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Abstract

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EXPERIMENTAL DETERMINATION OF THE ENTHALPY OF CORUNDUM (Al_2O_3) AT TEMPERATURES FROM 500 TO 2000°

Experimental data on the enthalpy and heat capacity of solid substances at present, as a rule, do not extend beyond temperatures of 1500-1600° ([1,2]). This is explained by methodological and technical difficulties in carrying out experiments at temperatures above 1600°. Meanwhile, in connection with the demands of modern technology, studies of the thermophysical properties of substances, including enthalpy and heat capacity, are urgently needed at temperatures considerably exceeding 1600°. With this in mind, a method was developed and, in accordance with it, an experimental installation was built for determining the enthalpy and heat capacity of solid substances up to temperatures of the order of 2400°.

The operation of the installation is based on the mixing method, using a massive metal calorimeter with a diathermic method of heat measurement. Heating of the specimen to a high temperature is carried out in a reconstructed furnace of the TVV-2 type with a tungsten heater. Between the furnace and the calorimeter there is a shutter device, whose shutter opens for the time during which the specimen falls into the calorimeter, and then closes again. The furnace and the calorimeter constitute a common sealed volume, which during the experiment is either under a vacuum of the order of 10^{-3} mm Hg, or in an inert argon atmosphere at a pressure of 1.05 ata.

The calorimetric system consists of a copper block, two platinum resistance thermometers, and a lever mechanism used to close the copper leaves of the calorimeter lid. Before the specimen falls, the leaves of the calorimeter lid are held by the lever mechanism in the open position. After the specimen has fallen, the closing of the leaves is effected automatically when the shutter of the shutter device closes.

The temperature of the calorimetric system was measured by two resistance thermometers—an outer and an inner one. The outer thermometer, with a resistance of about 200 ohms, is laid bifilarly in a two-start groove cut in the cylindrical surface of the copper block. The inner thermometer, having a resistance of about 50 ohms, in the form of a spiral of platinum wire, is wound

Graph of the enthalpy of corundum versus temperature. Vertical axis: i, kcal/kg, from 0 to 600. Horizontal axis: temperature in °C, from 0 to about 2000. Legend: solid circles–MEI experiments; open circles–(10); open circles–(6); open squares–(11); open triangles–(9); dashed line–(7); diamonds–(8); inverted triangles–(13).

Figure 1: Graph of the enthalpy of corundum versus temperature. Vertical axis: i, kcal/kg, from 0 to 600. Horizontal axis: temperature in °C, from 0 to about 2000. Legend: solid circles–MEI experiments; open circles–(10); open circles –(6); open squares–(11); open triangles–(9); dashed line–(7); diamonds–(8); inverted triangles–(13).

bifilarly on a copper helical frame. The thermometer is placed in a blind hole in the copper block. By careful fitting of the dimensions, good thermal contact was ensured between the thermometer frame and the block. Both thermometers were made of spectrally pure platinum wire 0.05 mm in diameter.

The copper block is enclosed in a metal shell. In order to reduce heat losses from the calorimetric system, the inner surfaces of the shell are carefully polished, and a cover of aluminum foil is tightly stretched over the copper block. In addition, between the shell and the block there is a system of shields made of polished aluminum foil, while the protruding parts of the calorimetric system are made of low-thermal-conductivity textolite.

The calorimeter shell is in a water thermostat, the constancy of whose temperature was maintained with an accuracy of $\pm 0.001^\circ$.

Fig. 1. Dependence of the enthalpy of corundum, measured from 0°C, on temperature.

Calibration of the calorimeter was carried out by heating it with an electric current. The work of the current Q was measured by the compensation method on a potentiometer, and it was assumed that 1 abs. joule = 0.2390 cal. From the calibration, the dependence of the heat value of the calorimeter H on the magnitude of the true temperature change of the calorimetric system Δt was determined:

$$H_i = \left(\frac{Q}{\Delta t}\right)_{\text{calibr}} = f(\Delta t). \tag{1}$$

To calculate Δt, graphs of the change in temperature of the calorimetric system with time were plotted from the experimental points. On the averaging straight lines of the initial and final periods, at the moments of the beginning τ_0 and the end τ_{p} of the main period, the apparent change in temperature of the calorimetric system $(t - t_0)$ and the magnitudes of the temperature drifts $(dt/d\tau)_0$ and $(dt/d\tau)_{\text{p}}$, corresponding to the temperatures t_0 and t_{p}, were found. The corrections for heat exchange δt and Δt in this case are equal to (3)

$$\delta t = k \int_{\tau_0}^{\tau_\text{p}} (t - t_k)\, d\tau, \qquad \Delta t = (t_\text{p} - t_0) + \delta t = t'_\text{p} - t_0, \tag{2}$$

where $t'_\text{p} = t_\text{p} + \delta t$ is the temperature of the calorimetric system at the end of the main period, taking into account the correction for heat exchange. The integral (2) is determined by graphical integration, while the cooling rate k and the convergence temperature t_k are determined by calculation:

$$k = -\frac{(dt/d\tau)_\text{p} - (dt/d\tau)_0}{t_\text{p} - t_0}; \tag{3}$$

$$t_k = \frac{(dt/d\tau)_\text{p} + (dt/d\tau)_0}{2k} + \frac{t^*_\text{p} + t_0}{2}. \tag{4}$$

The amount of heat introduced by the specimen into the calorimeter is found from the measured value of Δt and the dependence (1) known from calibration:

$$Q = H\Delta t = \left(\frac{Q}{\Delta t}\right)_\text{calibr} \Delta t. \tag{5}$$

Since the initial temperature of the main period during calibration and in the experiments for determining enthalpy was set the same ($t_0 = 22^\circ$), an unambiguous relationship was obtained between Q, H, and Δt (1), and the values of Δt in the numerator and denominator of formula (5) were equal. Owing to this method of calibration, the parabolic dependence of the resistance of the platinum thermometer can, with an insignificant error (4), be replaced by a linear one over the interval $\Delta t \leq 10^\circ$; in this case the coefficient of proportionality between temperature and resistance will also be an unambiguous function of Δt and will cancel in the final result (5).

Thus, the construction of the graphs $t = f(\tau)$ and the calculation by formulas (1)–(5) were carried out directly from the values of the electrical resistance of the thermometers, while from the calibration of the calorimeter the dependence $H = (Q/\Delta R)_\text{calibr} = f(\Delta R)$ was determined.

In all, 28 calibration points were obtained for each thermometer. The scatter of the points relative to the averaging straight line obtained by the method of least squares does not exceed ±0.2% for both the external and the internal thermometer. The root-mean-square deviation is ±0.08%. The change in the heat value of the calorimeter per 1° is 0.07%.

In the course of calibration the following points were clarified:

1) Experiments with different shapes of the temperature curve in the main period agreed within the accuracy of the calibration, although the time for introducing one and the same amount of heat differed by a factor of 2–3.

2) On the basis of graphs $(dt/d\tau)_\mathrm{p} = f(t_\mathrm{p} - t_k)$ and $(dt/d\tau)_0 = f(t_0 - t_k)$, constructed from the experimental data, it was found that the conditions of heat exchange in the calorimeter are practically independent of the direction of the heat flux,

and the limits of applicability of the cooling law on which the calculation of δt (2) is based are restricted by the temperature difference $(t - t_k) \leqslant 5 \div 6^\circ$. Taking this into account, the investigations were carried out at $\Delta t = 3 \div 8^\circ$; moreover, owing to the selection for each experiment of the corresponding thermostat temperature (almost equal to t_k), the value $\delta t/\Delta t$ did not exceed 5%.

3) The measurements of the amount of heat on the two thermometers agreed well (discrepancy of $\sim \pm 0.1\%$), and this gives grounds for recommending, in similar investigations, the use of the more convenient internal thermometers.

The first experiments on the apparatus that had been constructed were devoted to the study of corundum (the α-modification of aluminum oxide) with the aim of refining the existing experimental data of other investigators up to 1550° and extending the range of investigation to 1993°, i.e., in essence, to the melting point of corundum $(2015 \div 2050^\circ)$. The investigation was carried out on 5 samples, which had a cylindrical shape, with heights of $43 \div 28$ mm and diameters of $21 \div 17$ mm. The aluminum oxide content in the sample was $99.8 \div 99.9\%$, and the sample weights were $17 \div 29$ g.

The temperature of the samples up to 1318° was measured with standard platinum-rhodium-platinum thermocouples of class II, and above this—with an optical pyrometer using a model of an absolute black body created in a cylindrical recess of the sample. The pyrometer, together with the three-sided glass prism through which the sample was observed, was checked against standard temperature lamps of class I at the All-Union Scientific Research Institute of the Committee of Standards, Measures, and Measuring Instruments. The samples in the furnace were suspended on a tungsten wire, which was burned through by an electric current in order to drop the sample into the calorimeter.

Proceeding from the special features of investigation at high temperatures (4), an ampoule was not used for corundum, and the heat losses by the sample during its fall into the calorimeter were determined by calculation from the known coefficient of total radiation of corundum (5).

In the temperature interval $498 \div 1993^\circ$, 30 experimental points were obtained, through which a smoothing curve was drawn. The results of the investigation are shown in the graph (see the experiments of the Moscow Power Engineering Institute), on which, for comparison, the experimental points of other authors are plotted. The experiments were carried out mainly in an argon medium, and they coincided with control experiments carried out in vacuum. The transition from high temperatures back to low ones did not affect the results of the investigation.

The experimental points obtained in the overlapping temperature region agree on average within ±0.5% with the data of (6) (500—1514°), (7) (1100—1400°), (8) (500—1300°), and within ±1% with the data of (9,10) (500—1550°). The new experimental data agree at 800—900° with the results of (11,12), and at 500—800° are higher by 1—0.2%, respectively. The experimental data of (13) at temperatures of 500—1100° lie below the experimental data obtained by 0.5—1%.

The limiting relative random error in determining the enthalpy in the present work when measuring the temperature with a thermocouple (500—1300°) is estimated as ±0.5%, and when measuring the temperature with a pyrometer (1300—2000°), ±0.9%.

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