A SIMPLE CONTINUOUS-FLOW CALORIMETER FOR MEASURING THE SPECIFIC HEAT OF GASES

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Inzhenerno-Fizicheskii Zhurnal, Vol. 13, No. 1, pp. 31–36, 1967

UDC 536.6

A bridge-type arrangement of a capillary continuous-flow calorimeter for measurement of the specific heat of gases at constant pressure is described. The method of the experiment is analyzed. The construction of the calorimeter and the results of tests of its operation are described.

It was suggested in [1, 2] that the relationship between the temperature distribution along a thin-walled tube heated by an electric current, and the specific heat of the gas flowing through it could be used to measure the specific heat of gases at constant pressure. The practical realization of this method, however, entails several difficulties (precise thermostatic control of the ends of the measuring tube, measurement of very small temperature differences), which complicate the apparatus and reduce the accuracy of measurement.

To overcome these difficulties we suggest that the measuring tubes should be incorporated in an electric bridge, as shown in Fig. 1. Two thin-walled metal tubes 1, soldered in parallel into conductors 3 and heated by an electric current, together with the measuring wires 2 form an electric bridge. When there is no flow of gas the temperature distribution along the tubes is symmetrical and the bridge is balanced. Gas flowing through the tubes in opposite directions upsets the symmetry of the temperature distributions and, hence, alters the electric resistance in the bridge arms. In the measuring diagonal of the bridge there appears a voltage which depends on the specific heat of the gas at constant pressure and its mass flow rate. The inevitable small fluctuations in the ambient temperature and the temperature of the ends of the measuring tubes have no effect on the results of the measurement, since the changes produced in the resistances in the bridge arms by these fluctuations cancel one another out.

Neglecting longitudinal flow of heat in the gas, which is not more than 0.1–0.2% of the heat flow through the walls of the measuring tubes, we can represent the temperature distribution along an electrically heated tube when heat transfer with the surrounding medium occurs and gas flows through it by a system of dimensionless heat-balance equations:

$$\frac{d^2\vartheta_c}{dX^2} - L_e\vartheta_w - L_i(\vartheta_w - \vartheta_g) + L_e = 0,$$

$$\vartheta_w - \vartheta_g - \frac{\text{Pe}}{4\,\text{Nu}}\frac{d_i}{l}\vartheta_g' = 0, \qquad (1)$$

where $X = x/l$ is the dimensionless coordinate; $\vartheta_w(X) = (t_w - t_0)/\Theta_0$ and $\vartheta_g(X) = (t_g - t_0)/\Theta_0$ are the dimensionless temperatures of the tube wall and gas;

$$\Theta_0 = \frac{I^2 R_0(1+\beta t_0)}{\alpha_e \pi d_e - \beta I^2 R_0},$$

$$L_e = \frac{4(\alpha_e \pi d_e - \beta I^2 R_0)}{\pi\lambda_w\left[\left(\frac{d_e}{d_i}\right)^2 - 1\right]}\left(\frac{l}{d_i}\right)^2,$$

$$L_i = \frac{4\alpha_i d_i}{\lambda_w\left[\left(\frac{d_e}{d_i}\right)^2 - 1\right]}\left(\frac{l}{d_i}\right)^2 = \frac{4\text{Nu}}{\left[\left(\frac{d_e}{d_i}\right)^2 - 1\right]}\frac{\lambda_g}{\lambda_w}\left(\frac{l}{d_i}\right)^2$$

are dimensionless coefficients.

In the case of low heating ($t_w - t_0 \sim 1°$ C) the physical properties of the tube material and the investigated gas can be regarded as independent of X. At low gas flow rates $[\text{Pe}(d_i/l) = (4GC_p/\pi l\lambda_g) < 1]$ the length of the entry region for stabilization of α_i is very small—less than 0.1 mm [4, 5].

Hence, α_i can be regarded as independent of X and the dimensionless heat transfer coefficient Nu in (1) as independent of the kind of gas [4]. In this case, eliminating ϑ_g from (1), we obtain a third-order equation

$$\frac{\text{Pe}}{4\text{Nu}}\frac{d_i}{l}\vartheta_w''' + \vartheta_w'' - \frac{\text{Pe}}{4\text{Nu}}\frac{d_i}{l}(L_i + L_e)\vartheta_w' - L_e\vartheta_w + L_e = 0, \qquad (2)$$

the solution of which for boundary conditions

$$\vartheta_w(X=0) = \vartheta_w(X=1) = \vartheta_g(X=0) = 0$$

has the form

$$\vartheta_w = 1 - \sum_{k=1,2,3} C_k \exp(\nu_k X),$$

where C_k are dimensionless solution coefficients determined from the boundary conditions $\nu_k = f_k(L_i, L_e, (\text{Pe}/4\text{Nu})(d_i/l))$ are the roots of the characteristic equation

$$\frac{\text{Pe}}{4\text{Nu}}\frac{d_i}{l}\nu_k^3 + \nu_k^2 - \frac{\text{Pe}}{4\text{Nu}}\frac{d_i}{l}(L_i + L_e)\nu_k - L_e = 0.$$

The relative unbalance of the bridge depends on the change in resistance in its arms:

$$\left|\frac{U}{E}\right| = \left[\int_0^{l/2} R(t_w)\,dx - \int_{l/2}^{l} R(t_w)\,dx\right] \Big/ \int_0^{l} R(t_w)\,dx =$$

$$= \beta\Theta_0\left[\int_0^{1/2}\sum_{k=1,2,3} C_k\exp(\nu_k X)\,dX - \int_{1/2}^{1}\sum_{k=1,2,3} C_k\exp(\nu_k X)\,dX\right] \Big/ \left[1 + \beta t_0 + \beta\Theta_0 - \beta\Theta_0\int_0^1\sum_{k=1,2,3} C_k\exp(\nu_k X)\,dX\right].$$

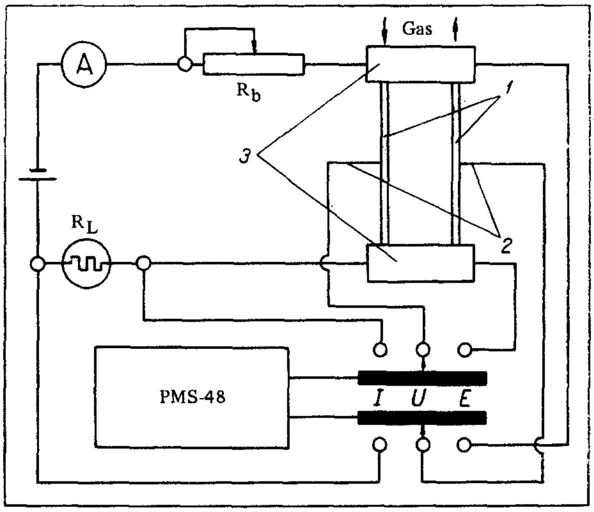

Fig. 1. Calorimeter circuit: A) ammeter; R_L) standard resistance coil; R_b) ballast resistor; PMS-48) dc potentiometer.

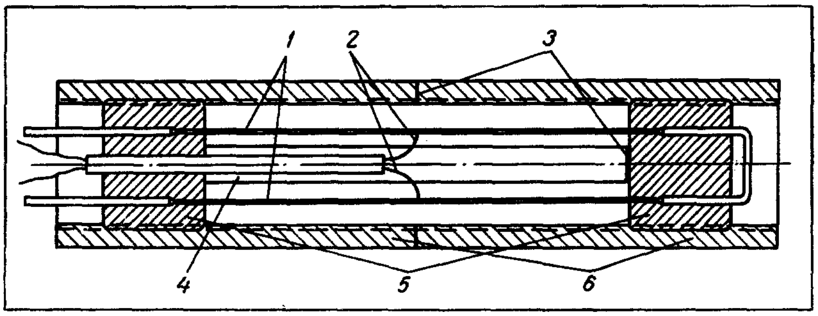

Fig. 2. Construction of calorimeter: 1) nickel tubes, cross section 1 × 0.05 mm, l = 100 mm; 2) nickel wires, diameter 0.1 mm; 3) mica spacers; 4) nickel reinforcing plate; 5) nickel current conductors; 6) thermostat units.

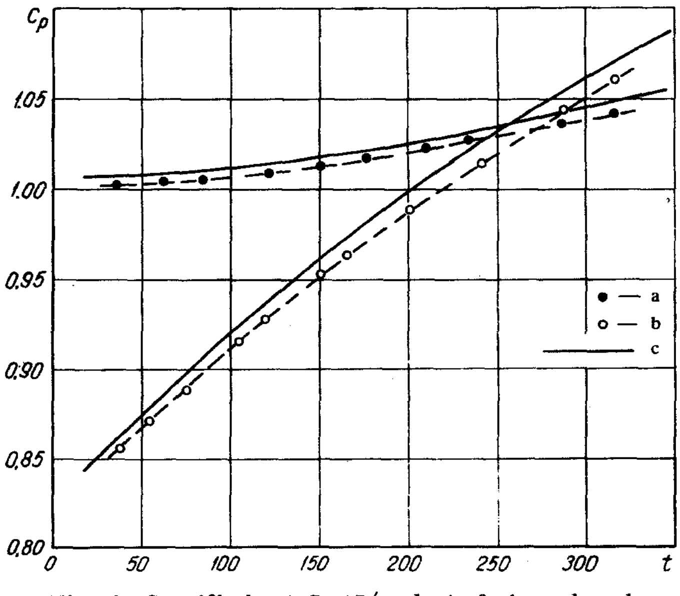

Fig. 3. Specific heat C_p (J/g · deg) of air and carbon dioxide: a) measured values for air; b) the same for carbon dioxide; c) from data of [3].

Eliminating Θ_0 and integrating, we obtain

$$\frac{1}{I^2}\left|\frac{U}{E}\right| = \beta R_0 \sum_{k=1,2,3} \frac{C_k}{\nu_k}\left[\exp\left(\frac{\nu_k}{2}\right)-1\right]^2 \Big/$$

$$\Big/ \alpha_e \pi d_e \left[1 - \frac{\beta I^2 R_0}{\alpha_e \pi d_e} \sum_{k=1,2,3} \frac{C_k}{\nu_k}(\exp \nu_k - 1)\right]. \quad (3)$$

For low gas flow rates we can expand the right side of (3) in a series of powers of the small parameter $(\mathrm{Pe}/4\mathrm{Nu})(d_i/l) \ll 1$ and obtain a relationship between the relative unbalance of the bridge and GC_p in explicit form

$$\frac{1}{I^2}\left|\frac{U}{E}\right| = AGC_p + \ldots, \quad (4)$$

where

$$A = \beta R_0 \left(1 - \frac{1}{\operatorname{ch}\frac{\sqrt{L_e}}{2}}\right)\left(1 - \frac{\frac{\sqrt{L_e}}{2}}{\operatorname{sh}\frac{\sqrt{L_e}}{2}}\right) \Big/ l(\alpha_e \pi d_e)^2 \times$$

$$\times \left[1 - \frac{\beta R_0 I^2}{\alpha_e \pi d_e}\left(1 + \frac{2}{\sqrt{L_e}} \operatorname{th}\frac{\sqrt{L_e}}{2}\right)\right]. \quad (5)$$

The value of the discarded terms in (4) for

$$\frac{\mathrm{Pe}}{4\,\mathrm{Nu}}\frac{d_i}{l} \leqslant 0.01 \quad (6)$$

is in hundredths of one percent of the first term. Condition (6) gives the permissible flow rates when (4) is used for calculation of specific heat.

To test the method we constructed a calorimeter, the design and main dimensions of which are shown in Fig. 2, and made measurements of the specific heat of air and carbon dioxide at atmospheric pressure in the temperature range 20–350° C.

To determine the specific heat we measured the relative unbalance of the bridge for several flow rates of the investigated gas, at constant t_0 and I. The gas flow rate was measured from the pressure drop on a capillary tube of diameter 0.4 mm and length 200 mm. The specific heat of the gas was calculated from the formula

$$C_p(t_0) = \frac{1}{A}\, d\left[\frac{1}{I^2}\frac{U}{E}\right] \Big/ dG.$$

The constant A, as expression (3) shows, depends only on the physical properties of the calorimeter tube material and quantities characterizing the heat exchange with the surroundings. Since these values are not known sufficiently accurately, the constant of the prebaked calorimeter and its temperature dependence were determined from calibration experiments with argon.

The results of measurements of the specific heat of air and carbon dioxide are shown in Fig. 3. The deviation of the experimental points from the mean value (dashed line) does not exceed 0.1%. The systematic deviation of the measured specific heats from published data (0.5% for air and 0.9% for carbon dioxide) is due mainly to the systematic error in measurements of the flow rate.

The results of the experimental tests and experience in operating the calorimeter indicate that the incorporation of the experimental tubes in an electric bridge increases the accuracy of the method and greatly facilitates its practical application. The calorimeter is small, simple in design, and can be used for measurement of the specific heat of gases with sufficient accuracy for many cases.

NOTATION

x is the coordinate along tube; t_w is the tube temperature; t_g is the gas temperature; t_0 is the ambient temperature; G is the gas flow rate, g/sec; C_p is the specific heat of gas at constant pressure, J/g · deg; ρ_g is the gas density, g/m^3; d_e and d_i are the external and internal diameters of tube, m; l is the tube length, m; β is the temperature coefficient of electrical resistance of tube material, 1/deg; R_0 is the resistivity of tube at 0° C, ohm/m; $R(t_w)$ is the same at t_w° C; λ_w and λ_g are the thermal conductivities of tube material and gas, W/m · deg; E and U are the voltage in supply and measuring diagonals of bridge, V; I is the current through tube, amp; α_e and α_i are the coefficients of heat transfer from tube surface and to gas flow, W/m^2 · deg; $\mathrm{Nu} = \alpha_i d_i/\lambda_g$ is the limiting value of Nusselt number for laminar flow [4]; Pe is the Peclet number.

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26 October 1966

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