width of specimen; d, S, perimeter and area of cross section; I, current strength; j, current density; H, magnetic field strength; T, absolute temperature; T_m, ambient temperature; λ , k, σ , R_H, thermal conductivity, thermal diffusivity, electrical conductivity, and Hall coefficient of investigated material; a, coefficient of heat transfer between specimen and surroundings; B(r, μ^*), coefficient dependent on scattering mechanism and degree of degeneracy of electron gas; k₀, e, Boltzmann constant and electron charge; w_E = AT, Ettingshausen heat released or absorbed on faces of specimen perpendicular to y axis; $\Phi(z)$, probability function; W_{μ,ν}(z), Whittaker function; D_{ν}(z), parabolic cylinder function; t, time; p, Laplace transform parameter.

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USE OF PERIODIC-HEATING METHOD FOR

MEASUREMENT OF THERMAL ACTIVITY

COEFFICIENT OF GASES

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A method of increasing the sensitivity of the circuit for measuring the thermal activity coefficient of gases by the periodic-heating method is proposed. The thermal activity of argon, carbon dioxide, and air at 1300°K was measured.

Among the new developing methods of measuring the thermophysical properties of substances the periodic-heating method merits great attention. This method consists essentially in recording the temperature fluctuations of a fast sensor (wire or foil) due to heating by alternating current in the medium under investigation. The method is based on the use of electronic circuitry, is suitable for automation, and can be used to carry out investigations in a wide range of temperature and pressure.

This method was first proposed in [1, 2], where it was used to determine the thermal activity coefficient of liquids (foil sensor) [1, 2]. Later, American authors [3, 4] used practically the same measuring circuit to determine the thermal conductivity of gases by means of wire sensors. This technique was subsequently developed successfully in [5, 6]. Some modifications of the method of measuring the thermal activity coefficients of fluids have been used in a series of investigations [7, 8].

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Fig. 1. Electric circuit for measuring thermal activity coefficient of gases.

The developed modifications of the alternating-heating method for gases have low sensitivity. The appreciable heat capacity of the sensors greatly reduces the sensitivity of the measuring technique and does not permit measurements in gases of relatively low density (e.g., in vapor at relatively low pressure). The amplitude of the temperature fluctuations of the sensor for small values of thermal activity coefficient depend weakly on the latter and are determined mainly by the thermal inertia of the sensor. Hence, an increase in sensitivity is a most urgent problem in the utilization of the alternating-heating method for the study of the properties of gases.

In this paper we describe a new method of increasing the sensitivity of measurements of the thermal activity of gases and discuss the experimental results.

An increase in the sensitivity of the measuring system is achieved by the use of differential circuits, which provide for compensation of the thermal inertia of the sensor. We propose a bridge circuit, one arm of which contains a sensor in vacuum, while the other contains a sensor in the gas under investigation. The unbalance of such a circuit would transmit the effect of the investigated gas as happens, for instance, in thermal gas analyzers.

Such a circuit can in principle be used in devices where the heating of the sensor relative to the cell walls is slight. In the most promising circuits designed for the investigation of gas properties, the sensor is heated well above the cell walls. This overheating is a method of creating sufficiently high temperatures, since the reference temperature in this case is that of the sensor. In such conditions the use of a simple differential circuit does not give the desired result. The introduction of gas into one of the arms greatly alters the heat transfer, and also greatly reduces the sensor temperature of the particular sensor by the passage of extra current through it is possible in principle. Both direct and alternating current, however, alter the power of the periodic heating, which again alter the conditions in which the particular sensor is situated. These difficulties were overcome by using a high-frequency (tens of kilohertz) additional voltage imposed on the sensor in the investigated gas for compensating heating. The high-frequency voltage does not cause changes in the power of periodic heating on the main frequency and gives the desired degree of freedom for independent regulation of the temperature of one of the sensors.

The circuit of the measuring device is shown in Fig. 1.

Two identical sensors (of platinum foil) Z_0 and Z_1 are connected in the arms of an ac bridge. The generator 1 and battery 3 produce a low-frequency signal containing a constant component at the input of the Wien bridge. The generator 4 effects high-frequency heating of the sensor Z_0 . The separating capacitor C_2 eliminates the effect of generator 4 on the dc balancing of the bridge. The incorporation of the capacitor C_2 ensures that balance of the bridge at the supply-voltage frequency is achieved in the presence of capacitor C_1 , which for convenience is a variable one.

The dc balance of the bridge is checked by a microvoltmeter 7 (F116-2). The ac unbalance of the bridge is amplified by an amplifier 6 (U2-6) tuned to the supply-voltage frequency. The filter 5 prevents the passage of the high-frequency signal to the input of amplifier 6.

The bridge unbalance signal is measured by comparing it with a reference signal supplied from generator 1 through the divider R_5-R_6 . The magnitude of the signal is determined from the readings of the voltmeter 2 and the resistance box R_5 .

The initial dc and ac balancing of the bridge is effected by the boxes R_1 and C_1 in conditions that are identical for both sensors (e.g., at a certain pressure of the investigated gas); if the gas pressure in one of the cells is altered and then the bridge is balanced for direct current by means of generator 4, the bridge unbalance signal at the supply-voltage frequency will be uniquely related to the thermal activity coefficient of the investigated gas.

TABLE 1. Comparison of Experimental and Published Data on Thermal Activity of Gases

Gas	(<i>b</i> , <i>b</i>) exp	$(b_{\mathfrak{d}}/b_{0}')$ from [9]
Air Carbon dioxide	1,03	1,01
Argon	0,626	0,620

The theory of the method, whose principles are expounded in [1], leads to the following relation between the magnitude of the signal on the bridge diagonal and the thermal activity coefficient of gases in conditions where $b_i/d \ll 1$ (i = 1, 2):

$$e = \frac{2 \sqrt{2} V_{-}^2 V_{-}^2 R_0^2 R_1 \alpha}{cm\omega d (R_0 + R_1)^4} [b_1 - b_2] \cos (\omega t - \pi/4).$$
(1)

The measured signal in this case is proportional to the difference in activity coefficients of the media. At a gas pressure on the order of tens to hundreds of mm Hg and for platinum sensors 5-6 μ m thick b/d = 0.01-0.05.

The sensitivity of the circuit with one sensor in these conditions would be given by the expression

$$e = \frac{2\sqrt{2}V_{-}^{2}V_{-}^{2}R_{0}^{2}R_{1}\alpha}{cm\omega(R_{0}+R_{1})^{4}}(1-b/d)\cos(\omega t-\varphi).$$
(2)

A 1% error in the measured value of e would give a 20-100% error in the determined activity coefficient b (95-99% of the thermal reaction is determined in this case by its heat capacity and the effect of the medium is barely detectable). In the differential circuit a 1% error in the measured signal e gives a 1% error in the activity coefficient. Thus, the described circuit ensures an increase in sensitivity by two orders.

The discussed method can be used in two variants: for absolute and relative measurements. In the first variant one of the sensors is contained in a vacuum $(b_1 = 0)$. In the second it is contained in some gas. The first variant requires no reference data, but it has the disadvantage that the temperature distribution along the sensor in a vacuum is slightly different from that in the medium under investigation. This necessitates the introduction of a correction for the temperature profile. For the case of gases in both arms this effect is much less. Of special interest in difference measurements are measurements in conditions where the cells contain the same gas, but at different pressures P and P₁. In this case for ideal gases we have

$$e = \frac{2\sqrt{2}V_{-}^{2}V_{-}R_{0}^{2}R_{1}\alpha}{cm\omega d(R_{0}+R_{1})^{4}}b_{0}[\sqrt{P/P_{0}}-\sqrt{P_{1}/P_{0}}].$$
(3)

Equation (3) can be used for different gases, forming the ratio:

$$\frac{e}{e'} = \frac{V_{=}^2 V_{\sim}}{V_{=}^2 V_{\sim}} \left[\frac{R_0^2 R_1}{R_0'^2 R_1'} \right] \left[\frac{R_0' + R_1'}{R_0 + R_1} \right]^4 \frac{b_0}{b_0'} \cdot \frac{\sqrt{P} - \sqrt{P_1'}}{\sqrt{P'} - \sqrt{P_1'}}.$$
(4)

This equation provides the basis for the relative variant of the method. Its advantage is the absence of information about the properties of the sensors in Eq. (4).

We give some results illustrating the operation of the device. Table 1 gives the values of b_0/b_0^{\dagger} obtained on the basis of (4) for air, carbon dioxide, and argon at sensor temperature 1300° K ($b_0^{\dagger} = 5.06 \text{ W} \cdot \sec^{1/2}/\text{m}^2 \cdot \text{K}$ is the thermal activity of nitrogen).

The obtained values, as can be seen, agree to within 2% with published values.

The experiment shows that at constant sensor temperature the ratio of the measured signal to \sqrt{P} is constant and is independent of the initial pressure at which the bridge is balanced. As an example, Fig. 2 gives the results of series of measurements of the bridge unbalance voltage in relation to the air pressure in the measuring cell for three frequencies of temperature oscillations: 20, 30, and 40 Hz. In the experiments the air pressure in the reference cell was $P_0 = 0.3$ atm. The results of the measurements confirm the linear relationship between the bridge unbalance voltage e and $\sqrt{P/P_0}$ in accordance with Eq. (3). The gradients of the lines in Fig. 2 depend on the thermal activity coefficient of the gas and the temperature oscillation frequency at constant heating power. The standard deviation of the points is ~1.5%, which gives ~3% for the confidence interval at the 0.95 significance level.





The systematic error of determination of the thermal activity coefficient, according to Eq. (4), is determined by the contribution of the errors $\delta R/R \sim 0.05\%$, $\delta (V/V')/(V/V') \sim 0.1\%$, $\delta (e/e')/(e/e') \sim 0.2\%$, $\delta P/P \sim 0.3\%$. The resultant systematic error is $\delta (b_0/b_0')/(b_0/b_0') \sim 1\%$. Besides this (particularly in the absolute variant of the method), possible contributions to the error due to the difference between actual experimental conditions and the ideal conditions on which the theory of the method is based must be taken into account.

Consideration of the temperature discontinuity at the foil-gas boundary leads to the following corrections for the constant and variable temperature components:

$$\Delta \overline{T} = g \left(\frac{d\overline{T}}{dx} \right)_{x=0}, \quad \frac{\Delta \theta_0}{\theta_0} = g \sqrt{\frac{\omega}{2d}}.$$
 (5)

For typical experimental conditions (gas pressure ~0.1 atm or more, $\omega/2\pi = 20-80$ Hz, $(d\overline{T}/dx)_{X=0} = 10^3$ K/cm) these corrections are negligibly small (~0.1%).

The role of radiative heat transfer in periodic-heating methods is small. The correction to Eq. (3) has the form

$$-\frac{\Delta b_0}{b_0} = \frac{2h}{c\rho\delta\omega} \,. \tag{6}$$

In typical conditions ($\overline{T} \sim 1300^{\circ}$ K) this correction does not exceed 0.5%.

An important question of the method when the sensor is highly heated is that of the reference temperature of the measurement results. It is known [1] that the depth of penetration of the medium by the temperature wave is given by $\sqrt{2a/\omega}$, which is tenths of a centimeter. Hence, the temperature oscillations of the sensor depend on the state of the gas in its immediate vicinity. An analytical treatment of this question necessitates the solution of the nonlinear heat-conduction equation for the medium. This equation is easily linearized in real conditions, when $\theta \ll \overline{T}$. In this case the propagation of the temperature wave in the medium is given by a linear differential equation with variable coefficients. The dependence of the coefficients on the coordinates in this case is determined by the constant temperature component in the medium. The solution of this equation near a foil sensor gives the correction to Eq. (3), determined by the gradient of the mean temperature at the sensor surface and the temperature coefficients of the thermophysical parameters referred to the sensor temperature

$$-\frac{\Delta b_0}{b_0} = \frac{\left(1+2\sqrt{2}\right)}{8\lambda_0} \left(\frac{d\lambda}{dT}\right)_0 \left(\frac{da}{dT}\right)_0 \left(\frac{d\bar{T}}{dx}\right)_0^2. \tag{7}$$

Specific estimates for real conditions and $(d\overline{T}/dx)_0 = 10^3 \text{ K/cm}$ give a value of ~0.5% for $\Delta b_0/b_0$. The frequency dependence of the correction (7) can be used to determine the thermal activity coefficient of the gas at the sensor temperature from the results of measurements of b_1 and b_2 at two frequencies ω_1 and ω_2 from the equation

$$b = \frac{b_2 \omega_2 - b_1 \omega_1}{\omega_2 - \omega_1}.$$
(8)

In the conditions of the experiment whose results are given in Fig. 2 the correction from Eq. (8) to the thermal activity coefficient (3) is $\sim 2\%$. As a whole the total systematic error of measurement of the thermal activity coefficient of gases is 2-3%.

NOTATION

a, thermal diffusivity of gas, $b = \sqrt{\lambda c_p \gamma}$ and b_0 , thermal activity coefficients of gas at pressures P and P₀; c and c_p, specific heats of sensor material and gas; $d = \sqrt{\omega/2} c \rho \delta$, a quantity characterizing the speed of response of the sensor; e, measured signal; g, temperature discontinuity coefficient; h, radiative heat transfer coefficient; m, mass of sensor; R₀ and R₁, resistance of sensor and bridge arm in series; T, mean gas temperature; θ_0 , amplitude of sensor temperature oscillations; V₌ and V_~, constant and variable voltage components at bridge input; $\alpha = I/R_0 \cdot dR_0/dT$, ρ , and δ , temperature coefficient of resistance, density, and thickness of sensor; γ and λ , density and thermal conductivity of gas; φ , difference in phase between temperature and power oscillations; ω , cyclic frequency of supply alternating current.

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KNUDSEN EFFECT IN DETERMINING THE THERMAL CONDUCTIVITY OF GASES BY THE COAXIAL-

CYLINDER METHOD

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The properties of the thermal conductivity of gases are investigated by the coaxial-cylinder method at low pressures. It is established that there is a temperature-jump effect, which must be taken into account, especially for light gases at $P \approx 1$ atm and room temperature.

Macroscopic transfer theory has been formulated for molecular free path lengths less than all the macroscopic parameters of the experiment. In this case the gas behaves as a continuous medium, and the concepts of local density, velocity, and temperature gradient have a perfectly definite physical meaning. In particular, in a pure gas, the thermal conductivity λ is defined as the coefficient of proportionality relating the energy flux \mathbf{q}_{c} to the thermodynamic force ∇T

$$\mathbf{q}_c = -\lambda \nabla T.$$

Experimental values of q_c and ∇T allow the value of λ to be determined.

In the commonly used steady-state methods (parallel-plate, coaxial-cylinder, or heated-fiber methods), ∇T , which is assumed to be unidirectional in the first of these methods and axisymmetry in the other two, is practically determined from the temperature difference between two solid surfaces bounding the investigated gas.

At low pressures this definition of the thermal conductivity is problematic, since the temperature gradient becomes discontinuous in the vicinity of the wall. For example, if two plane-parallel solid walls at tem-

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