DYNAMIC METHOD OF MEASURING THE THERMAL CONDUCTIVITY OF GASES AT HIGH TEMPERATURES

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The author proposes a method of measuring and a formula for calculating the thermal conductivity of gases during monotonic heating.

Thermophysical measurements are made basically on specimens of simple shapes (plate, cylinder, sphere) inside which a one-dimensional temperature field $t(r, \tau)$ with a sufficiently small drop is artificially maintained.

The following nonlinear equation of heat conduction is valid for calculating the temperature field in such specimens:

$$\nabla^2 t + \frac{1}{\lambda} \cdot \frac{d\lambda}{dt} \left(\frac{\partial t}{\partial r} \right)^2 = \frac{1}{a} \cdot \frac{\partial t}{\partial \tau}. \tag{1}$$

Generally, the coefficients $a(t)$, $\lambda(t)$, $c(t)$, and $\gamma(t)$ are arbitrary functions of the temperature.

An analytic solution can be obtained only in individual special cases where the temperature-dependence of the thermophysical properties is subject to simplifying constraints and where either rigorous or approximate transformations may reduce the equation to a linear one.

The simplest case is

$$a(t) = \text{const}; \quad \lambda(t) = \text{const}; \quad c(t) = \text{const}; \quad \gamma(t) = \text{const}. \tag{2}$$

With (2), Eq. (1) transforms into the ordinary linear equation of heat conduction

$$\nabla^2 t = \frac{1}{a} \cdot \frac{\partial t}{\partial \tau}, \tag{3}$$

which has been solved in [1] for various different boundary conditions.

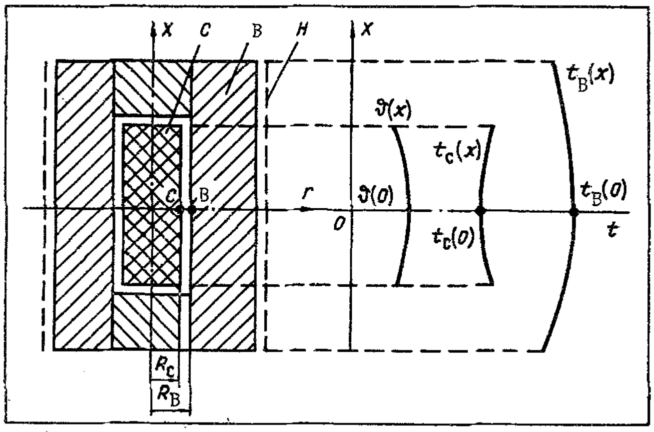

Fig. 1. Basic schematic diagram of a λ-calorimeter: C) copper road; B) metal block; H) heater.

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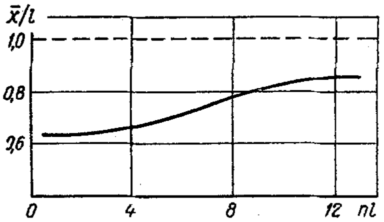

Fig. 2. Ratio $\bar{x}/l = f(nl)$ for real λ-calorimeters.

Almost all existing methods of thermophysical measurements are based on regularities in the solution to Eq. (3). With any other assumptions concerning the functional relations $a(t)$, $\lambda(t)$, $c(t)$, and $\gamma(t)$ than those in (2), Eq. (2) will remain nonlinear and will require approximate methods of solution.

Thermophysical measurements usually involve a small temperature drop $\vartheta(r, \tau)$. This allows us to represent the parameters a, λ, c, and γ on intervals commensurable with $\vartheta(r, \tau)$ as Taylor series expansions of the respective functions in powers of $\vartheta(r, \tau)$:

$$\begin{aligned} a &= a_0(1 + k_a\vartheta + n_a\vartheta^2 + \cdots); & \lambda &= \lambda_0(1 + k_\lambda\vartheta + n_\lambda\vartheta^2 + \cdots); \\ c &= c_0(1 + k_c\vartheta + n_c\vartheta^2 + \cdots); & \gamma &= \gamma_0(1 + k_\gamma\vartheta + n_\gamma\vartheta^2 + \cdots), \end{aligned} \tag{4}$$

The power series in (4) are absolutely convergent. The rate of their convergence is directly related to the magnitude of the temperature drop ϑ and can be controlled by the experimenter.

An analysis of published data shows that, within the temperature ranges between phase transformations, the relative coefficients remain usually $|k_i| \le 3 \cdot 10^{-3}$ deg^{-1} and $|n_i| \le 3 \cdot 10^{-6}$ deg^{-2}, making the conditions for the optimum convergence of series (4)

$$|k_i\vartheta| \leqslant 0.1 \quad \text{and} \quad |n_i\vartheta^2| \leqslant 0.01 \tag{5}$$

easily realizable in thermophysical measurements. For instance, conditions (5) allow measurements with $\vartheta = 10$–100°C, and with $\vartheta \le 5$°C we have for series (4):

$$|k_i\vartheta| \leqslant 0.01 \quad \text{and} \quad |n_i\vartheta^2| \leqslant 0.0001. \tag{6}$$

If conditions (6) are satisfied, then the thermophysical parameters can be represented as linear functions of the temperature drop ϑ.

The basic principle of a λ-calorimeter is shown schematically in Fig. 1. The temperature distribution in the active zone of this calorimeter is also indicated here.

The calorimeter consists of a metal block B and a solid copper rod C mounted coaxially. Between them there is a rather narrow gap filled during the experiment with the test gas. The calorimeter is heated monotonically by a heater H spread uniformly over the outside surface of the block.

Generally, the heat can be transmitted through the gap by conduction, convection, and radiation. Convection can usually be eliminated from gaseous interlayers without major difficulties. The radiative component is appreciable at high temperatures, however, and must be accounted for.

The temperature drops will be referred to the rod temperature:

$$\vartheta(r, \tau) = t(r, \tau) - t_c(\tau). \tag{7}$$

The thermal flux through the gaseous interlayer is determined by the heat capacity $C_C(t)$ and the heating rate $b_C(\tau)$ of the rod:

$$Q(\tau) = C_c(t)\, b_c(\tau). \tag{8}$$

The thermal flux penetrates through the gap by conduction Q_λ and by radiation Q_r:

$$Q(\tau) = Q_\lambda(\tau) + Q_r(\tau). \tag{9}$$

The following expression applies to the radiated flux Q_r

$$Q_л(\tau) = \varepsilon_0\sigma_0 2\pi R_c l\,(T_B^4 - T_c^4). \tag{10}$$

The Fourier equation applies to the conduction flux Q_λ:

$$Q_\lambda(\tau) = \lambda(t)\, 2\pi r l \frac{dt}{dr}. \tag{11}$$

Integrating (11) from $r = R_C$ to $r = R_B$ and retaining only the linear term in series (4) will yield

$$\lambda(\bar{t}) = \frac{Q_\lambda}{4\pi l\vartheta_{BC}} \ln\frac{R_B}{R_c} = \frac{Q - Q_r}{2\pi l\vartheta_{BC}} \ln\frac{R_B}{R_c}, \tag{12}$$

where $\bar{t} = t_C + 1/2\vartheta_{BC}$.

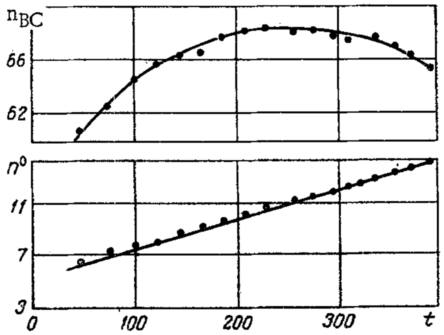

Fig. 3

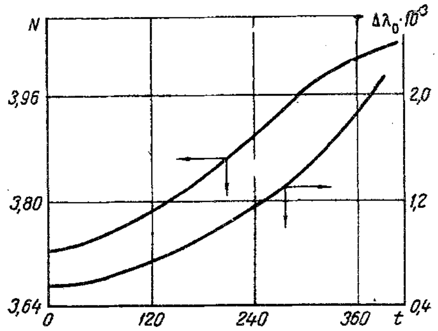

Fig. 4

Fig. 3. Temperature drops during measurements (n_{div}) and during calibration (n^0_{div}).

Fig. 4. "Instrument constants" as functions of the temperature: N (J/m · deg), $\Delta\lambda_0$ (W/m · deg), t (°C).

At a small temperature difference ($\vartheta_{BC}/2\bar{T} < 0.05$) expression (10) becomes

$$Q_r(\tau) = 4\varepsilon_0\sigma_0 2\pi R_c l \bar{T}^3 \vartheta_{BC}. \tag{13}$$

Consequently, formula (12) can be rewritten as

$$\lambda(\bar{t}) = \frac{C_c b_c}{2\pi l \vartheta_{BC}} \ln\frac{R_B}{R_c} - \Delta\lambda_r(\bar{t}), \tag{14}$$

where

$$\Delta\lambda_l(\bar{t}) = 4\varepsilon_0\sigma_0 R_c \bar{T}^3 \ln\frac{R_B}{R_c}.$$

According to the design formula (14), the determination of $\lambda(\bar{t})$ requires a measurement of $b_C(\tau)$ and of drop ϑ_{BC} across the layer. Another mode of temperature measurements is also possible, where the time lag $\tau_{CB}(t)$ of the rod temperature $t_C(\tau)$ is recorded directly. The respective signals $E_C(\tau)$ and $E_B(\tau)$ are recorded through a potentiometer, while the time delay of signal E_C relative to signal E_B is recorded directly at preselected fixed temperature levels E(t).

For the other mode of temperature measurements the design formula becomes

$$\lambda(t) = \frac{C_c}{2\pi l \tau_{CB}(t)} \ln\frac{R_B}{R_c}(1 + \Delta\sigma) - \Delta\lambda_l(t), \tag{15}$$

where

$$\Delta\sigma = -1/2\,(2k_c + k_{V,\tau} - k_\lambda)\, b_c \tau_{CB}. \tag{16}$$

Considering that $k_C + k_{V,\tau} - k_\lambda = k_\vartheta$, one can transform (16) into

$$\Delta\sigma = -\frac{1}{2}(k_c + k_\vartheta)\, b_c \tau_{CB} = -\frac{1}{2}(k_c + k_\vartheta)\, \vartheta_{BC}. \tag{17}$$

The correction $\Delta\sigma$ in terms of (17) is more convenient for practical use.

These design formulas, which reflect the basic features of the method, do not incorporate a number of corrections involved in making this method technically feasible and, therefore, are not yet workable. Such major corrections include: a correction for the readings of thermocouples which measure the temperature drop across the layer, a correction for the heat transfer from block to rod through stray heat paths, and a correction for possibly anisothermal active rod and block surfaces. The first of these corrections must be usually made to account for stray emfs in the thermocouple circuits, for the not quite identical calibration characteristics of the thermocouples, and for the rather large distance from the active junctions of the thermocouples to the plane surfaces of the block and the rod. When the thermocouples are installed permanently, this correction depends only on the temperature level and on the heating rate and can thus be determined from calibration tests and defined as an "instrument constant." The second correction accounts, generally, for radiative heat transfer through the layer of test substance, also for heat leakage along the

TABLE 1. Test Values of Thermal Conductivity for Air and Water Vapor at Various Temperatures

t, °C	$\lambda\cdot10^4$, W/m·deg		t, °C	$\lambda\cdot10^4$, W/m·deg	
	air	water vapor		air	water vapor
150	347	280	319	458	467
207	385	341	336	462	484
227	400	365	354	477	502
246	411	385	363	484	510
265	422	406	380	489	532
284	433	426	396	497	550
302	442	445	404	508	558

rod fasteners and the thermocouple wires. The correction for radiation depends essentially on the nature of the test substance and it must be determined from data on the integral transmittivity of the layer as a function of the temperature. If the substance is almost perfectly nonabsorbing, then the correction $\Delta\lambda_r$ becomes an "instrument constant" and can be found from calibration tests. The correction for heat leakage along the rod fasteners and the thermocouple wires $\Delta\lambda_T$ can, in the case of a permanent installation, be always treated as an "instrument constant" and determined analytically.

The design formulas (14) and (15) with these two corrections become

$$\lambda(\bar{t}) = \frac{C_c}{2\pi l}\cdot\frac{b_c}{(\vartheta_{BC}-\vartheta^0)}\ln\frac{R_B}{R_c} - \Delta\lambda_0, \tag{18}$$

$$\lambda(t) = \frac{1}{2\pi l}\cdot\frac{C_c}{(\tau_{CB}-\tau^0)}\ln\frac{R_B}{R_c}(1+\Delta\sigma) - \Delta\lambda_0. \tag{19}$$

Here $\Delta\lambda_0 = \Delta\lambda_r + \Delta\lambda_T$.

Corrections $\vartheta^0(\tau)$ and $\tau^0(t)$ are "instrument constants" and can be found from a calibration test duplicating a measurement with the rod inserted into the block along a sliding fit.

A quantitative consideration of the systematic error due to anisothermal active block and rod surfaces is fraught with technical difficulties. For instance, it requires a larger number of thermocouples in the block and in the rod, to be located within the most characteristic zones of the test layer, and it requires a precise calibration of the calorimeter. In our calorimeter setup there are two main factors which make the active surfaces of the test layer anisothermal. These are the heating of the rod from its ends and the inevitable heat loss through the block ends. For a quantitative evaluation of the temperature field we will use the solution to the problem concerning the heating of a short rod [3].

The temperature field in the block within the zone of the test layer is a parabolic function of the coordinate:

$$t_B(x,\tau) = t_B(0,\tau) - \Delta t_B\frac{x^2}{l^2}, \quad \Delta t_B = \frac{q_T}{2\lambda_B}\cdot\frac{l^2}{L}. \tag{20}$$

The temperature field in the rod satisfies the equation of heat conduction:

$$\frac{d^2t_c}{dx^2} + n^2(t_B - t_c) = \frac{b_c}{a_c}, \quad n^2 = \frac{2\lambda}{\lambda_c R_c\delta} \tag{21}$$

with the boundary conditions

$$\left.\frac{dt_c}{dx}\right|_{x=0} = 0; \quad \left.\frac{dt_c}{dx}\right|_{x=l} = \frac{\lambda}{\lambda_c}\cdot\frac{\vartheta_T}{\delta}, \quad \vartheta_T = t_B(l) - t_c(l). \tag{22}$$

The general solution to Eq. (21) is

$$t_c(x,\tau) = t_B(x,\tau) - \frac{1}{n^2l^2}\left(2\Delta t_B + \frac{b_c}{a_c}l^2\right) + \left(2\Delta t_B + \frac{\lambda}{\lambda_c}\frac{l}{\delta}\cdot\vartheta_T\right)\frac{\operatorname{ch} nx}{nl\operatorname{sh} nl}. \tag{23}$$

From (23) follows the temperature drop $\vartheta_L(x,\tau)$ across the cylindrical part of the layer

$$\vartheta_L(x,\tau) = \frac{1}{n^2l^2}\left(2\Delta t_B + \frac{b_c}{a_c}l^2\right) - \left(2\Delta t_B + \frac{\lambda}{\lambda_c}\frac{l}{\delta}\vartheta_T\right)\frac{\operatorname{ch} nx}{nl\operatorname{sh} nl}. \tag{24}$$

Considering that $(2l + R_C)\bar{\vartheta}_\delta = 2l\bar{\vartheta}_L + R_C\vartheta_T$, we have

$$\vartheta_L(x, \tau) = \bar{\vartheta}_\delta + \left(2\Delta t_B + \frac{\lambda}{\lambda_c}\cdot\frac{l}{\delta}\vartheta_T\right)\left[\frac{R_c}{2l+R_c}\left(\frac{\operatorname{ch} nl}{nl \operatorname{sh} nl} - \frac{1}{n^2l^2}\right) - \left(\frac{\operatorname{ch} nx}{nl \operatorname{sh} nl} - \frac{1}{n^2l^2}\right)\right]. \tag{25}$$

Relation (25) yields the section $\bar{x}$ where the temperature drop is equal to the mean-over-the-surface temperature drop, i.e., where the condition $\vartheta_L(\bar{x}, \tau) = \bar{\vartheta}_\delta(\tau)$ is satisfied. Coordinate $\bar{x}$ can be determined here from the following equation:

$$\operatorname{ch} n\bar{x} = \frac{R_c}{2l+R_c}\operatorname{ch} nl + \frac{2l}{2l+R_c}\cdot\frac{\operatorname{sh} nl}{nl}. \tag{26}$$

The curve $\bar{x}/l = f(nl)$ shown in Fig. 2 covers almost all calorimeters used in practice. It can be seen here that within the range $nl < 4$, which is of most practical significance, the ratio $\bar{x}/l = \text{const}$ so that the formula

$$\bar{x} = l\sqrt{1/3\left(1 + \frac{2R_c}{2l+R_c}\right)} \tag{27}$$

applies.

Thus, if thermocouples B and C are located at section $\bar{x}$ according to (27), the temperature drop across the test layer will be equal to the mean-over-the-surface drop and no correction for anisothermy should (to the first approximation) be necessary. If this condition holds true, then $\bar{\vartheta}_\delta$ and the measured temperature drop $\vartheta_L(\bar{x})$ are related as follows:

$$\bar{\vartheta}_\delta = \vartheta_L(\bar{x})(1 - \Delta\sigma_T), \tag{28}$$

with $\Delta\sigma_T$ denoting a correction for the axial temperature drop along the rod

$$\Delta\sigma_T = \frac{1}{270}\cdot\frac{2\lambda}{\lambda_c}\cdot\frac{l^2}{\delta R_c}\cdot\frac{\lambda l}{\lambda_c\delta}\left[1 + \frac{4R_c}{2l+R_c} - \frac{5}{4}\cdot\frac{R_c^2}{(2l+R_c)^2}\right]. \tag{29}$$

Correction $\Delta\sigma_T$ involves rather determinate parameters and its exact magnitude can be found analytically. For an estimate of the allowable Δt_B across the block segment [0, 1] it is convenient to use the inequality

$$\Delta t_B \leqslant \frac{270\bar{\vartheta}_\delta\Delta}{\frac{2\lambda}{\lambda_c}\cdot\frac{l^2}{\delta R_c}\left[1 + \frac{4R_c}{2l+R_c} - \frac{5}{4}\cdot\frac{R_c^2}{(2l+R_c)^2}\right]}, \tag{30}$$

where Δ is the relative error within which the temperature drop Δt_B may be disregarded.

If $\bar{\vartheta}_\delta$ is measured not with one but with two pairs of thermocouples installed at sections $\bar{x}$ and $-\bar{x}$ equidistant from the center, then correction $\Delta\sigma_T$ may most often be omitted.

In many cases a precise isothermism at the boundaries of the test layer is attained rather easily and, therefore, it is possible to remove any constraints on the coordinate of the thermocouples B and C location. With certain conditions for measuring $\bar{\vartheta}_\delta$ defined, for example, one may use thermocouples located at the center section ($\bar{x} = 0$). In order to determine these test conditions, we will make use of relation (25). It follows from here that $\vartheta_L(0, \tau) = \bar{\vartheta}_\delta(\tau)$, if the condition

$$\left(\frac{2\Delta t_B}{\bar{\vartheta}_\delta} + \frac{R_c}{2l}n^2l^2\right)\left[\frac{R_c}{2l+R_c}\left(\frac{\operatorname{ch} nl}{nl \operatorname{sh} nl} - \frac{1}{n^2l^2}\right) - \left(\frac{1}{nl \operatorname{sh} nl} - \frac{1}{n^2l^2}\right)\right] \leqslant \Delta \tag{31}$$

is satisfied, with Δ denoting the allowable relative error due to anisothermy.

In this way, each correction has a distinct structure and can be determined analytically with sufficient accuracy. Expressions (29)-(31) may be considered the basis for an optimum calorimeter design.

It would be desirable to simplify the design formulas somewhat from the practical standpoint. Considering that

$$\delta = R_B - R_c, \quad \bar{R} = R_B - \frac{1}{2}\delta, \quad \vartheta_{BC} = n_{BC}k_u k_t, \quad b = \frac{\Delta t}{\Delta\tau} = k_t\frac{\Delta E}{\Delta\tau}$$

and expanding $\ln R_B/R_C$ into a power series in terms of $\delta/2\bar{R}$, we can rewrite formulas (18) and (19) as

$$\lambda(\bar{t}) = \frac{N(t)}{k_u(n_{BC} - n^0)}\left(\frac{\Delta E}{\Delta\tau}\right) - \Delta\lambda_0, \tag{32}$$

$$\lambda(t) = \frac{N(t)}{(\tau_{CB} - \tau_0)}(1 + \Delta\sigma) - \Delta\lambda_0. \tag{33}$$

Here $N(t) = \delta C_C/\bar{F}$.

In order to verify this method experimentally, the author has built an instrument according to the design described thoroughly in [4]. Numerous measurements have revealed the effectiveness of both the instrument and the procedure. The $n_{BC}(t)$ curve and the $n^0(t)$ curve shown in Fig. 3 are based on calibration tests and measurements with air. Temperature measurements were made with Nichrome–constantan thermocouples 0.2 mm in diameter and calibrated at the D. I. Mendeleev VNIIM. The temperature drop and the heating rate were measured with a model R-306 low-resistance potentiometer of class 0.015 accuracy in conjunction with a model M17/4 mirror galvanometer. The time was recorded by means of a model 51-SD two-hand stopwatch with 0.1 sec divisions.

Parameter N(t) appears to be an "instrument constant" and can be easily calculated as a function of the temperature. For a copper rod R_C = 5 mm and l = 68 mm the values of N(t) are given in Fig. 4. Here are also shown the calculated values of $\Delta\lambda_0 = \Delta\lambda_r + \Delta\lambda_T$.

The results of control tests for determining $\lambda(t)$ of air and water vapor are given in Table 1. Our data agree closely with reliable published data [5, 6].

We note, in conclusion, that numerous tests performed at higher temperatures have shown this method to be applicable to measuring $\lambda(t)$ of gases up to 1000°C. This study is of interest on its own account and the results will be reported in a separate article.

NOTATION

$a(t)$	is the thermal diffusivity;
$\lambda(t)$	is the thermal conductivity;
$\gamma(t)$	is the density;
$\lambda_C(t)$	is the thermal conductivity of rod material;
τ	is the time;
$k_i = 1/i\,(di/dt)$	is a relative temperature coefficient;
$n_i = 1/2i\,(d^2i/dt^2)$	is a relative temperature coefficient;
Q_λ	is the thermal flux conducted;
Q_r	is the thermal flux radiated;
ε_0	is the referred emissivity;
σ_0	is the Stefan–Boltzmann constant;
R_C, R_B	are the radius of rod and of block respectively;
δ	is the thickness of gas interlayer;
$\tau_{CB}(t)$	is the time lag;
$\Delta\sigma$	is the correction;
$\Delta\lambda_0$	is the correction for radiation and for heat leakage;
ϑ^0, τ^0	are the corrections for the thermocouple readings;
q_T	is the thermal flux density;
2L	is the height of block;
λ_B	is the thermal conductivity of block material;
$2l$	is the height of rod;
$\bar{\vartheta}_\delta$	is the mean-over-the-surface temperature drop across the interlayer;
L	is the mean-over-the-surface temperature drop across the cylindrical part of the layer;
Δt_B	is the temperature drop across the block;
$\bar{F}$	is the mean surface of the layer;
ΔE, $\Delta\tau$	are the increment of the thermocouple emf and the time corresponding to it;
$\bar{x}$	is the coordinate;

k_t is the temperature coefficient of a thermocouple;
k_u is the galvanometer sensitivity;
n is the temperature drop, measured in divisions of the galvanometer scale.

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