LITERATURE CITED

1. V. Kh. Goikhman and V. M. Gol'dfarb, in: Plasmochemical Reactions and Processes [in Russian], Nauka, Moscow (1977), p. 232.
2. G. B. Sinyarev, Tr. Mosk. Vyssh. Tekh. Uchil., No. 159, 35 (1973).
3. G. B. Sinyarev, B. G. Trusov, and L. E. Slyn'ko, Tr. Mosk. Vyssh. Tekh. Uchil., No. 159, 60 (1973).
4. V. P. Glushko (ed.), Thermodynamic Properties of Individual Substances [in Russian], Vols. 1 and 2, Nauka, Moscow (1962).
5. JANAF Thermochemical Tables, 2nd ed., Nat. Bur. Stand., Washington, USA (1971).
6. L. V. Gurvich and N. P. Rtishcheva, Teplofiz. Vys. Temp., No. 1 (1965).
7. I. B. Rozhdestvenskii, B. N. Gutov, and N. A. Zhigul'skaya, in: Collection of Researches of the G. M. Krzhizhanovskii Power Institute [in Russian], No. 7 (1973).
8. V. A. Kireev, Methods of Practical Computations in the Thermodynamics of Chemical Reactions [in Russian], Khimiya, Moscow (1975).
9. K. Wicks and F. E. Block, Thermodynamic Properties of 65 Elements, Their Oxides, Halides, and Nitrides [Russian translation], Metallurgiya, Moscow (1965).
10. M. Kh. Karapet'yants and M. L. Karpet'yants, Fundamental Thermodynamic Constants of Inorganic and Organic Substances [in Russian], Khimiya, Moscow (1968).
11. V. P. Glushko (ed.), Thermal Constants of Substances [in Russian], Vols. 1-7, Moscow (1965-1974).
12. Ya. I. Gerasimov, A. N. Krestovnikov, and A. S. Shakhov, Chemical Thermodynamics in Nonferrous Metallurgy [in Russian], Vol. 7, Metallurgizdat, Moscow (1975).

DEVICE FOR MEASUREMENT OF HEAT CAPACITY OF SMALL SPECIMENS IN THE RANGE 10-20°K

K. R. Zhdanov, É. V. Matizen,
A. A. Nikoforov, and M. A. Starikov

UDC 536.2.083

The construction of a calorimeter for rapid measurement of heat capacity by the cooling method is described.

In the technology of producing materials with certain properties (i.e., superconductors) the need often arises for rapid low-temperature measurements of the heat capacity of a large number of small specimens no more than 0.05 cm^3 in volume. One of the methods which may be used is that of continuous cooling of the specimen. In this method the decrease in specimen enthalpy per unit time is equal to the thermal flux through the heat sink. The equation describing the cooling process has the form

$$C(T)\dot{T} = -W(T, T_0). \tag{1}$$

The heat power $W(T, T_0)$ may be determined in individual measurements. In experiment the temperature of the cooling specimen is measured as a function of time. The rate of temperature change is found by numerical differentiation. The literature describes the use of such a method for measurement of heat capacity at temperatures below 4.4°K [1, 2].

Heat capacity may also be measured during the process of continuous heating [3]. However, the cooling method is more easily realizable, since it does not require total adiabatization of the specimen; the only requirement is constancy of heat sink conditions from experiment to experiment. The experimental point density with the cooling method can be made extremely high (up to 100 points per degree).

A block diagram of the device which realizes the cooling method is shown in Fig. 1. The specimen is heated to a temperature T and heating is terminated, so that the specimen cools through the heat sink to the "bath" temperature T_0. The voltage across the resistance

---

Institute of Inorganic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 37, No. 6, pp. 1068-1973, December, 1979. Original article submitted January 21, 1979.

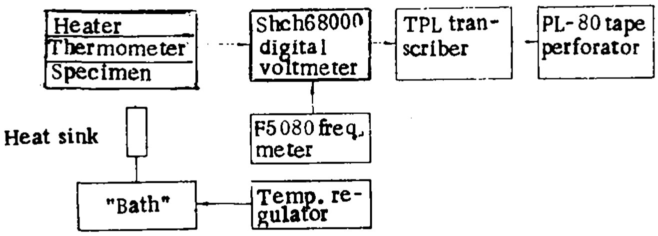

Fig. 1. Block diagram of calorimeter.

thermometer is measured by an Shch68000 digital voltmeter at time intervals determined by an F5080 frequency meter-chronometer. Measurement results are passed through a TPL transcriber to a PL-80 tape perforator. The measurement period is chosen so that the temperature steps comprise approximately 0.01°K.

The total cooling time depends on the heat capacity of the specimen, comprising 20 to 60 min with the construction described. This permits elimination of random error in multiple measurements.

The bath temperature T_0 is maintained constant in all measurements. A thermostat mechanism ensuring stabilization to an accuracy of 10^{-3}°K is provided.

Measurement results were processed by a Minsk-32 computer. A time—temperature dependence was interpolated and its derivative calculated with use of cubic splines with smoothing [4]. The cryostat construction is shown in Fig. 2. The calorimeter was designed for measurement of heat capacity of specimens in the form of plates 8 mm in diameter. It is important that temperature gradients in the specimen be negligibly small during cooling. For the stationary case these gradients can be estimated from the expression $\Delta T = hW(T, T_0)/2kS$ [3]. Thus the method described can be used for measurements of thin specimens with good thermal conductivity.

The substrate for the specimen is a copper plate 8 mm in diameter and 0.1 mm thick, suspended on silk threads. A germanium crystal is soldered to the bottom of the substrate and serves as a resistance thermometer. A manganin heater element is glued to the substrate. The electrical leads of the thermometer and heater simultaneously function as the heat sink. They are made of manganin wires 0.075 mm in diameter and ∿3 cm long. The heat sink leads are terminated in a copper block, the "bath," whose temperature is maintained constant and equal to T_0.

The electrical leads coming from the "bath" are wound on another copper block, which is threaded into the copper cup and has good thermal contact with the liquid helium. The calorimeter electrical leads are connected to the measurement equipment through a vacuum coupling. The calorimeter and specimen are inserted into the cryostat through the cap with a removable rod. Three to five minutes are required for a change of specimens. Total time for a specimen measurement, considering time needed for filling with helium, is ∿2-3 h. Before filling with helium the outer calorimeter volume is evacuated to a pressure of not more than 10^{-4} Pa.

Thermometer calibration in the temperature range 14-20°K was performed using saturated hydrogen vapor, and from 2 to 4.2°K with saturated helium vapor [5]. The thermometer resistance as a function of temperature over the entire range 2-20°K was approximated by a polynomial of the form

$$\frac{1}{T} = \sum_{k=0}^{n} A_k (\ln R)^k \tag{2}$$

by the method of least squares. At n = 5 the mean square deviation of the relatively smoothed curve of Eq. (2) comprises 0.01°K.

The heat sink function $W(T, T_0)$ was determined in individual measurements. Upon passage of a current i through the heater with resistance r a power $P = i^2 r$ is liberated. The specimen should heat up according to the law

$$C(T)\dot{T} = P - W(T, T_0) \tag{3}$$

to a temperature T_1, at which the power dissipated in the heater is equal to the power loss through the heat sink, i.e., $W(T_1, T_0) = P$.

If we neglect the dependence of heat capacity on temperature in the immediate vicinity of T_1, then Eq. (3) may be rewritten in the form

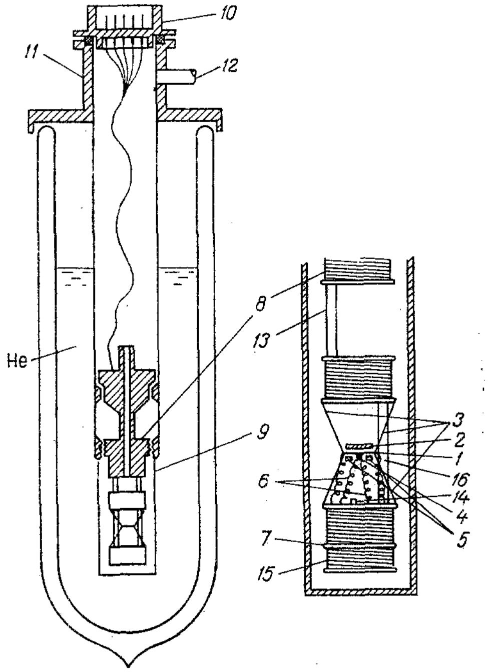

Fig. 2. Diagram of cryostat and calorimeter: 1) specimen substrate; 2) specimen; 3) silk threads; 4) thermometer; 5) heater; 6) thermometer and heater leads; 7) "bath"; 8) copper block; 9) copper cup; 10) vacuum coupling; 11) cryostat lid; 12) vacuum line; 13) three teflon supports (only one shown); 14) "bath" thermometer; 15) three copper braces (only one shown).

$$\dot{T} = -\frac{1}{\tau}(T - T_1), \tag{4}$$

where $1/\tau = [1/C(T_1)](dW/dT)|_{T=T_1}$.

To determine T_1 the specimen temperature was recorded from the time of heater turn-on. Numerical differentiation provided the value of the derivative $\dot{T}$ as a function of temperature. T_1 and τ in Eq. (4) were calculated by the method of least squares. The average error in determination of T_1 comprised ~ 10^{-3}°K.

The power dissipated in the connecting leads was considered in the usual manner, i.e., it was assumed that half this power was transmitted to the specimen and half to the "bath." No correction was introduced for temperature dependence of the connecting lead resistance [6], since its maximum value was less than 1% according to our estimates.

The heatsink function temperature dependence obtained in this manner was approximated by a polynomial of the form

$$W(T,\ T_0) = \sum_{k=1}^{4} B_k (T^k - T_0^k). \tag{5}$$

Scattering of experimental points relative to the curve of Eq. (5) comprised ∿1%.

Our estimates indicate that heat loss through the residual gas does not exceed 0.02% of the value of $W(T, T_0)$. Upon specimen change heat transfer by radiation may change slightly, but is less than 2% of the total heat transfer and may be neglected.

The power dissipated in the thermometer depends on temperature and current. If all measurements are performed at one and the same current, this power can be considered by including it in the determination of $W(T, T_0)$.

Good thermal contact of specimen and thermometer is usually assisted by some kind of glue, vacuum grease, varnish, or indium solder [1, 7-9]. A shortcoming of such "glues" is that it is difficult to remove their residues when changing specimens.

In the construction described here the specimen is attached to the substrate with a measured quantity of water. Immediately after insertion of the specimen into the calorimeter the entire construction is cooled with liquid nitrogen. Since the saturated vapor pressure of water at room temperature is quite high, the danger exists that during the cooling process some of the water may evaporate, leading to differing amounts of water being present in individual experiments. Four trials were made of one and the same copper specimen, 0.08525 g in mass, with the specimen removed and reinstalled for each measurement. Comparison of the data obtained shows that there was no significant systemic error.

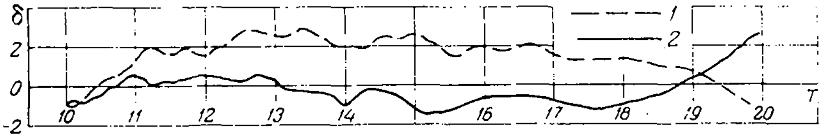

Fig. 3. Relative deviation of measured heat capacity C_e of copper (1) and tin (2) from smoothed data obtained in adiabatic calorimeter, C_a; $\delta = (C_e - C_a)/C_a$, %; T, °K.

The quality of the thermal contact between specimen and substrate produced by the water was verified in the following manner. At the times of heater turn-on and turn-off relaxation processes occur in the heater–thermometer–substrate–specimen system with a time constant τ_0. They characterize the thermal conductivity and capacity of the individual components of the measurement circuit, including the contact [3]. Measurements revealed that $\tau_0 < 1$ sec. Thus the steady state temperature difference between thermometer and specimen $\Delta T \sim \tau_0 \cdot \dot{T}$ does not exceed a few mdeg K, since usually $\dot{T} \sim (1-8)\cdot 10^{-3}$deg K/sec.

To verify calorimeter operation the heat capacities of white tin and copper were measured. In order to eliminate the heat capacity of the measurement circuit, measurements were performed twice, with specimens of one and the same material, but of two different masses (m_1 and m_2). In this case the heat capacity per mole of material can be expressed in the form:

$$C_M = \frac{MW(T, T_0)}{m_1 - m_2} (\dot{T}_1^{-1} - \dot{T}_2^{-1}).$$

The tin specimens had masses of 0.09419 and 0.04297 g, while the copper specimens were 0.08525 and 0.22492 g. Experimental data were compared with smoothed heat capacity values of these specimens obtained in the adiabatic calorimeter of [10, 11]. Results of this comparison for the temperature range 10-20°K are shown in Fig. 3.

Multiple measurements of the temperature behavior of one and the same specimen revealed that the rate of temperature change was reproducible to an accuracy of better than 1%, i.e., $\delta\dot{T}/\dot{T} < 0.01$. It can be shown that in such a case the error in heat-capacity determination comprises $\delta C_M/C_M \simeq (C_1 + C_2 + C_0)/(C_1 - C_2)\delta\dot{T}/\dot{T}$. In the temperature interval studied this uncertainly comprises 1.6% for tin and 3.5% for copper.

It should be noted that the temperature range in which the heat capacity measurements were performed could be expanded. For an increase in the direction of lower temperatures, it would be necessary to decrease the "bath" temperature T_0. If the measurements above 20°K were necessary, the thermometer could be calibrated for that range with a platinum resistance thermometer.

Thus, the equipment described makes possible rapid measurement of heat capacity of specimens with volume not exceeding 0.05 cm^3 with accuracy sufficient for a number of purposes. The calorimeter construction developed here also permits heat capacity measurements by the thermal relaxation method [9], continuous heating [3], heating by ac current [12], and the modified pulse method [13]. The measurement apparatus may be used for direct input of data into a computer.

NOTATION

T, temperature, °K; T_0, "bath" temperature, °K; $\dot{T} = dT/dt$, rate of temperature change, °K sec; C(T), specimen heat capacity, J/°K; C_M, molar heat capacity, J/mole/°K; M, molecular mass of material, g; m_1, m_2, specimen masses, g; $\dot{T}_1$, $\dot{T}_2$, cooling rates of specimens with masses m_1 and m_2, °K/sec; h, specimen thickness, m; S, specimen area, m^2; k, thermal conductivity coefficient, W/m/deg.

LITERATURE CITED

1. T. Haseda and A. R. Miedema, Physica, 27, 1102 (1961).
2. A. Comberg, S. Ewert, and W. Sanger, Cryogenics, 18, 79 (1978).
3. Cochran, Schiffman, and Neybor, PNI, No. 4, 116 (1966).
4. S. B. Stechkin and Yu. N. Subbotin, Splines in Computational Mathematics [in Russian], Nauka, Moscow (1976).
5. M. P. Malkov, I. B. Danilov, A. G. Zel'dovich, and A. B. Fradkov, Handbook of Physicotechnical Fundamentals of Cryogenics [in Russian], Énergiya, Moscow (1973).

6. Neybor, PNI, No. 4, 113 (1966).
7. Low-Temperature Calorimetery [Russian translation], Mir (1971).
8. Moses, Ben-Aroya, and Lupu, PNI, No. 8, 161 (1977).
9. Bachman et al., PNI, No. 2, 21 (1972).
10. V. N. Naumov and V. V. Nogteva, Seventh All-Union Conference on Calorimetry (Expanded Summaries of Reports) [in Russian], Moscow (1977), p. 488.
11. V. N. Naumov, V. V. Nogteva, and I. E. Paukov, Zh. Fiz. Khim., 53, 497 (1979).
12. P. F. Sullivan and G. Seidel, Phys. Rev., 173, 679 (1968).
13. Fagaly and Bon, PNI, No. 11, 143 (1977).

INVESTIGATION OF 10.6 μ ABSORPTION COEFFICIENT FOR CARBON DIOXIDE MOLECULES AT TEMPERATURES UP TO 3500°K

I. E. Zabelinskii, N. A. Fomin,
and O. P. Shatalov

UDC 621.378.33

Experimental data are used to analyze features of resonance absorption processes in the high-temperature region, where the influence of hot transitions is appreciable.

At present a considerable amount of information has accumulated on the behavior of the absorption coefficient at low and intermediate temperatures. By measuring the 10.6 μ radiation absorption coefficient in test cells, investigators have studied the α(T) relationship up to temperatures of ∿650°K [1-6]. The development of gasdynamic lasers [7] has led to a need to analyze absorption processes at higher temperatures. These investigations were conducted using the region behind the front of a shock wave in shock tubes as the absorbing cell: in [8] absorption coefficient data were obtained up to temperatures of ∿1600°K, and in [9, 10] measurements were made up to ∿ 2100°K.

Meanwhile, absorption of 10.6 μ radiation by CO_2 molecules at higher temperatures is scientific interest, e.g., in analyzing recombination processes, in investigating spectral processes in dense gases, and also in investigation of the characteristics of high-temperature gasdynamic lasers [11].

The present paper uses experimental data on the resonance absorption in carbon dioxide at high temperatures, obtained in a large-diameter shock tube (the VUT-1 facility at the Institute of Mechanics, M. V. Lomonosov Moscow State University), to discuss features of the absorption process in the high-temperature region (up to 3500°K).

Description of the Facility. The experiments were conducted in a shock tube of internal diameter 493 mm (see, e.g., [12]). The radiative absorption was investigated behind the incident shock front in pure CO_2 and in CO_2 + Ar mixtures. Argon of special purity (99.98%) and specially dried carbon dioxide gas (the drying agent was P_2O_5) were used. The shock tube was pumped down to $2 \cdot 10^{-2}$ torr. The rate of inflow of air due to imperfect sealing of the shock tube and desorption of gas from the walls did not exceed 10^{-3} torr/min.

The gas mixture was made up in a special mixer, and was mixed beforehand (by a fan mounted inside the mixer) for several minutes prior to each shock tube filling. The pressure in the shock tube after filling with gas was measured with an oil manometer to an accuracy of better than 1%. The initial pressure was 3-60 torr. The shock wave speed was measured from the signals of piezoelectric sensors (located along the shock tube section) to an accuracy of better than 2%. Radiation from a type GL-23 laser, modulated by a mechanical shutter, passed through the shock tube via a BaF_2 window and fell on a semiconductor detector (germanium, doped with gold), from which the signal was recorded on an oscilloscope. At the same time, part of the laser radiation was directed to an infrared monochromator via a semitransparent

---

Institute of Mechanics, M. V. Lomonosov Moscow State University, Moscow. A. V. Lykov Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 37, No. 6, pp. 1074-1082, December, 1979. Original article submitted November 21, 1978.

0022-0841/79/3706-1461$07.50