MEASUREMENT OF THE SPECIFIC HEAT OF LIQUIDS WITH AN ELECTRONIC CALORIMETER

K. N. Chakalev and L. K. Belopukhov

Inzhenerno-Fizicheskii Zhurnal, Vol. 14, No. 4, pp. 698–704, 1968

UDC 536.22.083

A method of determining the specific heat of liquids is described. The test liquid is placed in a special steel container. The sample is heated by electron bombardment with an electron beam focused by electrostatic lenses.

A number of problems of nonstationary heat transfer were examined in [1–3]. The experimental solution of these problems became possible only as a result of the development of a method of controlling the heat flow to the test sample, i.e., of obtaining a given heat flow in the form of a function of time. Electron bombardment, which is practically inertialess and, in principle, permits an unlimited increase in heat flux intensity, was selected for this purpose.

In our apparatus the specimen is placed in a vacuum chamber and plays the part of anode (Fig. 1). The electron source, an oxide-coated cathode, is placed at a certain distance from the anode. Thanks to the potential difference between anode and cathode, by means of focusing elements it is possible to obtain an electron flow in the direction of the specimen (anode). Under electron bombardment the heat released in a surface layer several tenths or hundredths of a micron thick is propagated into the specimen as a result of heat heat conduction. This provides the basis for treating the problem as a case of heat transfer with boundary conditions of the second kind.

The heat flow depends on the electron energy and the flux density $j = I/S$,

$$q = j\Delta\varphi. \tag{1}$$

Thus, a predetermined variation of the heat flow to the sample surface can be obtained by varying the electron flux density or anode voltage.

In our experiments one of the methods of varying j was to vary the control electrode (grid) voltage. This makes possible both a smooth variation from zero or some initial value and a pulsed variation with variable pulse shape, as well as thermal waves of various configuration.

Apart from the actual magnitude of the heat flux, its distribution over the heat transfer surface is also important in creating given boundary conditions. Thus the current density should be uniform over the working section of the electron beam. Accordingly, we introduced an auxiliary anode designed to surround the bombarded surface so as to intercept some of the electrons. In this way, on focusing the beam we were able to obtain a broad maximum of the frequency of electron impact on the sample surface. As measurements of the current flowing through the sample and the auxiliary anode showed, this arrangement made it possible to obtain either an almost uniform impact density on the bombarded surface or, given suitable focusing, a density with a sharp maximum at the center.

The effect of the errors possible in various operating regimes were analyzed in [1, 2] and corrections determined. These include the errors due to radiation, heat losses through the leads, inaccurate positioning of the thermocouple junctions, secondary electron emission, etc.

The possibility of obtaining the required boundary conditions enabled us to use the apparatus for testing and developing methods of calculating heat transfer boundary conditions from the change of temperature in the specimen [2], including such complicated processes as those in which heat transfer is accompanied by phase changes at the surface and when the heat flow in the solid phase and the rate of migration of the phase transition front are among the quantities to be determined.

In [1] electronic heating was used to determine the specific heat and thermal conductivity of solids for a given constant heat flux.

The test specimen was a cylinder 5 mm in diameter and 10–15 mm long. One end of the cylinder was subjected to electron bombardment. The lateral surface and the other end were screened. The low pressure inside the apparatus (10^{-6}–10^{-7} mm) and screening ensured reliable isolation of the lateral surface, and thus the sample could be regarded as a model of an infinite plate.

In our view the method has the following advantages. The electronic calorimeter is suitable for use as a ready-made industrial test instrument as well as for use in the research laboratory. Use of the relations of nonstationary heat transfer makes it possible to determine specific heat and thermal conductivity simultaneously, from the data of a single experiment. There is no need to use a heat transfer agent as the calorimetric fluid. It is possible to use quite small amounts of test material without loss of accuracy. This is often a decisive factor.

Subsequent investigations showed that the method is applicable to liquid heat transfer agents as well as to solids. For a specific heat determination the liquid is placed in a metal container. This is a cylindrical vessel with a profiled bottom (Fig. 2), so that the thermocouple junction can be located in the center of the container.

The test liquid is introduced through a branchpiece using a syringe, after which the branch is sealed. The length of the branch is sufficient to prevent significant heating of the mass of liquid in the container during sealing.

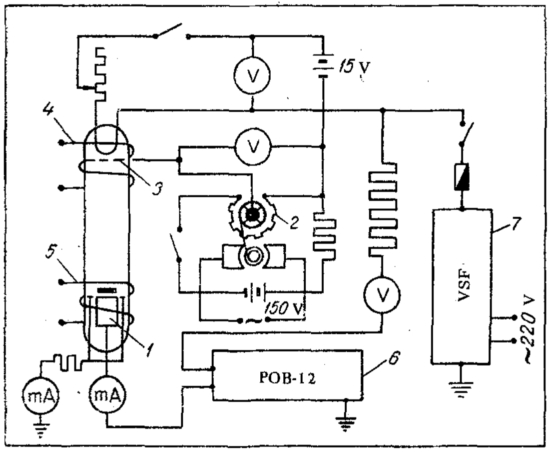

Fig. 1. Circuit diagram of electronic calorimeter: 1) specimen-anode, 2) device for automatically varying control electrode voltage, 3) control electrode, 4) magnetic lens, 5) guide coil, 6) oscillograph, 7) high-voltage rectifier.

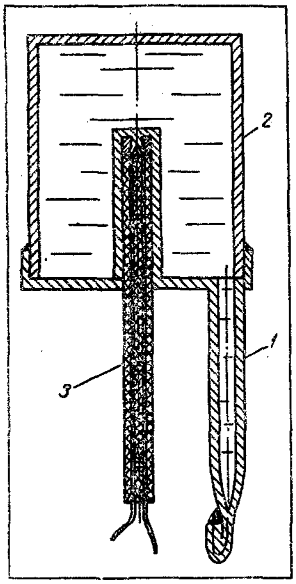

Fig. 2. Container used for measuring specific heat of liquids: 1) branch piece for filling container; 2) body of container; 3) thermocouple.

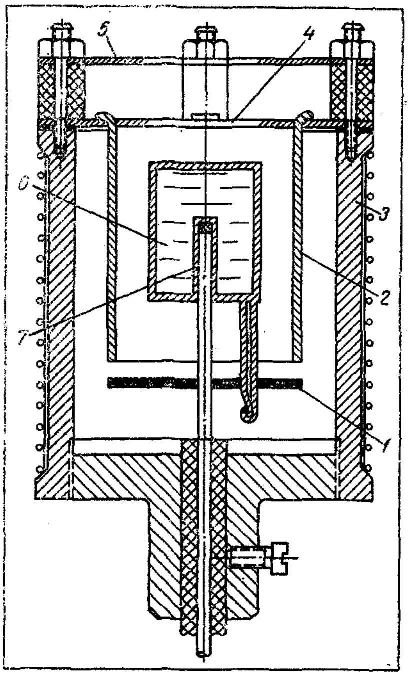

Fig. 3. Diagram showing the container mounting: 1 and 2) screens; 3) furnace; 4 and 5) diaphragms; 6) container with test liquid; 7) thermocouple.

The design of the container and the filling technique should provide for a perfect seal and sufficient mechanical strength to avoid rupture when the coefficients of thermal expansion of the container material and the test substance are not the same.

The container should be made of material with a low specific heat, and its mass should be as small as possible. These requirements are intended to ensure that most of the energy is absorbed by the test substance. Otherwise the accuracy of the measurements would be considerably reduced.

The specific heat of the container material should be known on the temperature interval investigated with an accuracy calculated not to reduce the accuracy with which the specific heat of the test substance is measured.

In our experiments we used a container made of 1Cr18Ni9Ti stainless steel. The thickness of the container wall was about 0.1 mm. The mass of the container was 1.2–1.3 g. For this grade of steel the temperature dependence of the specific heat is given by the formula [4]

$$c_p = 117 + 5.8\cdot 10^{-2}t - 0.21\cdot 10^{-4}t^2. \tag{2}$$

In the apparatus we employed electrostatic focusing of the electron beam. The object of focusing was to create a uniform distribution of electron flux on the end face of the container and also to eliminate the dynatron effect (Fig. 3). At large electron energies the dynatron effect (the knocking of electrons out of the container material) may be very considerable.

In order to return secondary emission electrons back to the anode (container), a ring-shaped antidynatron electrode was mounted in its immediate vicinity. A potential of 15 V was applied to this electrode. Since the maximum secondary electron energy is of the order of 10 eV, this potential was sufficient to return secondary electrons to the anode. Thus, the errors associated with secondary emission can be reduced considerably.

In order to exclude secondary-emission errors at the antidynatron ring itself, it was preceded by another ring of the same material. If a potential of +15 V is applied to this ring relative to the anode, then the two rings together will constitute a system of electrostatic lens-diaphragms serving to collimate the beam of electrons from the cathode. For the electron flux to be parallel after leaving the second ring, it is necessary to arrange the lenses so that their focal points coincide.

The focal length of an electron lens-diaphragm is given by the formula

$$|f| = \frac{4|u_0|}{E_1 - E_0}. \tag{3}$$

In our apparatus it may be assumed that the field strength on the diaphragm axis is determined only by the potential difference between cathode and anode and hence is equal to $\Delta\varphi/l$, where l is the distance between cathode and anode. Remote from the diaphragm axis the field may be assumed homogeneous and its strength equal to

$$\frac{15-(-15)}{2f} = \frac{30}{2f} = \frac{15}{f}.$$

For the focal length we have

$$f = \frac{4\cdot 15}{\dfrac{\Delta\varphi}{l} - \dfrac{15}{f}}$$

or

$$f = \frac{75l}{\Delta\varphi}. \tag{4}$$

In our case $l = 20$ cm, $\Delta\varphi = 2000$ V. We have $f = 0.75$ cm, and the distance between the diaphragm rings is 1.5 cm. Formerly, the electron beam was focused magnetically, but since this requires a considerable induction, the coil becomes inconveniently clumsy.

In measuring thermal parameters at temperatures above 150° C it is necessary to preheat the container and test substance. This is done with a furnace, a massive brass vessel with a nichrome heater coil. The test specimen or container and sample is placed in this vessel. The inside walls of the furnace form a screen whose emission balances the radiant heat losses from the sample.

To establish even closer equilibrium between the heat fluxes emitted and absorbed by the sample, one or two additional brass-foil screens may be introduced into the furnace (between the sample and the vessel walls). Thus, it was found possible to minimize the radiative losses through the side walls. The rate of cooling provides a check on how small these losses are. If during the time required to measure the specific heat on the given temperature interval the cooling rate is so small that the temperature reduction can be neglected, then the radiative heat losses through the lateral surface are also negligibly small. Such checks were made in all our experiments. When the test temperature is raised and the radiative losses are large and can not be neglected, it is necessary to introduce a correction, which is easily computed from the sample cooling rate.

We employed the following measuring apparatus. The current through the sample was measured with an M-182 milliammeter, the anode voltage with an M-91 shunted microammeter. The temperature was registered with an EPP-09 potentiometer or oscillographed on a Siemens oscillograph. The anode current and voltage were also oscillographed.

In conclusion we present a scheme for calculating the specific heat and the determination of the instrument error.

The energy of the bombarding electrons is distributed over the entire container and the test liquid. Then the heat balance equation will be

$$Q_{\text{total}} = Q_{\text{container}} + Q_{\text{liquid}} = c_c m_c (t_c^{\text{fin}} - t_c^{\text{in}}) + c_l m_l (t_l^{\text{fin}} - t_l^{\text{in}}). \tag{5}$$

Determining Q_{total} in terms of the specific heat flux from (1) and substituting in (5), we have

$$\Delta\varphi I \Delta\tau = c_c m_c \Delta t_c + c_l m_l \Delta t_l. \qquad (6)$$

The time of linear temperature rise is taken as the time $\Delta\tau$. For sufficiently small temperature differences, if the heat transfer processes in the sample may be assumed regular, the differences Δt_c and Δt_l may be considered equal. Then for experiments with the same container the expression for the specific heat may be written in the form

$$c_l = k_1 \frac{\Delta\varphi I \Delta\tau}{\Delta t} - k_2, \qquad (7)$$

where k_1 and k_2 are constant coefficients.

In this case the relative measuring error

$$\frac{dc_l}{c_l} = \frac{d(\Delta\varphi)}{\Delta\varphi} + \frac{dI}{I} + \frac{d(\Delta\tau)}{\Delta\tau} + \frac{d(\Delta t)}{\Delta t}. \qquad (8)$$

Assuming that we are able to measure the quantities in (7) with an error

$$d(\Delta\varphi) = 10 \text{ V} \quad dI = 2\cdot 10^{-6} \text{ A} \quad d(\Delta\tau) = 0.1 \text{ sec}$$
$$d(\Delta t) = 10^{-2} \text{ deg}$$

we can calculate the relative error for the optimum operating regime. Thus, for example, in one of the experiments to determine the specific heat the values of the quantities in Eq. (7) were as follows:

$$\Delta\varphi = 2500 \text{ V} \quad I = 1.5\cdot 10^{-3} \text{ A} \quad \Delta\tau = 20 \text{ sec} \quad \Delta t = 5^\circ.$$

Then the relative error

$$\frac{dc}{c} = \frac{10}{2500} + \frac{2\cdot 10^{-6}}{1.5\cdot 10^{-3}} + \frac{0.1}{20} + \frac{0.01}{5} =$$
$$= 0.0123 = 1.23\%.$$

We have tested containers filled with water, glycerol, and a number of special heat transfer agents on the temperature interval from 20 to 400° C (in individual cases). The agreement with the published data and the results of other methods was found to be good. Thus, the relative error in determining the specific heat of water on the interval 20–100° C did not exceed 0.53% as compared with the published data.

NOTATION

$\Delta\varphi$ is the potential difference between cathode and anode (container); j is the electron flux density; I is the current; S is the area of bombarded container surface; c is the specific heat; u_0 is the diaphragm potential; E_1 is the electric field strength on diaphragm axis; E_0 is the electric field strength remote from diaphragm axis; l is the distance between cathode and anode; f is the focal length of the electron lens-diaphragm; Q_{total} is the quantity of heat expended on heating the container and the specimen; Q_c is the heat expended on heating container; Q_l is the heat expended on heating the test liquid; m_c is the mass of the container; m_l is the mass of the test liquid; c_c is the specific heat of the container; c_l is the specific heat of the test liquid; t_c^{in} and t_c^{fin} denote the container temperature, first and second measurements; t_l^{in} and t_l^{fin} denote the test-liquid temperature, first and second measurements; $\Delta\tau$ is the time interval of linear variation in container temperature; Δt_c is the variation of container temperature during the time $\Delta\tau$; Δt_l is the variation in the test-liquid temperature during the time $\Delta\tau$; $d(\Delta\varphi)$, dI, $d(\Delta\tau)$, and $d(\Delta t)$ are the absolute errors in measuring potential, time, and temperature.

REFERENCES

1. E. V. Kudryavtsev and K. N. Chakalev, IFZh, no. 1, 1960.

2. E. V. Kudryavtsev and K. N. Chakalev, 1-st Interuniversity Conf. on the Theory of Similarity and its Applications in Heat Engineering [in Russian], Trudy MIIT, Moscow, no. 139, 1961.

3. K. N. Chakalev, IFZh, no. 4, 1962.

4. Thermophysical Properties, Handbook edited by N. B. Vargaftik [in Russian], GEI, Moscow-Leningrad, 1956.

13 July 1967

Krzhizhanovskii Power Engineering Institute, Moscow