# THERMAL CONDUCTIVITY DETERMINATION FOR NONMETALLIC MEDIA BY THE CYLINDRICAL PROBE METHOD

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The problem of thermal conductivity for an infinitely long composite cylinder is solved. The solution obtained permits analysis of a probe of finite dimensions and the contact resistance between probe and casing. The experimental methodology is described and results are presented for determination of thermal conductivity of aqueous solutions of nitric and sulfuric acid at low temperatures.

A variant of the cylindrical probe method has been proposed for investigations of the thermal conductivity of chemically active substances. In using a cylindrical probe with an external protective shield, it is important, on the one hand, to consider the effect of the shield thickness, and on the other hand, the contact resistance which exists between the interior surface of the shield and the measurement heater element, both of which factors influence the final form of the equation used in calculating results. This problem has not been solved to date.

We will examine the problem of development of a temperature field, created by a composite infinite cylinder in an unbounded medium, the interior portion of the cylinder being a volume heat source. It is assumed that the Fourier number of this internal portion is sufficiently small. This permits one to neglect the temperature distribution over the cross section of the interior portion of the cylinder. The external portion of the composite cylinder is a thin-walled casing. A thermal contact resistance exists between the internal and external portions of the cylinder. The exterior surface of the cylinder has perfect contact with the surrounding medium.

The problem may be formulated as follows:

$$\frac{\partial T_2(r,\tau)}{\partial r^2} + \frac{1}{r}\cdot\frac{\partial T_2(r,\tau)}{\partial r} = \frac{1}{a_2}\cdot\frac{\partial T_2(r,\tau)}{\partial \tau}, \quad r_1 < r < r_2, \quad \tau > 0, \tag{1}$$

$$\frac{\partial^2 T_3(r,\tau)}{\partial r^2} + \frac{1}{r}\cdot\frac{\partial T_3(r,\tau)}{\partial r} = \frac{1}{a_3}\cdot\frac{\partial T_3(r,\tau)}{\partial \tau}, \quad r_2 < r < \infty, \quad \tau > 0, \tag{2}$$

$$T_1(0) = T_2(r,\ 0) = T_3(r,\ 0), \tag{3}$$

$$-\lambda_2 \frac{\partial T_2(r,\tau)}{\partial r} = -\lambda_3 \frac{\partial T_3(r_2,\tau)}{\partial r}, \tag{4}$$

$$-\lambda_2 \frac{\partial T_2(r_1,\tau)}{\partial r} = H\left[T_1(\tau) - T_2(r_1\ \tau)\right], \tag{5}$$

$$-\lambda_2 \frac{\partial T_2(r_1,\tau)}{\partial r} = \frac{r_1}{2}\left[\omega - c_1\rho_1 \frac{\partial T_1(\tau)}{\partial \tau}\right], \tag{6}$$

or

$$-\lambda_2 \frac{\partial T_2(r,\tau)}{\partial r} = Q - \frac{\alpha}{2}\cdot\frac{\partial T_1(\tau)}{\partial \tau}, \tag{6^a}$$

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$$T_2(r_2, \tau) = T_3(r_2, \tau), \tag{7}$$

$$T_3(r, \tau) < \infty, \tag{8}$$

wherein the designations $Q = \omega r_1/2$; $\alpha = r_1 \rho_1 c_1$.

Employing the Laplace transform relative to time $\tau$ and solving the system so obtained for $\overline{T}_1(p)$, we have

$$\overline{T}_1(p) = \frac{Q}{p} \cdot \frac{\left[1 + \frac{Hr_1}{\lambda_2}\Delta\right]}{H + \frac{\alpha p}{2}\left[1 + \frac{Hr_1}{\lambda_2}\Delta\right]}, \tag{9}$$

where

$$\Delta = \frac{y\{K_1(y)I_0(x) + I_1(y)K_0(x)\}K_0(z) + K_\lambda z\,[I_0(y)K_0(x) - K_0(y)I_1(x)]\,K_1(z)}{y\left\{x\,[K_1(x)I_1(y) - I_1(x)K_1(y)]\,K_0(z) + K_\lambda z\,\frac{r_1}{r_2}\,[I_0(y)K_1(x) + I_1(x)K_0(y)]\right.},$$

$$x = q_2 r_1; \quad y = q_2 r_2; \quad z = q_3 r_3.$$

The function $\overline{T}_1(p)$ branches at $p = 0$. Thus, in returning to the original with the Laplace inversion formula, an integration contour must be selected with a profile along the negative real semiaxes. On this contour and within it, $\overline{T}_3(p)$ is a single-valued function of p and has no poles. This is easily established by using the asymptotic expression for cylindrical functions $I_\nu(x) \simeq (1/\sqrt{2\pi x})\exp(x)$, $K_\nu(x) \simeq \sqrt{\pi/2x}\exp(-x)$ and studying the behavior of the function in question for large p values.

On the basis of residue theory and Jordan's lemma, the contour integral can be found by integration along the line of the profile and low curvature.

Employing the method proposed by Golstein in [3], we expand the function $\overline{T}_1(p)$ into a series in low powers of p

$$\overline{T}_1(p) \simeq -\frac{r_1 Q}{2\lambda_3}\left[\frac{1}{p}\ln\left(\frac{\beta p}{w}\right) + \frac{r_1^2}{4a_3}\{2\ln(\beta p) - \ln^2(\beta p) - 2\} + \frac{r_1\alpha}{4\lambda_3}\ln^2\left(\frac{\beta p}{w}\right) + O(p)\right], \tag{10}$$

where

$$\beta = \frac{r_1^2\exp(2\gamma)}{4a_3}\ \ln w = \frac{2\lambda_3}{r_1 H} + \frac{2\lambda_3}{\lambda_2}\ln\frac{r_2}{r_1},$$

and $\gamma$ is Euler's constant.

Integrating Eq. (10) by terms, and using the values of the Eq. (10) integrals along the chosen contour of Eq. (1), we obtain, for large Fo

$$T_1(\tau) \simeq \frac{r_1 Q}{2\lambda_3}\left[\ln 4\mathrm{Fo} - \gamma + \frac{2\lambda_3}{r_1 H} + 2K_\lambda \ln\frac{r_2}{r_1} + \frac{1}{2\mathrm{Fo}}\right.$$

$$\left.\times\left\{\ln 4\mathrm{Fo} - \gamma + 1 - \frac{\alpha a_3}{r_1\lambda_3}\left(\ln 4\mathrm{Fo} - \gamma + \frac{2\lambda_3}{r_1 H} + 2K_\lambda \ln\frac{r_2}{r_1}\right)\right\} + O\left(\frac{1}{\mathrm{Fo}^2}\right)\right., \tag{11}$$

where $\mathrm{Fo} = a_3\tau/r_1^2$.

It follows from Eq. (11) that the curve of $T_1$ as a function of ln Fo has a rectilinear asymptote with an angular coefficient equal to $r_1 Q/2\lambda_3$:

$$T_1(\tau) \simeq \frac{r_1 Q}{2\lambda_3}\left[\ln 4\mathrm{Fo} - \gamma + \frac{2\lambda_3}{r_1 H} + 2K_\lambda \ln\frac{r_2}{r_1}\right]. \tag{12}$$

On the basis of Eq. (12), it is simple to determine the thermal conductivity of the external medium. Knowing the values $T_1(\tau_1)$ and $T_1(\tau_2)$ at differing times, we find

$$T_1(\tau_2) - T_1(\tau_1) = \frac{r_1 Q}{2\lambda_3}\ln\frac{\tau_2}{\tau_1}. \tag{13}$$

Hence

$$\lambda_3 = K_1 \frac{\ln \frac{\tau_2}{\tau_1}}{T_1(\tau_2) - T_1(\tau_1)}, \tag{14}$$

where

$$K_1 = \frac{r_1 Q}{2}.$$

The thermal conductivity of the external medium is determined by Eq. (12)

$$a_3 = \frac{K_2}{\tau} \exp\left(\lambda_3 K_3 + T_1(\tau) \frac{\lambda_3}{K_1}\right), \tag{15}$$

where

$$K_1 = \frac{r_1 Q}{2}; \quad K_2 = \frac{r_1^2}{4} \exp(\gamma); \quad K_3 = \frac{2}{r_1 H} + \frac{2}{\lambda_2} \ln \frac{r_2}{r_1}.$$

On the basis of the method described above, a device was constructed for determination of thermal conductivity of substances in the liquid and solid states.

Sulfuric and nitric acids were studied, their thermal conductivities being determined over the temperature interval –180 to +20°C. A variant of the probe method was employed.

The formula for calculation of the thermal conductivity of the substances studied has the form

$$\lambda = K_1 \frac{\ln \frac{\tau_2}{\tau_1}}{\vartheta(\tau_2) - \vartheta(\tau_1)}. \tag{16}$$

The probe constant $K_1$ is found experimentally with a reference liquid.

A diagram of the apparatus is presented in Fig. 1.

The measurement chamber 3 is constructed of stainless steel in the form of a cylinder. Internal chamber dimensions are: diameter, 40 mm; height, 140 mm. The weight, wall thickness, and other characteristics of the chamber have negligible significance when determining thermal conductivity by the probe method.

The resistance thermometer 5 and heater 4 are wound on the surface of the measurement chamber, and are designed to stabilize the temperature of the chamber and substance being studied.

The measurement probe is mounted coaxially within the chamber. Probe dimensions are: working length (heater length), 55 mm; diameter, 1.2 mm. The probe has a combined heater and resistance thermometer.

The excess probe temperature during the heating process in the substances studied did not exceed 0.5°C. This permitted relating the thermal conductivity values obtained to the initial temperature and neglecting changes in power input values produced by changes in the resistance of the probe heater–thermometer.

The change in power dissipation in the heater–thermometer produced by change in its resistance from start to end of heating is

$$\Delta P = I^2 \Delta R = I^2 R_0 \beta \Delta t. \tag{17}$$

The ratio of the power increment $\Delta P$ to the power $P_t$ is

$$\frac{\Delta P}{P_t} = \frac{I^2 R_0 \beta \Delta t}{I^2 R_0 (1 + \beta t)} = \frac{\beta \Delta t}{1 + \beta t}. \tag{18}$$

For a copper conductor at $t = 0°\mathrm{C}$ $\Delta P / P_t = 0.2\%$, and at $t = -196°\mathrm{C}$ $\Delta P / P_t = 1\%$.

The excess temperature value is found by

$$\Delta t = \frac{\Delta U}{I R_0 \beta}. \tag{19}$$

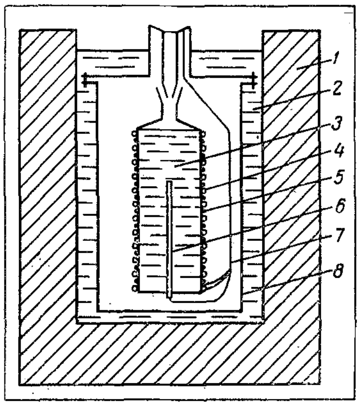

Fig. 1

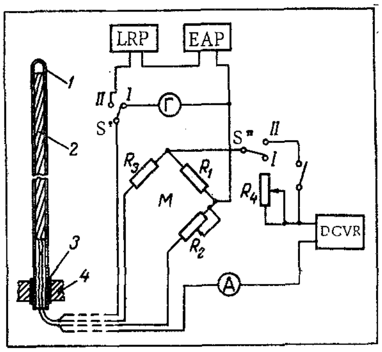

Fig. 2

Fig. 1. Diagram of apparatus. 1) Dewar flask; 2) liquid nitrogen; 3) measurement chamber containing substance to be studied; 4) measurement chamber heater; 5) measurement chamber thermometer; 6) probe; 7) leads; 8) low-temperature vessel.

Fig. 2. Electrical diagram of probe temperature measuring and recording system. 1) Probe envelope; 2) heater — thermometer winding; 3) interlayer; 4) measurement chamber bottom.

Measurement and recording of temperature are performed with a bridge circuit M (Fig. 2), in one of the legs of which the probe heater-thermometer is connected. The value of the resistance $R_{h\text{-}t}$ is determined from the ratios of the bridge leg resistances at balance

$$R_{h\text{-}t} = \frac{R_2 \cdot R_3}{R_1}. \tag{20}$$

In balancing the circuit, switch S is placed in position I, the bridge current then being determined by $R_4$. In position II the measurement diagonal is connected to the electronic automatic potentiometer EAP, and the bridge is fed directly from the dc voltage regulator DCVR. If the unbalance voltage during probe heating exceeds 10 mV, unbalance voltage compensation steps are manually switched in with the low resistance potentiometer LRP, ensuring that the EAP carriage returns to its initial position. This affords convenience in registration and interpretation of the thermograms.

In studying thermal conductivity with the probe method, it is necessary that there be an equality and constancy of temperature at every point within the volume of the medium studied. The necessary temperature values are produced by the thermostat system.

Experiments were conducted as follows. Initially, the probe constant $K_1$ was determined. The probe constant was calculated from a thermogram taken with glycerine, then verified with mineral oil and distilled water thermograms. Mineral oil, glycerine, and water were chosen since they have low, average, and maximum thermal conductivities among nonmetallic liquids.

The thermograms obtained on the EAP were graphically constructed in new coordinates ($\Delta U$, $\ln \tau$). The asymptote to the function $\Delta U = f(\ln \tau)$ thus obtained was constructed.

Using the known thermal conductivity of the substance, the constant $K_1$ can be found from the formula

$$K_1 = \lambda_e \mathrm{tg}\, \alpha_e, \tag{21}$$

where

$$\mathrm{tg}\, \alpha_e = \frac{\vartheta(\tau_2) - \vartheta(\tau_1)}{\ln \frac{\tau_2}{\tau_1}}.$$

The formula for determination of the thermal conductivity of the substance to be studied has the form

$$\lambda = K_1 \frac{1}{\mathrm{tg}\, \alpha}. \tag{22}$$

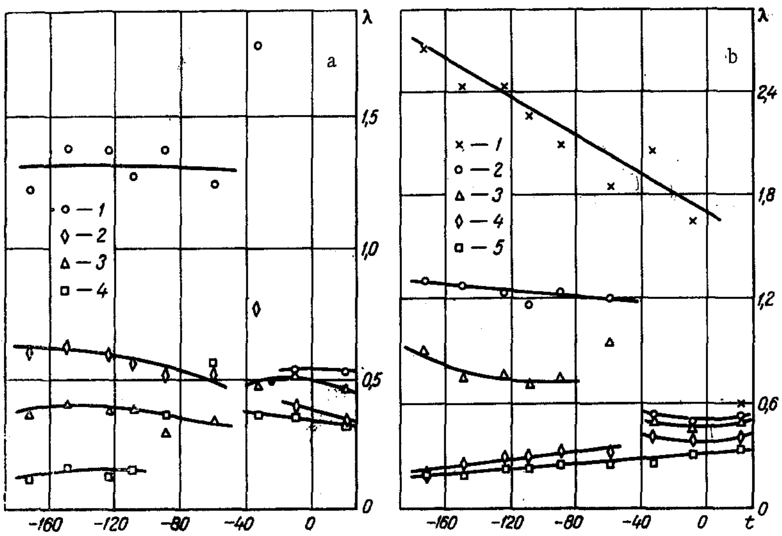

Fig. 3. Thermal conductivity of aqueous solutions of nitric (a) and sulfuric (b) acid versus temperature. a: 1) composition $HNO_3$ 25%, $H_2O$ 75%; 2) $HNO_3$ 50%, $H_2O$ 50%; 3) $HNO_3$ 72%, $N_2O_4$ 3%, $H_2O$ 25%; 4) $HNO_3$ 95%, $N_2O_4$ 3%, $H_2O$ 2% (molar concentrations). b: 1) composition $H_2O$ 100%; 2) $H_2SO_4$ 25%, $H_2O$ 75%; 3) $H_2SO_4$ 50%, $H_2O$ 50%; 4) $H_2SO_4$ 75%, $H_2O$ 25%; 5) $H_2SO_4$ 94%, $H_2O$ 6% (weight concentrations); λ, W/m · deg; t, °C.

Knowing the angle of inclination of the asymptote to the function $\Delta U = f(\ln \tau)$, constructed graphically from the thermogram of probe heating in the substance to be studied (in the same coordinate scale, in which $K_1$ was found), and knowing the value of $K_1$, we determine the thermal conductivity of the substance.

Since the thermogram is constructed in the coordinates ($\Delta U$, $\ln \tau$) the above statements are valid only for fixed temperature. This is due to the fact that the coefficient of proportionality between $\Delta U$ and probe temperature changes and is dependent on probe current.

For any arbitrary temperature, Eq. (22) can be rewritten, allowing for Eq. (19), in the form

$$\lambda = \frac{I_T}{I_1} K_1 \frac{1}{\operatorname{tg} \alpha}. \qquad (23)$$

The probe current $I_T$ is determined from temperature T by the condition that

$$I_T^2 R_{h\text{-}t} = \text{const}.$$

The error in determination of λ is no greater than 7%.

Reproducibility of results at every fixed temperature was within the limits of 1%.

The results obtained for thermal conductivity for the solutions mentioned above are presented in Fig. 3.

The aqueous acid solutions were produced from chemically pure sulfuric and nitric acid, obtained by double distillation of the commercial products.

Sulfuric acid concentration was determined by density, with a relative error no greater than 1%.

Analysis of the nitric acid was conducted by the volume method with titration with a base. The error in determining concentration was 1%. Calculation of the nitrogen tetroxide content was done by the manganometric method, with error no greater than 1%.

The thermal conductivity values of the 25 and 75% nitric acid solutions at T = −35°C are significantly higher than those at the neighboring points of the temperature interval. The same is true of the 25% sulfuric acid solution at T = −60°C. This is evidently due to the fact that these temperatures are within the region of a phase shift, where Eq. (22) for determining thermal conductivity requires refinement.

## NOTATION

| | |
|---|---|
| $T_1(\tau)$ | is the temperature of the interior portion of the composite cylinder; |
| $T_2(r, \tau)$ | is the temperature of the compound cylinder envelope; |
| $T_3(r, \tau)$ | is the temperature of the external medium; |
| $\lambda$, $c_1$, $\rho_1$ | are the thermal conductivity, specific heat flux, and density of interior part of cylinder; |
| $\lambda_2$, $a_2$ | are the thermal conductivity and thermal diffusivity of compound cylinder envelope; |
| $\lambda_3$, $a_3$ | are the thermal conductivity and thermal diffusivity of external medium; |
| $\omega$ | is the power of volume heat source; |
| $r_1$ | is the radius of interior portion of composite cylinder; |
| $r_2$ | is the external radius of composite cylinder envelope; |
| $H = 1/R$ | where R is thermal resistance between interior portion and envelope of cylinder; |
| $I_0(x)$, $I_1(x)$, $K_0(x)$, $K_1(x)$ | are the modified Bessel functions of the first and second types of zeroth and first order, respectively; |
| $\vartheta$ | is the excess probe temperature; |
| $\beta$ | is the temperature resistance coefficient; |
| $I_1$ | is the probe current at temperature at which $K_1$ is determined; |
| $I_T$ | is the probe current at temperature T. |

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