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Measurement of Heat Capacity by Adiabatic Calorimetry and Calculation of Thermodynamic Functions of Standard Substances: Copper, Benzoic Acid, and Heptane (For Calibration of an Adiabatic Calorimeter)

Mira R. Bissengaliyeva,*,† Daniil B. Gogol,† Shynar T. Taymasova,† and Nuraly S. Bekturganov‡

Institute of Complex Development of Mineral Resources, 5 Ippodromnaya St., Karaganda, 100019, Kazakhstan, and SC,
National Scientific-Technological Holding, Parasat, Republic Ave. 18, Astana, 010000, Kazakhstan

Measurements of the heat capacity of standard specimens of copper, benzoic acid, and heptane and their thermodynamic functions of molar heat capacity, change in entropy, and enthalpy have been carried out at a low-temperature thermal-physical installation in the temperature range (4.2 up to 320) K using the method of adiabatic calorimetry. The obtained data are in good agreement with the recommended values. The relative uncertainty limits of the calorimetric unit: ± 1.43 % at $T = 5$ K, ± 0.75 % at $T = 10$ K, ± 0.23 % at $T = 40$ K, and less than ± 0.11 % for the temperature range (90 up to 298.15) K have been determined according to the experimental data of measurements of the certified measure of oxygen-free electronic (OFE) grade copper heat capacity. According to the heptane heat capacity measurement, the values of its enthalpy and entropy of fusion at $T_{\text{fus}} = 182.54$ K, $\Delta H_{\text{fus}} = (14047 \pm 19.6)$ $\text{J}\cdot\text{mol}^{-1}$ and $\Delta S_{\text{fus}} = (76.96 \pm 0.11)$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, have been determined. These values are also in a satisfactory agreement with the reference data.

Introduction

Measurements of the heat capacity of reference substances are a necessary condition for carrying out precise calorimetric investigations and estimating the uncertainty of calorimeters. The main requirements for the standard specimens of heat capacity measurements include the stability of metrological performance and physical-chemical properties in the widest possible range of temperatures, the availability and possibility to obtain them in high-purity state, nonhygroscopicity, chemical stability, the absence of phase transitions in a changeable temperature range (except for the cases when enthalpy and entropy phase transitions are being determined), and so forth. One of the mandatory requirements for the certified measurement of heat capacity is the availability of the standard polynomial of heat capacity measurement, which is necessary while calculating a calorimeter value of uncertainty. Among such substances recommended as standard materials for adiabatic calorimetry by Sabbah et al.[1] are copper, benzoic acid, and heptane, used in temperature ranges (1 up to 300) K, (10 up to 350) K, and (10 up to 400) K, respectively. The present paper describes the design and process of determining performance reliability of the low-temperature thermophysical installation which was used to carry out the experimental measurements of the heat capacity of the specimens of natural minerals (hemimorphite, pyromorphite, antlerite, smithsonite, cerussite, wulfenite) studied by us.

Experimental Section

Description of the Installation and Parameters of the Heat Capacity Measurement. A low-temperature calorimetric installation produced by the firm "Termax" (Moscow, 2005)[2] consists of cryostat BKT-10.04 with a temperature range from (1.5 up to 350) K, a low-temperature calorimeter with a variation range from (4.2 up to 350) K, data collection and processing system AK-9.02, and an exhaust cart.

An inner capillary and a cooling chamber provide cooling of the calorimeter to the lowest temperature equal to the boiling temperature of the cooling liquid. The cryostat outer vacuum jacket is a pipe 127 cm in length and 44 mm in diameter, which is immersed into a standard liquid helium storage dewar with a 50.8 mm neck. A flange between the pipe and the cryostat head is tightened with an easily movable vacuum joining of PneEroup type, which is disjointed to place a specimen. On the cryostat head there is a vacuum valve, gas connections, and a RS32 connector to connect AK-9.02 data collection and processing system. A calorimetric cell is situated inside two screens, one nested into another. The inner screen is adiabatic, and the outer one serves for additional temperature insulation (Figure 1).

The installation embodies the classical adiabatic method of heat capacity determination, at which temperature of the screen surrounding a specimen being measured is maintained equal to the specimen temperature, that is, the body being measured is in adiabatic or, more precisely, in quasi-adiabatic conditions. The specimen under investigation is placed inside a titanium container with a volume of 1 cm^3, which is tightly inserted into a thin cylindrical heating case. The heater is made of manganin wire of 0.06 mm in diameter covered with one layer of copper foil 0.03 mm thick; the wire is coined around the case. Eleven junctions of thermocouples of copper−iron/chromel are glued to the foil; twelve junctions are on the inner surface of the copper adiabatic screen. The screen temperature is measured with an iron−rhodium resistance thermometer RIRT-3, calibrated at NPO "VNIIFTRI" (Moscow) according to the International Temperature Scale ITS-90 ($R_0 = 50\ \Omega$); the thermometer is located on the base of the adiabatic screen. During the heat capacity measurements the screen temperature is maintained

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* Corresponding author. E-mail: mirabis@ipkon.kz, 160655@mail.ru. Fax: +7-7212-414520.

† Institute of Complex Development of Mineral Resources.

‡ SC, National Scientific-Technological Holding.

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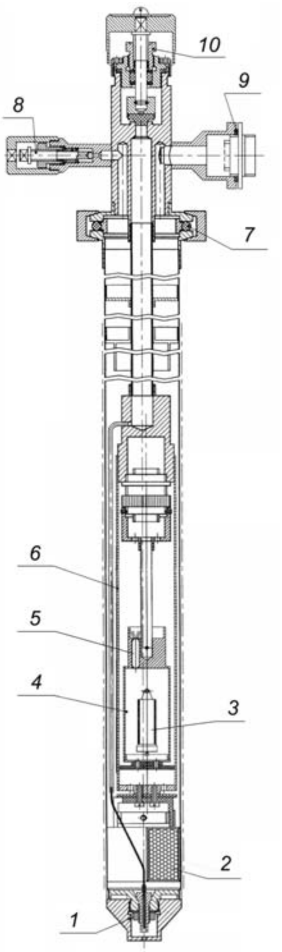

Figure 1. Scheme of a low-temperature calorimetric installation: 1, capillary; 2, charcoal getter; 3, sample container and heating tube; 4, inner adiabatic shield; 5, Fe/Rh resistance thermometer; 6, outer shield; 7, vacuum tight; 8, vacuum valve; 9, RS32 socket; 10, capillary valve.

equal to the temperature of calorimeter (the heater + container) correct to the some tenth of millikelvin. The container titanium lid is tightened with indium gasket and locked with a nut made of beryllium bronze. The container filled with a specimen is kept in vacuum ($p \approx 3$ Pa) for 15 min and then filled with gaseous helium at a pressure of 4 kPa at room temperature.

For the purpose of the experiment automation a measuring and controlling device of the AK-9.02 data collection and processing system functioning together with an IBM personal computer (PC) has been used. The AK-9.02 system is designed to measure voltage and resistance in the direct-current circuits. Reference resistors of (10, 100, and 1000) Ω provide the relative precision of measurements at the level not worse than $1 \cdot 10^{-5}$. Four digital-to-analog converters provide out voltages in the range (0 up to 20) V with a relative discreteness of 0.02 %. The system functions under the control of the software from the external computer, which gives commands via a bit-serial interface and gets the data of measurements from the system. On the computer's command the system independently carries out the programs of measurement and regulation recorded in the internal memory of the system microprocessors and requires a minimal exchange with the host computer.

The heating periods are from (50 to 100) s at $T = (4$ to $20)$ K, 150 s at $T = (20$ to $70)$ K, and 600 s at $T > 70$ K. The periods of drift (temperature displacement of the calorimeter at time interval $\Delta\tau$) measurements are from (60 to 200) s at $T = (4$ to $20)$ K, 240 s at $T = (20$ to $70)$ K, and 600 s at $T > 70$ K. The temperature steps of measurements are from (0.2 to 1) K at $T = (4$ to $20)$ K, 2 K at $T = (20$ to $70)$ K, and 3 K at $T > 70$ K.

Results and Discussion

Low-Temperature Measurements of Standard Specimens of the Heat Capacity Measurements in the Range from (4.2 to 320) K. The heat capacity references (calibration instruments) are used to evaluate reliability of a calorimetric installation; heat parameters of the calibration instruments are used at calorimetric measurements. Research laboratories usually use measures of the specific heat capacity from various materials being working standards since the substances differing in aggregative states, and thermal and physical characteristics are measured in calorimeters. Copper, benzoic acid, and heptane are among other working standards.

Measurement of the Heat Capacity of Oxygen-Free Electronic (OFE) Grade Copper. Measurements of the heat capacity of a standard specimen, OFE grade copper (annealed oxygen-free copper) in the titanium container, are carried out at a low-temperature thermophysical installation in the temperature range from (4.2 to 320) K.[3] The standard specimen of the heat capacity measurement, OFE grade copper GOST 859-78, is produced and certified in the Metrological Cryogenic Center of NPO "VNIIFTRI". The primary substance content in the specimen made in the form of a cylinder is not less than 99.995 % (the specimen mass was 7.42925 g).

The experimental values of copper heat capacity and thermodynamic functions are given in Table 1 of the Supporting Information. The temperature dependence of copper heat capacity in the measured temperature range has been smoothed according to the approximating spline method by the third power polynomials $C_p/\mathrm{J \cdot mol^{-1} \cdot K^{-1}} = a_0 + a_1(T/\mathrm{K}) + a_2(T/\mathrm{K})^2 + a_3(T/\mathrm{K})^3$; their coefficients are given in Table 1. The graphical extrapolation of copper heat capacity to absolute zero below $T = 4.5$ K has been performed according to the Debye T^3 law taking into account the electron component using the formula: $C_p/\mathrm{J \cdot mol^{-1} \cdot K^{-1}} = a(T/\mathrm{K})^3 + b(T/\mathrm{K})$, where $a = 4.8870 \cdot 10^{-5}$ and $b = 6.7325 \cdot 10^{-4}$, for the temperature range from (4.34 up to 5.62) K.

Figure 2 shows deviations of the experimental values of the heat capacity of the copper standard specimen from the smoothed curve in the temperature range from (4.3 up to 320) K. The copper thermodynamic functions calculated based on the polynomial coefficients are given in Table 2. The data on the copper heat capacity in helium and nitrogen areas resulting from mathematic treatment are given in Figures 3 and 4 in comparison with the values obtained by other authors.

As it seen from Figures 3 and 4, the experimental values of the copper heat capacity obtained by us and the data obtained by authors Rybkin et al.,[4] Stevens and Boerio-Goates,[5] Furukawa et al.,[6] White and Collocott,[7] and Blokhin et al.[8] relative to the values of Sabbah et al.[1] are in good agreement. A relative uncertainty of the heat capacity measurement in helium area was 0.5 %, and in the temperature range from (80 up to 320) K it did not exceed 0.2 % from the data recommended by Sabbah et al.

Determination of the Calorimetric Installation Uncertainty. The procedures for evaluation of the experimental uncertainty of the installation are taken from a low-temperature thermophysical unit TAU-1 manual written by the designers of this unit (Rybkin et al.).[4,10]

The installation uncertainty was determined by means of calculating deviations of the heat capacity values measured

Table 1. Coefficients of the Heat Capacity Polynomials of a Standard OFE Grade Copper Specimen for the Range $T = 4.5$ K up to 320 K at Different Temperature Ranges ΔT

	coefficients of polynomial $C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = a_0 + a_1(T/\text{K}) + a_2(T/\text{K})^2 + a_3(T/\text{K})^3$			
ΔT/K	a_0	a_1	a_2	a_3
4.5 to 5.5	−0.065005	0.0421651	$-8.7718\cdot10^{-3}$	$6.6299\cdot10^{-4}$
5.5 to 8	0.048611	−0.0208889	$3.1556\cdot10^{-3}$	$-1.0419\cdot10^{-4}$
8 to 13	0.022531	−0.0050360	$4.1684\cdot10^{-4}$	$4.1349\cdot10^{-5}$
13 to 20	−0.131088	0.0303737	$-2.3826\cdot10^{-3}$	$1.1720\cdot10^{-4}$
20 to 30	0.968573	−0.1266262	$5.1522\cdot10^{-3}$	$-4.5447\cdot10^{-6}$
30 to 50	2.203518	−0.2684105	$1.0491\cdot10^{-2}$	$-7.0706\cdot10^{-5}$
50 to 80	−5.902888	0.1933105	$1.7042\cdot10^{-3}$	$-1.4804\cdot10^{-5}$
80 to 120	−14.42312	0.5358163	$-2.8991\cdot10^{-3}$	$5.8601\cdot10^{-6}$
120 to 170	−9.251221	0.4124027	$-1.9199\cdot10^{-3}$	$3.2788\cdot10^{-6}$
170 to 220	2.781384	0.2001573	$-6.6799\cdot10^{-4}$	$8.0924\cdot10^{-7}$
220 to 270	18.18368	0.0085765	$1.2289\cdot10^{-4}$	$-2.7389\cdot10^{-7}$
270 to 320	33.52463	−0.1302450	$5.2397\cdot10^{-4}$	$-6.3449\cdot10^{-7}$

experimentally using this installation from those indicated in its value certificate in percentage terms. For this purpose the experimental values of the specific heat capacity were determined near (5, 10, 40, 90, 120, 200, 270, and 298.15) K. Five measurements were carried out at each temperature.

Each of the obtained values $C(T_i)$ taken from the experimental record has been reduced to the integral value of temperature T close to the average temperature near to (5, 10, 40, 90, 120, 200, 270, and 298.15) K. The reduced values $C(T)$ have been calculated by the formula:

$$C(T) = C(T_i) + \Delta C/\Delta T\cdot(T - T_i) \tag{1}$$

where $\Delta C/\Delta T$ is the value of a derivative for each experimentally measured point taken according to the standard copper heat capacity polynomial from the certificate of measure.

The deviation random component has been calculated in percentage terms by formula:

$$\mathring{\Delta} = \alpha\sqrt{\frac{\sum_{1}^{n}[(C(T) - \bar{C}(T))/\bar{C}(T)]^2}{n - 1}}\cdot 100 \tag{2}$$

where α is the Student coefficient ($\alpha = 2.78$ for $n = 5$ and confidence probability 0.95); n is the number of measurements; $\bar{C}(T)$ is an average from n values $C(T)$ reduced to temperature T.

The systematic component of deviation has been calculated in percentage terms by the formula:

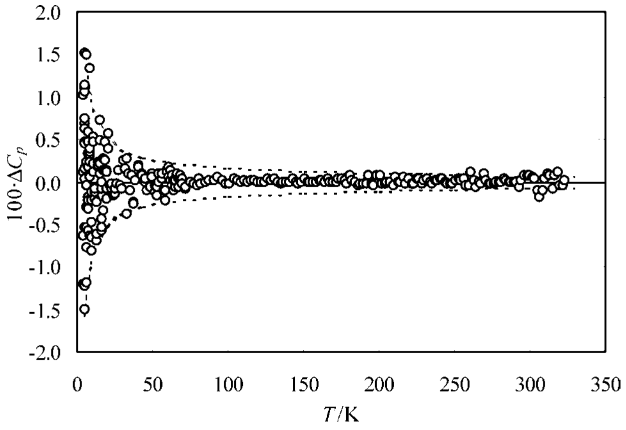

Figure 2. Relative deviations $\Delta C_p = (C_{p,\text{exp}} - C_{p,\text{fit}})/C_{p,\text{fit}}$ of experimental values of the heat capacity of the copper standard specimen $C_{p,\text{exp}}$ from the smoothed ones $C_{p,\text{fit}}$ in the range (5 to 320) K.

Table 2. Molar Thermodynamic Functions of OFE Grade Copper Standard Specimen ($M = 63.546$ g·mol^{-1})

T K	$C_{p,\text{m}}$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\Delta_0^T S^\circ_\text{m}$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\Delta_0^T H^\circ_\text{m}$ $\text{J}\cdot\text{mol}^{-1}$
5	0.0094	0.0054	0.0160
10	0.0552	0.0228	0.1543
15	0.184	0.0658	0.7055
20	0.461	0.152	2.2391
25	0.952	0.303	5.6696
30	1.684	0.538	12.160
35	2.630	0.866	22.871
40	3.728	1.288	38.713
45	4.927	1.795	60.321
50	6.173	2.379	88.064
55	7.421	3.026	122.06
60	8.633	3.724	162.22
65	9.797	4.461	208.31
70	10.90	5.228	260.09
75	11.94	6.016	317.21
80	12.89	6.817	379.31
85	13.77	7.625	446.00
90	14.59	8.436	516.94
95	15.34	9.245	591.79
100	16.03	10.05	670.23
110	17.24	11.64	836.74
120	18.25	13.18	1014.3
130	19.12	14.68	1201.3
140	19.85	16.12	1396.3
150	20.48	17.51	1598.0
160	21.01	18.85	1805.5
170	21.48	20.14	2018.0
180	21.89	21.38	2234.9
190	22.25	22.57	2455.6
200	22.57	23.72	2679.7
210	22.85	24.83	2906.8
220	23.10	25.90	3136.6
230	23.32	26.93	3368.7
240	23.53	27.93	3603.0
250	23.73	28.89	3839.4
260	23.91	29.83	4077.6
270	24.07	30.73	4317.4
273.15	24.11	31.01	4393.3
280	24.21	31.61	4558.8
290	24.34	32.46	4801.6
298.15	24.45 ± 0.03	33.14 ± 0.04	5000.4 ± 4.4
300	24.48	33.29	5045.7
310	24.60	34.09	5291.1
320	24.71	34.88	5537.6

where $C_0(T)$ is the value of the measured specific heat capacity at temperature T taken from its certificate.

After this an uncertainty of the tested installation for temperatures near (5, 10, 40, 90, 120, 200, 270, and 298.15) K has been determined by the formula:

$$\Delta_C = \frac{\bar{C}(T) - C_0(T)}{C_0(T)} \cdot 100 \qquad (3)$$

$$\Delta = \sqrt{\mathring{\Delta}^2 + {\Delta_C}^2 + {\Delta_M}^2} \qquad (4)$$

where Δ_M is the measured uncertainty from its certificate which is equal to (0.4 up to 0.05) % at temperatures from (4 up to 40) K and 0.05 % at temperatures from (40 up to 300) K. The batch of standard samples of heat capacity measurements to which our sample belongs has been certified in a high-precision sample calorimetric unit of the first level in accordance with the requirements of the USSR State Standard with the indicated uncertainty of 0.05 % at temperatures of (40 up to 300) K and the uncertainty of (0.4 up to 0.05) % at (4 up to 40) K. When calculating, this uncertainty was included into the value of uncertainty of our unit. The deviations of our data from those of other authors are shown in Figures 3 and 4, which do not reflect the degree of accuracy of the unit itself but depend on the degree of purity of a sample used, the presence of impurities, conditions of measurements, and so forth.

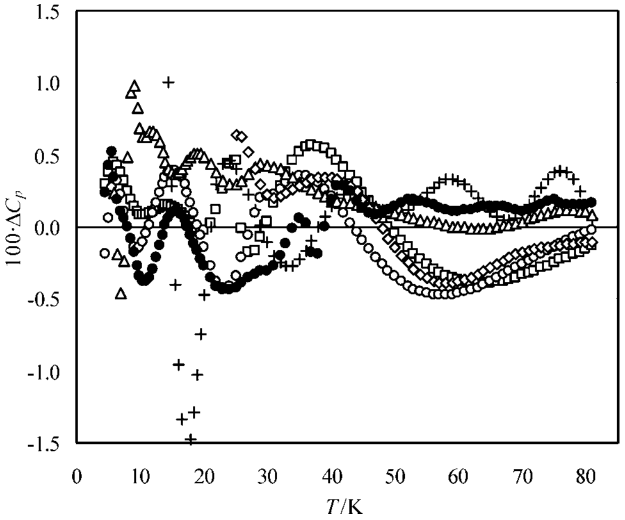

Figure 3. Relative deviations $\Delta C_p = (C_{p,\mathrm{exp}} - C_{p,\mathrm{std}})/C_{p,\mathrm{std}}$ of the heat capacity experimental values of the standard copper specimen $C_{p,\mathrm{exp}}$ from the recommended by Sabbah et al.[1] values $C_{p,\mathrm{std}}$ in the range (5 to 80) K: ●, this work; ○, ref 4; +, ref 5; □, ref 6; ◇, ref 7; △, ref 8.

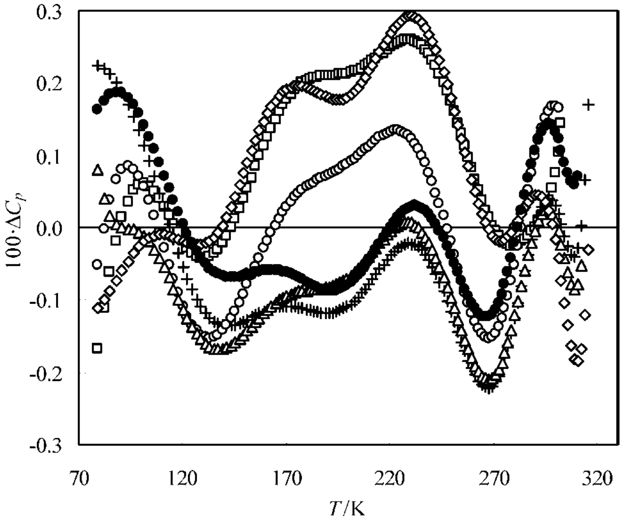

Figure 4. Relative deviations $\Delta C_p = (C_{p,\mathrm{exp}} - C_{p,\mathrm{std}})/C_{p,\mathrm{std}}$ of experimental values of the heat capacity of the standard copper specimen $C_{p,\mathrm{exp}}$ from the recommended by Sabbah et al.[1] values $C_{p,\mathrm{std}}$ in the range (80 to 320) K: ●, this work; ○, ref 4; +, ref 5; □, ref 6; ◇, ref 7; △, ref 8.

The standard copper heat capacity value has been calculated as the difference between the measured value of the heat capacity and the value of polynomial heat capacity for the empty container at a corresponding temperature. As a result of mathematical treatment of the heat capacity values obtained by the above-mentioned procedure the uncertainty magnitudes of measurement at the low-temperature thermophysical installation have been calculated. The initial data, the reduced values of the heat capacity, and the results of the calculation of the low-temperature thermophysical installation uncertainty are presented in Table 3.

As it results from the data processing of the experimental measurements of the standard specimen heat capacity measure - OFE grade copper, the relative uncertainty of the heat capacity measurement at the low-temperature thermophysical installation easily falls within the permissible limits while measuring the standard specimen. The permissible limits are given in the installation manual: ± 0.025 % at $T = (4$ up to $40)$ K and ± 0.007 % at $T = (40$ up to $370)$ K.

Measurement of the Heat Capacity of K-1 Grade Benzoic Acid. Benzoic acid C_6H_5COOH of K-1 grade (purity 99.993 %) is produced in the VNIIM named after Mendeleev (St. Petersburg). Benzoic acid C_6H_5COOH is recommended as the reference substance when measuring the heat capacity in the temperature range from (10 up to 350) K.[1] It is not recommended to use this substance at temperatures close to the fusion temperature (395.5 K) and above due to its corrosiveness.

The measurements of benzoic acid heat capacity in the helium area of temperatures have been carried out at a low-temperature thermophysical installation in the range from (4.2 up to 85) K. The specimen mass is 0.6144 g. The measurements in nitrogen area have been carried in the temperature range from (80 up to 350) K; the specimen mass is 0.6047 g. The masses are given with buoyancy correction at atmosphere conditions of 290 K and 720 mmHg.

The measurements of benzoic acid heat capacity have been carried out at 199 experimental points. The heat capacity measurements of benzoic acid have resulted in five series of measurements in the helium area and one series in the nitrogen area.

The experimental values of benzoic acid heat capacity are given in Table 5 of the Supporting Information. The experimental dependence $C_p(T)$ of the standard specimen of K-1 grade benzoic acid has been smoothed by the polynomials which coefficients are given in Table 4. Extrapolation to the absolute zero has been performed according to the Debye T^3 law: $C_p/\mathrm{J \cdot mol^{-1} \cdot K^{-1}} = a(T/\mathrm{K})^3$, where $a = 1.9373 \cdot 10^{-3}$ in the temperature range from (4.32 up to 6.09) K.

An average scatter of points from the smoothed curve (maximal relative deviation of the experimental values within the temperature range) in the temperature range from (4.3 up to 10) K was not more than 1.5 %, from (10 up to 60) K not more than 0.6 %, and in the range from (60 up to 320) K it did not exceed 0.20 % (Figure 5).

The experimental data obtained have been compared with the results given in works by Furukawa et al.,[9] Blokhin et al.,[8] and Sabbah et al.[1] relative to the results of the metrological work[10] specially performed for the reliable determination of the benzoic acid heat capacity. Figures 6 and 7 show the deviations of the present work data from the data given in the metrological work[10] in comparison with other experimental measurements.

Table 3. Calculation of the Uncertainty of the Low-Temperature Thermophysical Installation at Temperatures (5, 10, 40, 90, 120, 200, 270, and 298.15) K

			C_{exp}	C_{pol}		C_{red}			
range/K	T/K	$T_{reduced}$/K	$J\cdot kg^{-1}\cdot K^{-1}$	$J\cdot kg^{-1}\cdot K^{-1}$	$\Delta C/\Delta T$	$J\cdot kg^{-1}\cdot K^{-1}$	$100\cdot\mathring{\Delta}$	$100\cdot\Delta_C$	$100\cdot\Delta$
5	4.3712	5.066	0.1106174	0.110530	0.0610787	0.1530549	1.3666	0.2105	±1.429
	4.7371		0.1318878	0.131601	0.0649629	0.1532541			
	5.0908		0.1540628	0.154677	0.0689121	0.1523537			
	5.3634		0.1758843	0.174406	0.0720869	0.1544457			
	5.7613		0.2068290	0.206456	0.0769290	0.1533403			
10	9.2984	10.507	0.7095423	0.709984	0.2400022	0.9996090	0.6555	−0.0483	±0.749
	9.7411		0.8045750	0.807828	0.2509761	0.9967976			
	9.9635		0.8586174	0.860554	0.2566641	0.9981143			
	10.8296		1.0933366	1.090371	0.2799767	1.0030161			
	11.7151		1.3697600	1.369510	0.3058183	1.0003009			
40	35.3378	39.287	42.439507	42.44429	3.4533692	56.077552	0.2153	0.0762	±0.234
	36.4808		46.316963	46.25674	3.5013906	56.142565			
	39.3526		56.334718	56.31898	3.6073985	56.098073			
	41.1550		63.033144	62.92556	3.6633962	56.189920			
	43.2371		70.805138	70.77025	3.7183643	56.117227			
90	85.4024	90.893	217.81159	217.8337	2.5392034	231.75334	0.0550	0.0087	±0.075
	88.2723		225.28641	225.2807	2.4782598	231.78119			
	91.0516		232.17326	232.1594	2.4206401	231.78935			
	93.7515		238.63689	238.5384	2.3658884	231.87400			
	96.3843		244.48611	244.4816	2.3138711	231.77995			
120	115.6605	120.075	280.69361	280.6718	1.5258695	287.42956	0.0315	−0.0086	±0.060
	117.9064		284.15552	284.1617	1.4968775	287.40165			
	120.1329		287.44176	287.4928	1.4690126	287.35670			
	122.3225		290.59332	290.6493	1.4422865	287.35178			
	124.4901		293.63017	293.6623	1.4166144	287.37568			
200	195.2580	200.59	352.70840	352.7898	0.4824433	355.28079	0.0426	−0.0183	±0.068
	197.0346		353.51761	353.6648	0.4774373	355.21509			
	202.3761		356.14683	356.1892	0.4629780	355.31990			
	204.1500		356.93946	356.9941	0.4583781	355.30763			
	205.9222		357.78217	357.7823	0.4538647	355.36207			
270	264.6596	269.748	377.17071	377.3327	0.2477475	378.43135	0.0759	−0.0083	±0.091
	266.3929		377.82562	377.7678	0.2460506	378.65114			
	268.0802		378.17155	378.1857	0.2444155	378.57919			
	271.4674		379.08110	379.0081	0.2412231	378.66634			
	274.8361		379.69309	379.8050	0.2381503	378.48136			
298.15	294.9798	298.342	384.20689	384.1808	0.1999526	384.87917	0.0758	0.0547	±0.106
	296.6616		384.79060	384.5190	0.1988299	385.12471			
	298.3431		385.13315	384.8533	0.1896511	385.13294			
	300.0241		385.42679	385.1838	0.1966092	385.09607			
	301.7051		385.74248	385.5107	0.1955304	385.08489			

Table 4. Coefficients of the Heat Capacity Polynomials of K-1 Grade Benzoic Acid Standard Specimen for the Range $T = 4.5$ K up to 320 K at Different Temperature Ranges ΔT

	coefficients of polynomial $C_p/J\cdot mol^{-1}\cdot K^{-1} = a_0 + a_1(T/K) + a_2(T/K)^2 + a_3(T/K)^3$			
ΔT/K	a_0	a_1	a_2	a_3
4.5 to 5.5	−5.582342	3.432392	−0.701030	$4.9480\cdot 10^{-2}$
5.5 to 8	1.093456	−0.483091	$6.7754\cdot 10^{-2}$	$-9.8218\cdot 10^{-4}$
8 to 12	3.302162	−1.166981	0.136311	$-3.1845\cdot 10^{-3}$
12 to 18	0.836344	−0.463321	$6.8371\cdot 10^{-2}$	$-9.8482\cdot 10^{-4}$
18 to 30	−4.527543	0.284904	$3.4155\cdot 10^{-2}$	$-4.7322\cdot 10^{-4}$
30 to 50	−19.66493	1.752160	$-1.3198\cdot 10^{-2}$	$3.5074\cdot 10^{-5}$
50 to 80	−36.84145	2.610135	$-2.7635\cdot 10^{-2}$	$1.1812\cdot 10^{-4}$
80 to 120	−12.05715	1.386420	$-8.7955\cdot 10^{-3}$	$2.5399\cdot 10^{-5}$
120 to 160	28.15622	0.371576	$-2.3989\cdot 10^{-4}$	$1.3140\cdot 10^{-6}$
160 to 200	23.24307	0.493570	$-1.1027\cdot 10^{-3}$	$3.1411\cdot 10^{-6}$
200 to 240	−205.3628	3.578471	$-1.4799\cdot 10^{-2}$	$2.3084\cdot 10^{-5}$
240 to 320	132.3876	−0.904405	$5.0431\cdot 10^{-3}$	$-6.1974\cdot 10^{-6}$

The deviations do not exceed 0.5 % above the temperature of 20 K and 0.05 % in the range from (280 up to 320) K, testifying the fidelity of the experimental data at low-temperature calorimetric measurements.

On the basis of the found polynomial coefficients of the heat capacity temperature dependence, we have calculated the thermodynamic functions of benzoic acid (Table 5). Because of the lack of standard heat capacity polynomials for benzoic and heptane, we did not use the evaluation procedure described for copper to evaluate thermodynamic uncertainties for these molecular substances. The uncertainties of integral thermodynamic functions were found by summing up (in the temperature range of (0 to 298.15) K) the absolute values of relative uncertainties in the heat capacity evaluation calculated for the corresponding temperature intervals. These values were found from the relative deviations of the experimental values from the smoothed ones according to the equations describing the corridor of uncertainties, which includes 95 % of the experimental data.

Measurement of the Heptane Heat Capacity. Normal heptane C_7H_{16} is recommended as a reference substance when measuring

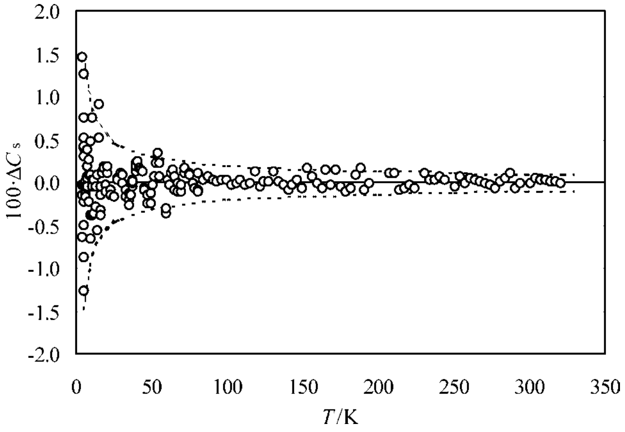

Figure 5. Relative deviations $\Delta C_s = (C_{s,exp} - C_{s,fit})/C_{s,fit}$ of experimental values of the heat capacity of the standard K-1 grade benzoic acid specimen $C_{s,exp}$ from the smoothed $C_{s,fit}$ in the range (4.5 to 320) K.

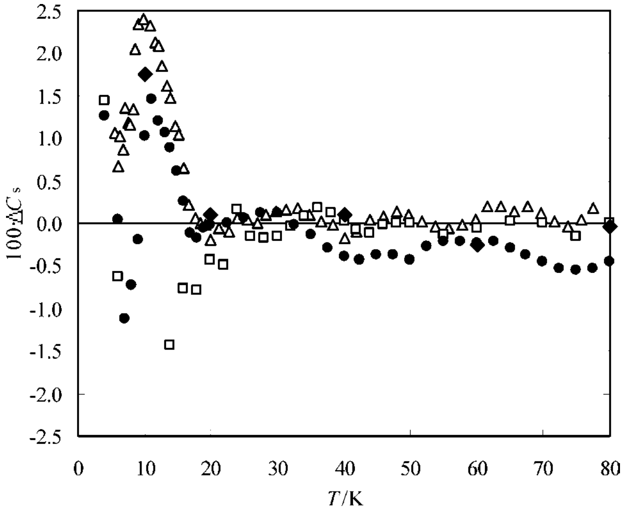

Figure 6. Relative deviations $\Delta C_s = (C_{s,exp} - C_{s,std})/C_{s,std}$ of experimental values of the heat capacity of the standard specimen of benzoic acid $C_{s,exp}$ from the recommended by Rybkin et al.[10] values $C_{s,std}$ in the range (5 to 80) K: ●, this work; ◆, ref 1; △, ref 8; □, ref 9.

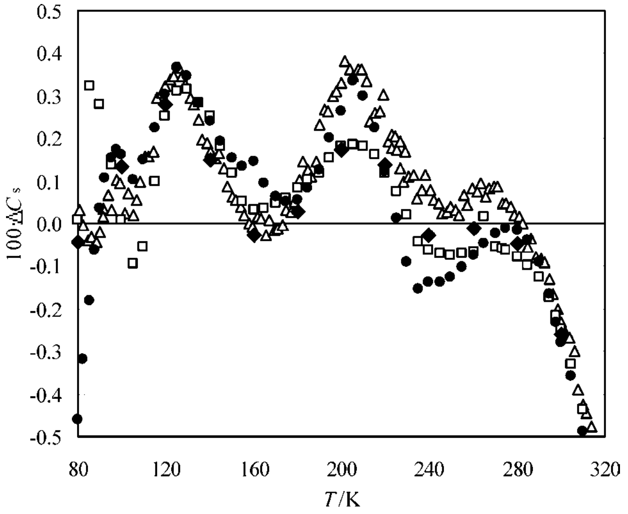

Figure 7. Relative deviations $\Delta C_s = (C_{s,exp} - C_{s,std})/C_{s,std}$ of experimental values of the heat capacity of the standard specimen of benzoic acid $C_{s,exp}$ from the recommended by Rybkin et al.[10] values $C_{s,std}$ (for the range up to 273.15 K) in the range (80 to 320) K: ●, this work; ◆, ref 1; △, ref 8; □, ref 9.

Table 5. Molar Thermodynamic Functions of K-1 Grade Benzoic Acid Standard Specimen ($M = 122.1232\ \mathrm{g \cdot mol^{-1}}$)

T	$C_{s,m}$	$\Delta_0^T S°_m$	$\Delta_0^T H°_m$
K	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$\mathrm{J \cdot mol^{-1}}$
5	0.2388	0.0806	0.3023
10	2.079	0.6776	5.1187
15	5.946	2.197	24.502
20	11.05	4.586	66.635
25	16.55	7.640	135.57
30	21.98	11.14	232.00
35	27.00	14.91	354.62
40	31.55	18.82	501.18
45	35.65	22.78	669.36
50	39.33	26.73	857.00
55	42.77	30.64	1062.5
60	45.80	34.49	1284.1
65	48.50	38.27	1519.9
70	50.97	41.95	1768.7
75	53.31	45.55	2029.4
80	55.59	49.06	2301.7
85	57.84	52.50	2585.2
90	59.99	55.87	2879.9
95	62.05	59.17	3185.0
100	64.03	62.40	3500.2
110	67.83	68.68	4159.7
120	71.55	74.75	4856.5
130	75.29	80.62	5590.8
140	79.08	86.34	6362.6
150	82.93	91.93	7172.6
160	86.85	97.40	8021.4
170	90.71	102.78	8909.2
180	94.68	108.08	9836.0
190	98.76	113.31	10803
200	102.98	118.48	11812
210	107.24	123.61	12863
220	111.40	128.69	13956
230	115.65	133.74	15091
240	120.13	138.75	16270
250	124.64	143.75	17494
260	129.23	148.73	18763
270	133.85	153.69	20079
273.15	135.31	155.25	20503
280	138.49	158.64	21440
290	143.08	163.58	22848
298.15	146.78 ± 0.16	167.60 ± 0.36	24029 ± 40
300	147.61	168.51	24302
310	152.03	173.42	25800
320	156.31	178.32	27342

the heat capacity and enthalpy in the temperature range from (10 up to 400) K.[1] Its advantages are as follows: chemical stability up to the critical temperature (540 K), the absence of unwanted transitions in the solid phase, and quick achievement of thermal equilibrium, as well as the possibility of easy purification by means of distillation.

Measurements of the heptane heat capacity in the helium area of temperatures have been carried out at the low-temperature thermophysical installation in the temperature range from (4.2 up to 85) K. Heptane in the quantity of 1 mL was placed into a titanium container, which was exhausted with vacuum pump. The specimen mass, determined after exhaustion, was 0.6338 g. Measurements in nitrogen area were performed in the temperature range from (80 up to 350) K; the specimen mass was 0.5255 g. The masses are given after buoyancy correction at 290 K, 720 mmHg, and outer volume of container of 1.38 cm^3. The container was subjected to only exhaustion, and it was not filled with helium for the avoidance of gas invasion in the liquid.

At the temperature 182.6 K a phase "solid−liquid" transition is observed, which serves a reference point at the calibration of calorimeters. The enthalpy of fusion of heptane is also a reference value.

The heptane heat capacity measurements resulted in obtaining 226 points in four series of measurements in the helium area

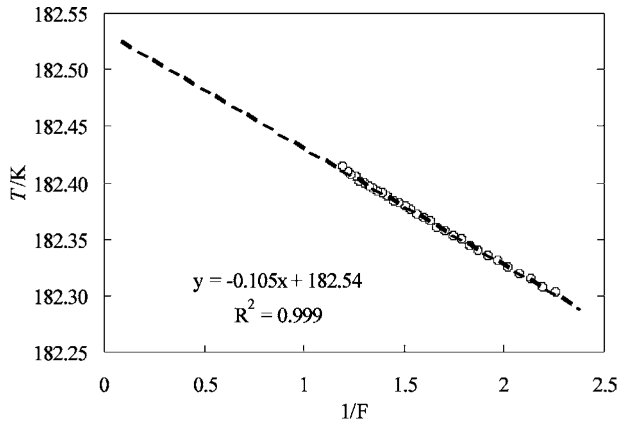

Figure 8. Dependence of heptane fusion temperature on a fraction of the sample fused.

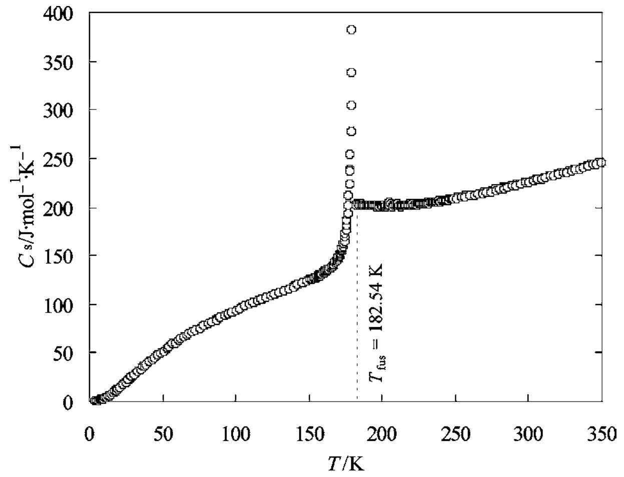

Figure 9. Experimental molar heat capacity of heptane at pressure of the saturated vapor C_s in the range T = (4.8 to 350) K.

and one series in the nitrogen area. The maximum value of the heat capacity registered at the point of phase transition for heptane at temperature 182.41 K is 38721 J·mol^{-1}·K^{-1}. The experimental values of the heptane heat capacity in the temperature range from (4.8 up to 350) K are given in Table 8 of the Supporting Information.

To evaluate a degree of heptane purity according to the fractional melting procedure, we used the series of heat capacity measurements carried out in the mode of introducing a constant amount of heat in the range from (150 up to 250) K with the pitch of 0.3 K, and the time of reaching temperature equilibrium was about half an hour. The triple point temperature for ideally pure heptane found by calculations is 182.54 K, and the decrease of fusion temperature for our specimen is 0.105 K (Figure 8). Taking into account the cryoscopic constants $a = 0.05074$ and $b = 0.00358$ calculated for our specimen, the purity of the given heptane specimen is 99.5 %. The impurity of 0.5 % according to the data of mass-spectrometric chromatography is represented by the heptane isomer 3-methylhexane.

The dependence of the molar heat capacity of the heptane standard specimen on temperature is presented in Figure 9.

The experimental values of the heptane heat capacity have been smoothed by the cubic polynomials of $C_p = a_0 + a_1T + a_2T^2 + a_3T^3$ type according to the method of spline approximation. Extrapolation to absolute zero has been performed according to the Debye T^3 law: $C_p = aT^3$, where $a = 1.73435 \cdot 10^{-3}$ for the temperature range below $T = 5$ K. Differentiation of the heat capacity temperature dependence in the area close to the phase transition shows that a bend of a heat capacity curve is observed at a temperature of about 140 K; consequently, a contribution of the heat effect of heptane fusion into the heat capacity begins at this temperature.

The left branch of the heptane heat capacity temperature dependence in the area of the phase transition in the temperature range from (180.28 up to 182.41) K has been described by the power equation of $C_p = a(T_c - T)^n$ type, which has shown the best agreement with the experimental data at critical temperature parameter T_c, equal to 182.54 K. Coefficients a and n in the straight-line equation found at linearization in logarithmic axis according to the least-squares method are 1834.316 and −1.5043, respectively.

The right branch of the heat capacity temperature dependence after the point of phase transition in the temperature range from (182.41 up to 185.57) K has been described by the equation of

Table 6. Coefficients of the Heat Capacity Polynomials of Heptane Standard Specimen for the Range T = 4.9 K up to 350 K at Different Temperature Ranges ΔT

	coefficients of polynomial C_p/J·mol^{-1}·K^{-1} = $a_0 + a_1(T/\mathrm{K}) + a_2(T/\mathrm{K})^2 + a_3(T/\mathrm{K})^3$			
ΔT/K	a_0	a_1	a_2	a_3
4.9 to 6	−0.664774	0.274863	$-3.7237 \cdot 10^{-2}$	$3.5453 \cdot 10^{-3}$
6 to 9	0.675555	−0.302310	$4.1920 \cdot 10^{-2}$	$1.7521 \cdot 10^{-4}$
9 to 15	1.14964	−0.478978	$6.1626 \cdot 10^{-2}$	$-4.8802 \cdot 10^{-4}$
15 to 21	3.95214	−1.03140	0.100102	$-1.4304 \cdot 10^{-3}$
21 to 30	9.05445	−1.44007	0.105696	$-1.3236 \cdot 10^{-3}$
30 to 50	−24.8542	2.06425	$-1.5801 \cdot 10^{-2}$	$8.8037 \cdot 10^{-5}$
50 to 70	−7.95059	0.814547	$1.3254 \cdot 10^{-2}$	$-1.2855 \cdot 10^{-4}$
70 to 100	99.5336	−2.39545	$3.9542 \cdot 10^{-2}$	$-1.6250 \cdot 10^{-4}$
100 to 140	−24.8068	2.00116	$-1.1271 \cdot 10^{-2}$	$3.0214 \cdot 10^{-5}$
140 to 155	−151.309	4.90324	$-3.3406 \cdot 10^{-2}$	$8.6355 \cdot 10^{-5}$
155 to 171.64	−14040.104	268.527	−1.70125	$3.6034 \cdot 10^{-3}$
171.64 to 180.28	−11806102.44	202947.615	−1162.819	2.22074
180.28 to 182.41	$C_p/\mathrm{J \cdot mol^{-1} \cdot K^{-1}} = 1834.316(182.54 - T/\mathrm{K})^{-1.5043}$			
182.41 to 185.57	$C_p/\mathrm{J \cdot mol^{-1} \cdot K^{-1}} = \dfrac{1}{1.5641 \cdot 10^{-3} T/\mathrm{K} - 0.28529}$			
185.57 to 210	−216.171	7.27266	$-4.1333 \cdot 10^{-2}$	$7.6898 \cdot 10^{-5}$
210 to 250	146.316	0.878572	$-5.2155 \cdot 10^{-3}$	$1.0758 \cdot 10^{-5}$
250 to 300	725.657	−6.05152	$2.2483 \cdot 10^{-2}$	$-2.6234 \cdot 10^{-5}$
300 to 350	−59.6268	2.22073	$-6.5447 \cdot 10^{-3}$	$7.6947 \cdot 10^{-6}$

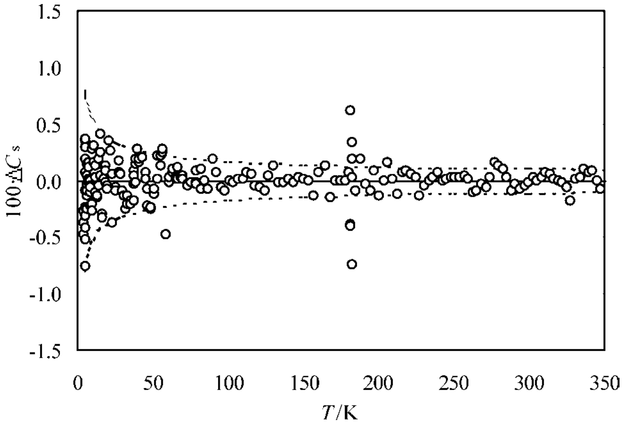

Figure 10. Relative deviations $\Delta C_s = (C_{s,exp} - C_{s,fit})/C_{s,fit}$ of experimental values of the heat capacity of heptane $C_{s,exp}$ from the smoothed values $C_{s,fit}$ in the range (4.8 to 350) K.

$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 1/[a(T/\text{K}) + b]$ type with coefficients $a = 1.5641\cdot10^{-3}$ and $b = -0.28529$.

After determination of amount of change of heptane thermodynamic functions at the phase transition, the heptane heat capacity has been calculated by extrapolation of the polynomial found for the range $T = (100 \text{ to } 140)$ K to the temperatures up to 182.54 K. In a similar way the polynomial for the range $T = (185 \text{ to } 210)$ K describing the heat capacity of the liquid on the other side of the phase transition has been extrapolated to the fusion temperature (Table 6).

The heat capacity experimental value deviations from the smoothed values go within the range of ± 0.8 % at temperatures up to 10 K, ± 0.5 % at $T = (10 \text{ up to } 30)$ K, ± 0.3 % at $T = (30 \text{ up to } 60)$ K, and less than ± 0.2 % for the rest of the temperature range. The corresponding corridor of uncertainties is marked on the diagram by a dashed line (Figure 10).

The thermodynamic functions of heptane (entropy and enthalpy) have been calculated by means of the found coefficients of the heat capacity equations according to the known integral relations in the corresponding temperature ranges. In the case of calculating entropy for the left branch of the phase transition of heptane in the interval from (180.28 up to 182.41) K for the integral

$$S(T) = \int_0^T \frac{a(T_c - T)^n}{T} dT$$

a mathematical solution has not been obtained; therefore, the entropy in this range has been determined by numerical integration according to the method of trapezoids with a variable-pitch from the tenth and hundredth parts of kelvin on the areas with a slight change of C_p/T value and up to some thousandths of kelvin in the areas with a sharp function increase.

To find the values of entropy and enthalpy at the heptane fusion point before and after the phase transition, the calculated values of the thermodynamic functions have been subjected to extrapolation by the third-power polynomials in temperature ranges from (100 up to 145) K and from (185 up to 300) K to temperature 182.54 K.

The tabulated values of the heptane thermodynamic functions, the heat capacity, entropy, and enthalpy, in the temperature range from (0 to 350) K are presented in Table 7.

The comparison of our experimental data on the heat capacity of heptane with the data obtained by a number of authors[11−15] is given in Figures 11 and 12 separately for the area before the phase transition and for the temperature range after the phase transition. The zero line in the graphs is the smoothed dependence of our experimental values of the heat capacity.

Table 7. Molar Thermodynamic Functions of Heptane (M = 100.2034 g·mol^{-1})

T / K	$C_{s,m}$ / J·mol^{-1}·K^{-1}	$\Delta_0^T S°_m$ / J·mol^{-1}·K^{-1}	$\Delta_0^T H°_m$ / J·mol^{-1}
5	0.2218	0.0723	0.2713
10	2.034	0.6524	4.9539
15	6.184	2.189	24.597
20	11.92	4.723	69.323
25	18.43	8.070	144.92
30	25.24	12.03	254.17
35	31.81	16.42	396.93
40	38.07	21.08	571.76
45	44.06	25.91	777.18
50	49.86	30.86	1012.1
55	55.55	35.88	1275.7
60	60.87	40.94	1566.9
65	65.69	46.01	1883.6
70	69.92	51.04	2222.9
75	73.74	55.99	2581.8
80	77.77	60.88	2960.5
85	81.81	65.71	3359.5
90	85.77	70.50	3778.5
95	89.51	75.24	4216.8
100	92.91	79.92	4673.0
105	96.03	84.53	5145.2
110	99.16	89.07	5633.2
115	102.22	93.54	6136.7
120	105.24	97.96	6655.3
125	108.24	102.31	7189.1
130	111.25	106.62	7737.8
135	114.28	110.87	8301.6
140	117.36	115.08	8880.6
145	120.50	119.26	9475.3
150	123.75	123.40	10084
155	127.11	127.51	10708
160	130.60	131.59	11348
165	134.26	135.66	12002
170	138.11	139.70	12670
175	142.16	143.74	13354
180	146.44	147.76	14053
182.54	148.71	149.80	14413
182.54	201.85	226.77	28460
185	201.54	229.34	28941
190	200.96	234.77	29959
195	200.50	239.98	30963
200	200.23	245.05	31965
210	200.46	254.82	33967
220	201.72	264.18	35977
230	203.38	273.18	38003
240	205.48	281.88	40047
250	208.08	290.32	42114
260	211.02	298.53	44209
270	214.39	306.56	46336
273.15	215.51	309.05	47013
280	218.01	314.42	48498
290	221.71	322.14	50696
298.15	224.69 ± 0.25	328.32 ± 0.52	52515 ± 71
300	225.35	329.71	52931
310	229.09	337.16	55203
320	232.97	344.50	57514
330	237.02	351.73	59863
340	241.29	358.87	62255
350	245.82	365.92	64690

In the temperature range before the phase transition our data on the heat capacity of heptane agree with the data from literature mainly within ± 1 %. More noticeable deviations occur in the temperature range from (140 to 180) K, that is, in the area of the extrapolated values, and also below $T = 20$ K. The greatest deviations are with the data by Ginnings and Furukawa,[11] up to 7.5 % at 15 K and up to 13 % at 10 K, which are also extrapolated. After the phase transition temperature,

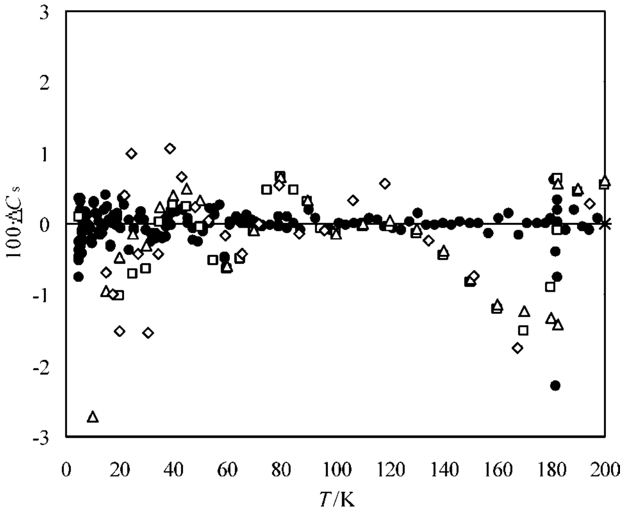

Figure 11. Relative deviations $\Delta C_s = (C_{s,exp} - C_{s,fit})/C_{s,fit}$ of experimental values of the heat capacity of heptane $C_{s,exp}$ from our smoothed values $C_{s,fit}$ in the area before the phase transition: ●, our experimental data; □, ref 11; △, ref 12; ◇, ref 13.

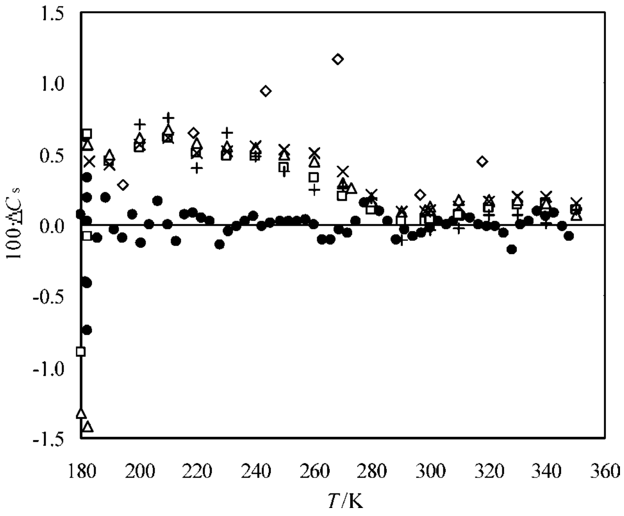

Figure 12. Relative deviations $\Delta C_s = (C_{s,exp} - C_{s,fit})/C_{s,fit}$ of experimental values of the heat capacity of heptane $C_{s,exp}$ from our smoothed values $C_{s,fit}$ in the area after the phase transition: ●, our experimental data; □, ref 11; △, ref 12; ◇, ref 13; +, ref 14; ×, ref 15.

divergence of the data does not exceed 0.7 % in the range from (180 to 270) K, and for temperatures from (270 to 350) K it is less than 0.2 %. Thus, the whole conformity of the measured heat capacity values to the known literature data is satisfactory.

The values of enthalpy and entropy of the phase transition (fusion) of heptane as well as the values of their uncertainties have been determined on the basis of the obtained values of enthalpy and entropy. Values of ΔH_{fus} and ΔS_{fus} were evaluated as the difference of these functions at the melting point before and after the phase transition. The data used for determination of ΔH_{fus} are presented in Table 8. The value of heptane fusion enthalpy is $\Delta H_{fus} = (14047 \pm 19.6)\ \mathrm{J \cdot mol^{-1}}$; the value of the phase transition entropy is $\Delta S_{fus} = (76.96 \pm 0.11)\ \mathrm{J \cdot mol^{-1}}$, that is, our fusion enthalpy data are consistent within uncertainty range with data of authors: $\Delta H_{fus} = (14022.5 \pm 19)\ \mathrm{J \cdot mol^{-1}}$,[16] $\Delta H_{fus} = (14061 \pm 48)\ \mathrm{J \cdot mol^{-1}}$.[17] The comparison of the data on enthalpy and entropy obtained by us with those obtained by a number of authors[11−13,16−23] is also given in Table 9.

Table 8. Data Used for Determination of ΔH_{fus}

before phase transition		after phase transition	
T	$\Delta_0^T H°_m$	T	$\Delta_0^T H°_m$
K	$\mathrm{J \cdot mol^{-1}}$	K	$\mathrm{J \cdot mol^{-1}}$
100	4673.04	185	28941.5
105	5145.19	185.57	29067.9
110	5633.20	190	29959.2
115	6136.68	195	30962.8
120	6655.35	200	31964.6
125	7189.07	210	33967.0
130	7737.79	220	35977.5
135	8301.59	230	38002.7
140	8880.64	240	40046.5
145	9475.30	250	42113.9
		260	44208.9
		270	46335.7
		273.15	47012.8
		280	48497.5
		290	50696.1
		298.15	52515.2
		300	52931.5

Table 9. Fusion Temperature T_{fus}, Enthalpy $\Delta_{fus}H$, and Entropy $\Delta_{fus}S$ of the Fusion of Heptane

T_{fus}	$\Delta_{fus}H$	$\Delta_{fus}S$	
K	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	ref
182.54 ± 0.01	14047 ± 19.6	76.96 ± 0.11	our data
182.57	13990		van Miltenburg et al.[18]
182.59	14053	76.96	Schaake et al.[19]
182.7	14059	77.0	Meijer et al.[20]
182.56	14061 ± 48	77.02	van Miltenburg[17]
182.56	14030.6	76.81	Oetting[21]
182.55	14037 ± 16.8	76.89	Huffman et al.[12]
182.55	14037	76.89	McCullough and Messerly[22]
182.56	14022.5 ± 19	76.81	Douglas et al.[16]
182.56	14022	76.81	Ginnings and Furukawa[11]
182.52	14040.7	76.93	Pitzer[13]
182.2	14163	77.73	Parks et al.[23]

Conclusion

The measurements of the heat capacity of standard specimens of copper, benzoic acid, and heptane carried out by the method of adiabatic calorimetry at the low-temperature thermophysical installation resulted in the determination of their standard thermodynamic functions. The data obtained show a good agreement with the data obtained by a number of authors and the recommended values.

The limits of relative uncertainty of the calorimetric installation: ± 1.43 % at $T = 5$ K, ± 0.75 % at $T = 10$ K, ± 0.23 % at $T = 40$ K, and less than ± 0.11 % for the temperature range from (90 to 298.15) K have been determined according to the experimental data on the measurement of the certified heat capacity of OFE grade copper.

On the basis of the data of measurements of the heat capacity of heptane, the values of its enthalpy and fusion entropy at $T = 182.54$ K, $\Delta H_{fus} = (14047 \pm 19.6)\ \mathrm{J \cdot mol^{-1}}$ and $\Delta S_{fus} = (76.96 \pm 0.11)\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, have been determined. These values are in a satisfactory agreement with the data obtained by other authors.

Thus, the results obtained testify a good accuracy of the calorimetric installation and adequacy of the obtained experimental data on the heat capacity of the solid bodies.

Supporting Information Available:

Table 1: Experimental values of the specific heat C_p of the standard specimen of OFE grade copper from $T = 4.3$ K up to

323.6 K. Table 5: Experimental values of the specific heat C_s of K-1 grade benzoic acid standard specimen at pressure of the saturated vapor in the range from $T = 4.3$ K up to 321.1 K. Table 8: Experimental values of the specific heat capacity C_s of heptane standard specimen at pressure of the saturated vapor in the range from $T = 4.8$ K up to 348.1 K. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

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