

# EFFECT OF RADIATION ON RESULTS OF RAPID THERMAL-CONDUCTIVITY MEASUREMENTS

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An approximate analysis is given of the effect of radiation on results of thermal-conductivity studies using measurements made during the stage of an irregular thermal regime.

In [1] a method was presented for rapid (duration up to 15 msec) measurement of the thermal conductivity of liquids, and it was noted that the effect of radiant heat exchange on the measurements decreased with decreasing duration of the measurement. Since the task of measuring molecular thermal conductivity is a complex metrological problem for a wide class of weakly absorbing liquids, it is desirable to analyze such measurements further.

In nonstationary methods characterized by a measurement time  $\tau$  over the course of which the probe temperature field  $T(x, \tau)$  remains localized within the inner portion of the volume of the specimen under study close to the heater, the liquids may be classified by the degree of their "transparency," using the concept of mean free path length of a photon  $\bar{l}$  and diffusion length of the temperature field  $l^* = (\alpha\tau)^{1/2}$ . Thus, a medium is considered strongly absorbing if

$$\bar{l}/l^* \ll 1, \quad (1)$$

while a medium is "transparent" if

$$\bar{l}/l^* \gg 1, \quad (2)$$

and finally, a medium is "gray" if the intermediate case is realized.

In essence, Eqs. (1) and (2) represent inequalities for the Knudsen number written for a photon gas. It is known that the condition for application of the Fourier law, by means of which the concept of thermal-conductivity coefficient is introduced, is the requirement of a small Knudsen number. From this it follows that writing the energy transfer equation for the photon gas is permissible only in case (1) and thus only in that case is the concept of radiative thermal conductivity  $\lambda_{\text{rad}}$  applicable.

As a rule, to calculate radiative thermal conductivity, as was demonstrated in [2], one can use the concepts of the molecular-kinetic theory of gases; the validity of an analogy between a gas of molecules and a photon gas follows from the generality of the energy transfer processes - transfer by oppositely directed motions of carriers. Using the analogy with thermal conductivity of gases to write the radiative thermal conductivity in the form

$$\lambda_{\text{rad}} = \frac{1}{3} C_v v \bar{l}$$

and considering that the heat capacity of a photon gas

$$C_v = \left( \frac{\partial E}{\partial T} \right)_v = \frac{16\sigma}{v} T_0^3,$$

finally we have

$$\lambda_{\text{rad}} = \frac{16}{3} \sigma T_0^3 \bar{l}$$

(the coefficient of refraction of the medium is taken as unity).

In the other limiting case, where Eq. (2) is fulfilled, the concept of radiative thermal conductivity has no sense. The effect of radiant energy transfer in this case appears only as a distorting factor produced by

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radiant heat loss from the heater surface and from the liquid volume in which a nonstationary temperature field is observed. It is with evaluating the factor that the present study will be concerned. It must be noted here that experimental methods for rapid measurement, e.g., of thermal activity  $\varepsilon = (\rho c \lambda)^{1/2}$  [3, 4] are characterized by short time, of the order of  $10^{-4}$  sec, which ensures fulfillment of Eq. (2) for the general case of weakly absorbing liquids.

The estimates of interest here will be made within the framework of the one-dimensional problem; i.e., we assume that the liquid under study occupies a semispace on the boundary of which is located a heater with zero intrinsic heat capacity. Beginning at time  $\tau = 0$  the heater creates a constant thermal flux per unit surface  $q_0$ .

We will assume further that the temperature field distribution around the heater  $T(x, \tau)$  is defined essentially by molecular thermal conductivity, with radiant effects appearing only as a small perturbation  $t$ . Then in accordance with [5]

$$T(x, \tau) = \frac{q_0}{\varepsilon} \tau^{1/2} \operatorname{ierfc} \frac{x}{2(a\tau)^{1/2}}. \quad (3)$$

The heater temperature ( $x = 0$ )

$$T(0, \tau) = \frac{2q_0}{\varepsilon\pi^{1/2}} \tau^{1/2}. \quad (4)$$

Hence for known  $T(0, \tau)$ ,  $\tau$  and  $q_0$  the thermal activity can be determined, so that for a known value of volume heat capacity the thermal-conductivity coefficient can also be determined. Turning to an evaluation of radiant effects, we will initially consider the effect of radiation from the heater surface. In the approximation of a blackbody the radiant flux per unit surface will be

$$q_{\text{rad}} = \sigma T_0^4.$$

Up to the moment of measurement this flux is compensated by an influx of energy from the surrounding medium; however, beginning at  $\tau = 0$  the heater temperature increases and an additional radiant flux  $\delta q_{\text{rad}}$  is emitted from its surface. Given  $T(0, \tau) \ll T_0$  this incremental flux can be written in the form

$$\delta q_{\text{rad}} = 4\sigma T_0^3 T(0, \tau) \quad (5)$$

or, with consideration of Eq. (4),

$$\delta q_{\text{rad}} = \frac{8\sigma T_0^3 q_0}{\varepsilon\pi^{1/2}} \tau^{1/2}. \quad (6)$$

Thus, the correction  $t$  must satisfy the equation

$$\frac{\partial t}{\partial \tau} = a \frac{\partial^2 t}{\partial x^2}$$

with initial and boundary conditions  $t(0, x) = 0$ ;  $t(\tau, \infty) = 0$ ;  $\lambda \partial t / \partial x|_{x=0} = -\delta q_{\text{rad}}$ . The solution of this problem for the coordinate  $x = 0$ ; i.e., the correction to the heater temperature has the form

$$t(0, \tau) = - \frac{4q_0\sigma T_0^3}{\varepsilon^2} \tau. \quad (7)$$

$$\frac{\delta \varepsilon}{\varepsilon} = 2\pi^{1/2} \frac{\sigma T_0^3}{\varepsilon} \tau^{1/2}. \quad (8)$$

We will now turn to an evaluation of the second factor, radiant energy loss from the liquid volume heated during the measurement process. It is known [6] that the volume radiation coefficient, defining the intensity of monochromatic radiation from a unit volume of matter into a unit solid angle is defined by the expression

$$I_v = \frac{k_v}{\pi} U(v, T_0).$$

The integral value of the volume radiation intensity

$$I = \int_0^{\infty} \int_0^{4\pi} I_{\nu} d\nu d\Omega = 4\bar{k}n^2\sigma T_0^4,$$

where  $\bar{k} = \int_0^{\infty} k_{\nu} U(\nu, T_0) d\nu / \int_0^{\infty} U(\nu, T_0) d\nu$  is the average value of the absorption coefficient.

In analogy with Eq. (5), the additional thermal flux upon heater switch-on has the form

$$\delta q(x, \tau) = \left( \frac{\partial I}{\partial T} \right)_{T=T_0} T(x, \tau). \quad (9)$$

From the physical viewpoint, upon fulfillment of Eq. (2), Eq. (9) determines the intensity of heat drains distributed within the volume. Consequently, the equation defining the temperature correction is written in the form

$$\frac{\partial t}{\partial \tau} = a \frac{\partial^2 t}{\partial x^2} - \frac{1}{\rho c} \delta q(x, \tau)$$

or, using Eq. (3) or Eq. (9):

$$\frac{\partial t}{\partial \tau} = a \frac{\partial^2 t}{\partial x^2} - \frac{q_0}{\rho c \varepsilon} \left( \frac{dI}{dT} \right)_{T=T_0} \tau^{1/2} \operatorname{ierfc} \frac{x}{2\sqrt{a\tau}} \quad (10)$$

with initial and boundary conditions  $t(0, x) = 0$ ,  $t(\nu, \infty) = 0$ ,  $\partial t / \partial x(\tau, 0) = 0$ .

The equation for the Laplace transform  $\tilde{t}(p, x) = L[t(\tau, x)]$  has the form

$$a \frac{d^2 \tilde{t}}{dx^2} - p \tilde{t} = \frac{q_0}{\rho c \varepsilon} \left( \frac{dI}{dT} \right)_{T=T_0} \frac{1}{2} p^{-3/2} \exp \left( -x \sqrt{\frac{p}{a}} \right). \quad (11)$$

With consideration of the boundary conditions, the solution of Eq. (11) is written as:

$$\tilde{t}(p, x) = -\frac{q_0}{\rho c \varepsilon} \left( \frac{dI}{dT} \right)_{T=T_0} \frac{1}{4p^{5/2}} \left( 1 + \sqrt{\frac{p}{a}} x \right) \exp \left( -\sqrt{\frac{p}{a}} x \right). \quad (12)$$

Since the measured quantity is the temperature of the boundary, in Eq. (12) we may set  $x = 0$ . Then

$$\tilde{t}(p, x) = -\frac{q_0}{\rho c \varepsilon} \left( \frac{dI}{dT} \right)_{T=T_0} \frac{1}{4p^{5/2}}.$$

Performing the reverse Laplace transform, we obtain

$$t(\tau, 0) = -\frac{q_0}{\rho c \varepsilon} \left( \frac{dI}{dT} \right)_{T=T_0} \frac{\tau^{3/2}}{3\sqrt{\pi}},$$

from which it follows that the relative error in the determination of thermal activity has the form

$$\frac{\delta \varepsilon}{\varepsilon} = \frac{8}{3} \frac{\bar{k}n^2\sigma T_0^3}{\rho c} \tau. \quad (13)$$

Thus Eqs. (8) and (13) define the amount of error in determination of thermal activity produced by neglect of radiant effects. In essence, the evaluations presented reflect the effect of radiant heat exchange on the thermal conductivity which enters into the expression for thermal activity. Considering that  $\delta \varepsilon / \varepsilon = \frac{1}{2} \delta \lambda / \lambda$ , for the error in thermal conductivity measurement we have

$$\frac{\delta \lambda}{\lambda} = \frac{4\pi^{1/2}\sigma T_0^3}{\varepsilon} \tau^{1/2}, \quad (14)$$

$$\frac{\delta \lambda}{\lambda} = \frac{16}{3} \frac{\bar{k}n^2\sigma T_0^3}{\rho c} \tau. \quad (15)$$

TABLE 1. Thermal Conductivity  
of a Number of Organic Liquids

Liquid	Thermal conductivity, W/m·deg
Benzene	0,146
Butyl acetate	0,139
Dichlorethane	0,132
Dioxane	0,170
Methylene chloride	0,136

Evaluations of Eqs. (14) and (15) obtained for the planar case may, as a first approximation, be applied to the case of a temperature field with cylindrical symmetry, and in particular, to the results of [1].

The characteristic peculiarity of Eqs. (14) and (15), which define the effect of radiation on the result of thermal conductivity measurements at high Knudsen numbers, is their time dependence: The effect of radiation decreases with reduction in the duration of the measurement process. For brief measurement times the effect is extremely low. For example, at  $\tau = 10^{-3}$  sec for a hypothetical semitransparent liquid with  $\bar{k} = 10^4 \text{ m}^{-1}$  (such a value characterizes the class of weakly absorbing liquids sufficiently accurately) the total value of the errors defined by Eqs. (14) and (15) is less than 0.1% at  $T_0 = 300^\circ\text{K}$ .

In connection with this, the methods for rapid measurement of semitransparent media take on special significance as a means of direct measurement of molecular thermal conductivity.

In particular, following the experimental method of [7], which is characterized by high accuracy of relative measurement (error not greater than 1%) the thermal conductivity of a number of semitransparent liquids was studied (see Table 1); measurements were performed at a temperature of  $20^\circ\text{C}$ . The study used platinum filaments  $1 \mu\text{m}$  in diameter; measurement pulse duration comprised 1 msec. Chemically pure grade toluol was used as a reference. In accordance with the recommendations of [8] its thermal conductivity with consideration of the radiation correction was taken as  $0,132 \text{ W/m}\cdot\text{deg}$ .

#### NOTATION

$\bar{l}$	is the mean-free path length of photon;
$l^*$	is the diffusion length of temperature field;
$C_V$	is the heat capacity of photon gas;
$v$	is the velocity of light;
$\lambda$	is the thermal conductivity;
$T_0$	is the temperature of medium;
$\tau$	is the time;
$T(x, \tau)$	is the temperature field distribution about heater;
$\sigma$	is the Stefan-Boltzmann constant;
$q_0$	is the specific heat flux;
$a$	is the thermal diffusivity;
$\varepsilon$	is the thermal activity;
$t$	is the temperature field perturbation by radiant effects;
$I_\nu$	is the volume coefficient of radiation at frequency $\nu$ ;
$U(\nu, T_0)$	is the Planck function;
$\Omega$	is the solid angle;
$n$	is the index of refraction of medium.

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## LIMITING POTENTIALITIES OF MICROCALORIMETERS

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An analysis is made of the limiting values of the minimum detectable power for conductive microcalorimeters with thermoelastic converters.

### 1. Statement of the Problem

Since any energy conversion is connected with heat release, the universal character of the information obtained as a result of measurements of thermal processes dictates the wide distribution of microcalorimetric methods in investigations of the thermodynamics and kinetics of physical, chemical, and biological processes, including manufacturing processes, in medicine and other fields. Rather sensitive and high-speed apparatus for general and special purposes have been developed to these ends.

The individual parameters and characteristics of microcalorimeters and the problems of the design and optimization of the constructions have been discussed in a number of reports [1-18]. Up to now, however, different and frequently contradictory concepts have been used in choosing the main parameters characterizing the relative potentialities of microcalorimeters. In this connection, in the light of the modern theory of measuring devices [19-22], it is desirable to start from an analysis of the noise arising primarily as a consequence of thermodynamic fluctuations. Such an approach was taken in [6] for isothermal and in [14] for continuous-flow microcalorimeters. The results of these reports provide an estimate of the minimum detectable power, but the interrelationship between this parameter and the energetic efficiency of the measuring converter being used and with the speed of response and accuracy of the instrument requires further investigation.

In the present report an analysis is made of the minimum detectable power for conductive microcalorimeters, the connection between this parameter and the speed of response is investigated, and the limiting potentialities of microcalorimeters, limited by thermodynamic fluctuations both in the instrument itself and in the recording apparatus, are determined.

The analysis of the limiting potentialities of a conductive microcalorimeter was carried out for a model (Fig. 1) which contains the following: A reaction chamber where the thermal power  $W_t$ , which varies with time, is released after being measured; a converter of thermal energy into a recordable signal, consisting of a thermoelastic battery, for example; a thermostat for the temperature  $T$  in which the reaction chamber and the converter are placed; a recorder of the microcalorimeter signal with an input resistance  $R_r$ , consisting of a linear measurement system such as a mirror galvanometer or photogalvanometric amplifier.

The calculations were made with allowance for the following limitations which occur in microcalorimeters.

1) The heat capacity of the converter is far less than the heat capacity of the reaction chamber filled with the test substance. This limitation means that the relation

$$\tau_c^0 \gg \tau_t^0 \quad (1)$$

between the time constant  $\tau_t^0$  of the converter itself and the time constant  $\tau_c^0$  of a converter having a heat capacity negligibly small in comparison with the heat capacity of the reaction chamber is valid. Since

$$\tau_t^0 = \frac{l^2}{\kappa c \delta}, \quad \tau_c^0 = \frac{Cl}{\kappa S} \quad (2)$$