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Heat capacity measurement with a heat flow calorimeter

B. Löwen, U. Peukert, S. Schulz *

Universität Dortmund, Lehrstuhl für Thermodynamik, D-44221 Dortmund, Germany

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Abstract

This paper deals with a new quasi-isothermal method for the measurement of heat capacities of pure solids and liquids in an LKB 2277 heat flow microcalorimeter TAM (thermal activity monitor). Deviations of less than 1% from literature data can be achieved.

It is shown that even excess heat capacities of binary mixtures can be determined. With a quasi-isothermal method, no heating up or cooling down of the calorimetric unit is needed; thus the temperature of the thermostat directly represents the test temperature.

Keywords: Calorimetry; Excess heat capacity; Heat capacity

1. Introduction

This paper is based on two previous studies by Löwen et al. [1,2], which also deal with the determination of specific heat capacities in an LKB 2277 microcalorimeter.

The first study [1] takes advantage of the static calibration of the calorimetric unit as described in the manual [3]. When the sample is supplied with a constant heat flow rate P_1 (see Fig. 1), a time constant can be derived from the experimental data. Using this time constant, the heat capacity of the specimen can be determined with an uncertainty of less than 5%.

The second study [2] is based on a dynamic calibration of the calorimeter as described in the manual [3] also. Now the sample is supplied with a heat flow rate $P_2(t)$ in two steps as shown in Fig. 1. A microprocessor incorporated in the

* Corresponding author.

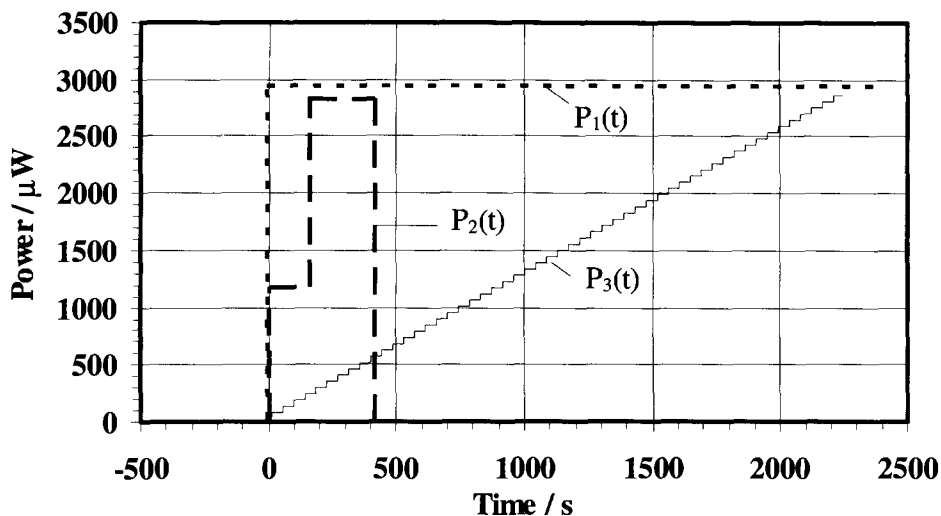


Fig. 1. Power input versus time of different quasi-isothermal methods for the measurement of heat capacities: $P_1(t)$, power input, Ref. [1]; $P_2(t)$, power input, Ref. [2]; $P_3(t)$, power input of the new method.

calorimetric unit calculates two time constants from the calorimetric signal, which are related to the specific heat capacity of the system. This method allows the determination of the specific heat capacity of materials with good thermal conductivities with an uncertainty of less than 4%.

The power input $P_3(t)$ of the new method is increased step by step with time as shown in Fig. 1. The measured output signal $\Phi(t)$ increases almost linearly. One can derive the specific heat capacity from the gradient of the response.

The proposed method is equally suitable for solids and liquids, which can be held in a 4 ml sample cup. In addition, tests were carried out to determine excess heat capacities of the system ethanol–water.

2. Measuring equipment and general principles

The measuring principle of the LKB 2277 heat flow microcalorimeter TAM is based on the Peltier effect. The heat flow rate between sample vessel and heat sink is detected by Peltier effect plates (see Fig. 2).

An electric calibration heater is placed below the sample cup. The measuring unit is linked to a computer, working with the TAM software DIGITAM from Thermometric, which stores the data sets obtained and controls the heat flow rate of the electrical calibration heater. The heat flow rate $P_3(t)$ is increased stepwise throughout all of the 51 levels (see Fig. 1) and is recorded by the computer using a number code (see Table 1). Every 45 s the power input is automatically increased by an

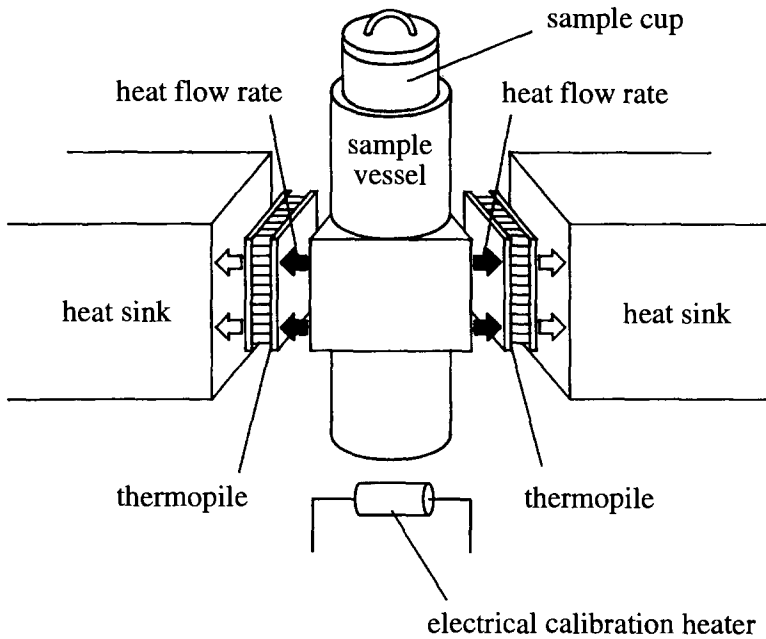


Fig. 2. Scheme of measuring set up.

amount of $56.8 \mu\text{W}$. A maximum power input of $2897 \mu\text{W}$ is reached after 2295 s (38.25 min).

Fig. 3 shows the response curve (power output) of an empty sample cup and of a water-filled cup to the thermal input of the calibration heater. The test temperature was 298.16 K. One can see, that, after a certain time, the power output increases almost linearly.

The determination of the specific heat capacity is based on Eq. (1), which is the first derivation of the heat balance equation of the sample vessel

$$\Phi(t) = (m_{\text{sample cup}} c_{p \text{ sample cup}} + m_{\text{sample}} c_{p \text{ sample}}) \frac{d(T(t) - T_U)}{dT} = A + Bt \quad (1)$$

The second derivation gives

$$\frac{d\Phi(t)}{dt} = (m_{\text{sample cup}} c_{p \text{ sample cup}} + m_{\text{sample}} c_{p \text{ sample}}) \frac{d^2(T(t) - T_U)}{dt^2} = B \quad (2)$$

where $\Phi(t)$ is the power output, m is the mass and c_p the specific isobaric heat capacity. $T(t) - T_U$ is the actual temperature difference between the sample vessel and the heat sink. A and B are constants of a linear fit, which are determined by linear regression using the data of the linear interval as shown in Fig. 3 by Δt . Assuming that the second derivation of the temperature difference is constant, the gradient B can be related to the heat capacity of the system sample cup/sample (see

Table 1
Number code for the control of the power input $P_3(t)$

Level n	Input number	Power input/ μW	Level n	Input number	Power input/ μW
1	139	56.8	27	722	1534.7
2	197	114.3	28	735	1590.5
3	241	171.0	29	748	1647.3
4	278	227.5	30	761	1705.0
5	311	284.8	31	774	1763.8
6	340	340.3	32	786	1818.9
7	368	398.7	33	798	1874.8
8	393	454.7	34	810	1931.6
9	417	512.0	35	822	1989.3
10	439	567.4	36	834	2047.8
11	461	625.7	37	845	2102.2
12	481	681.2	38	857	2162.3
13	501	739.0	39	868	2218.2
14	520	796.1	40	879	2274.8
15	538	852.2	41	890	2332.1
16	556	910.1	42	901	2390.1
17	573	966.6	43	911	2443.4
18	590	1024.9	44	922	2502.8
19	606	1081.2	45	932	2557.3
20	622	1139.0	46	943	2618.1
21	637	1194.6	47	953	2673.9
22	652	1251.6	48	963	2730.3
23	666	1305.9	49	973	2787.3
24	681	1365.4	50	983	2844.9
25	695	1422.1	51	992	2897.2
26	709	1480.0			

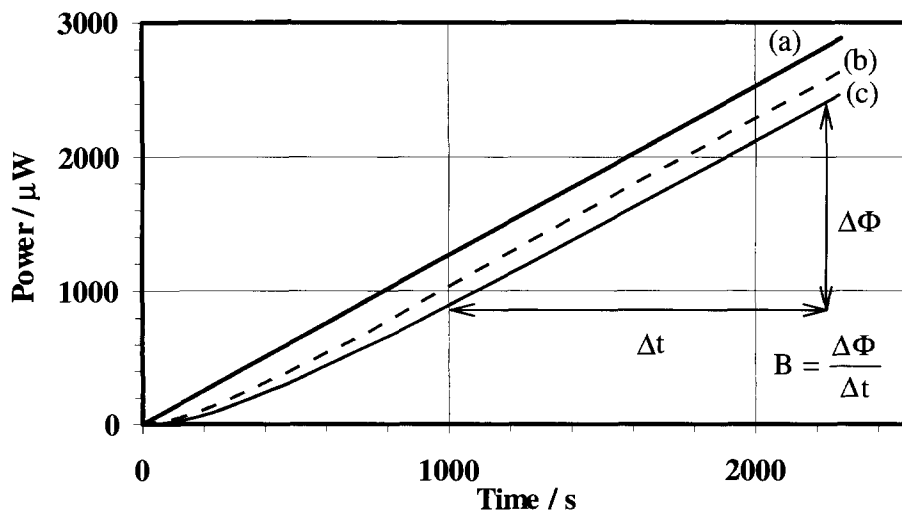


Fig. 3. Curve (a), power input signal $P_3(t)$ (linear regression); curve (b), power output of an empty sample cup; curve (c), power output of a sample cup filled with 4.29 g water.

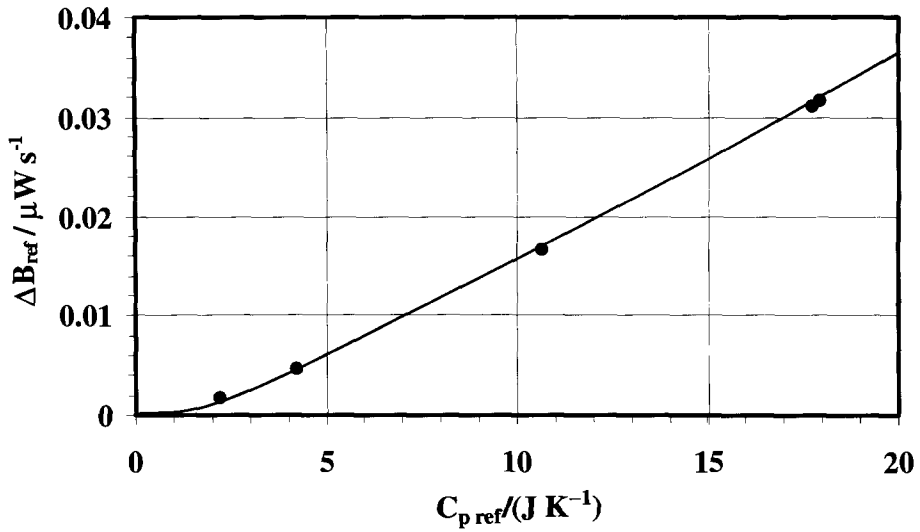


Fig. 4. Calibration curve, ΔB_{ref} as a function of heat capacity using water as reference material: —, fit (Eq. (5)); ●, experimental data.

Table 2

Experimental data for the determination of the calibration curve with water as reference material

m_{ref}/g	$C_{p \text{ ref}}/(\text{J K}^{-1})$	$\Delta B_{\text{ref}}/(\mu\text{W s}^{-1})$
0.529	2.21	0.0017
1.011	4.22	0.0047
2.551	10.66	0.0167
4.291	17.93	0.0311

$$c_{p, \text{H}_2\text{O}} = 4.18 \text{ J g}^{-1} \text{ K}^{-1} [5]; T = 298.16 \text{ K.}$$

Table 3

B_{ref} values from repeated tests with bi-distilled water

No. of test	$B_{\text{ref}}/(\mu\text{W s}^{-1})$
1	1.2664
2	1.2665
3	1.2660
4	1.2663
Mean value/ $(\mu\text{W s}^{-1})$	1.2663
Standard deviation	$\pm 0.022\%$

Sample mass, 0.529 g; $T = 298.16 \text{ K.}$

Table 4

Experimental results for some metals at $T = 298.16$ K

Material	m/g	$B_{\text{sample}}/(\mu\text{W s}^{-1})$	$c_{p \text{ lit}}/(\text{J g}^{-1} \text{K}^{-1})$	$c_{p \text{ sample}}/(\text{J g}^{-1} \text{K}^{-1})$	Deviation/%
Cu	33.286	1.2464	0.385	0.387	+0.71
Ti	16.858	1.2541	0.523	0.521	-0.35
Cr	26.908	1.2481	0.449	0.447	-0.42

Literature values are taken from Barin [6].

Table 5

Experimental results for some organic compounds at $T = 298.16$ K

Material	m/g	$B_{\text{sample}}/(\mu\text{W s}^{-1})$	$c_{p \text{ lit}}/(\text{J g}^{-1} \text{K}^{-1})$	$c_{p \text{ sample}}/(\text{J g}^{-1} \text{K}^{-1})$	Deviation/%
Ethanol	3.867	1.2602	2.42	2.44	+0.64
1-Propanol	3.072	1.2562	2.48	2.49	+0.23
2-Propanol	3.010	1.2595	2.55	2.57	+0.62
<i>n</i> -Heptane	2.613	1.2629	2.24	2.23	-0.45
Cyclohexane	2.962	1.2601	1.85	1.87	+0.88

Literature values are taken from Blanke [5].

Eq. (2)). This assumption is justified as long as the heating rate is relatively small and the heat is evenly distributed throughout the entire sample [4].

3. Performance of the test

In order to determine the heat capacity three tests are necessary.

1. At first, measurements must be carried out with an empty sample cup in order to determine the gradient B_0 , which represents the heat capacity of the empty sample cup.

2. Measurements must then be performed with a reference material, e.g. bi-distilled water, in order to determine the calibration curve. The mass of the reference material can be varied for different runs. Thus the gradient B_{ref} is detected and the difference ΔB_{ref} between the gradients B_0 and B_{ref} can be calculated

$$\Delta B_{\text{ref}} = B_0 - B_{\text{ref}} \quad (3)$$

In Fig. 4, ΔB_{ref} is shown as a function of the heat capacity $C_{p \text{ ref}}$

$$C_{p \text{ ref}} = m_{\text{ref}} c_{p \text{ ref}} \quad (4)$$

water being used as a reference material. Measured values are given in Table 2. All of them are correlated with the fit

$$\Delta B_{\text{ref}} = \frac{C_{p \text{ ref}}}{C_1 + \frac{C_2}{C_{p \text{ ref}}}} \quad (5)$$

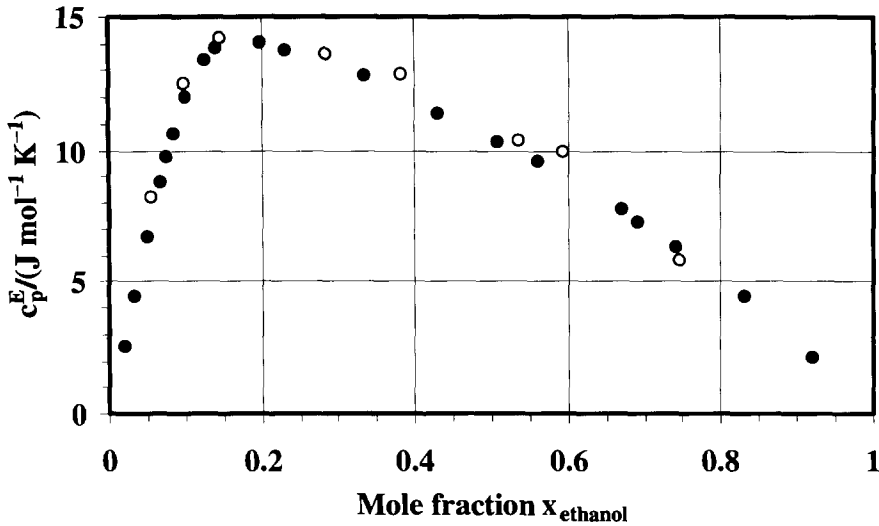


Fig. 5. Excess heat capacity of the system ethanol–water as a function of the mole fraction x_{ethanol} , $T = 298.16 \text{ K}$: O, experimental data; ●, Grolier et al. [7].

The values C_1 and C_2 vary around $C_1 \approx 500 \text{ s}^2 \text{ K}^{-1}$ and $C_2 \approx 1100 \text{ J s}^2 \text{ K}^{-2}$, according to whatever sample vessel and sample cup are used.

3. Finally, measurements are performed with the specimen placed in the sample cup. The gradient B_{sample} is derived from the experimental data. ΔB_{sample} is calculated as the difference between B_0 and B_{sample} . Using the constants C_1 and C_2 obtained from Eq. (5), the heat capacity $C_{p \text{ sample}}$ is determined from

$$\Delta B_{\text{sample}} = \frac{C_{p \text{ sample}}}{C_1 + \frac{C_2}{C_{p \text{ sample}}}} \quad (6)$$

and the specific isobaric heat capacity of the specimen from

$$C_{p \text{ sample}} = m_{\text{sample}} c_{p \text{ sample}} \quad (7)$$

4. Results and assessment

Table 3 gives a series of measurements when using a sample cup filled with water. The low standard deviation guarantees a high repeatability of the method.

Table 4 lists the experimental data and results of solid copper, titanium and chromium at a temperature of 298.76 K; literature data for c_p were taken from Barin [6] for comparison. Deviations are calculated as the difference between the measured and literature value divided by the literature value and are listed in percent. The results in Table 4 show deviations below 1%. Because the deviations are positive and negative, no systematic error seems to be present.

Table 6

Experimental data of the excess heat capacities c_p^E of the ethanol–water system at $T = 298.16$ K

x_{ethanol}	$c_p^E/(\text{J g}^{-1} \text{K}^{-1})$	x_{ethanol}	$c_p^E/(\text{J g}^{-1} \text{K}^{-1})$
0.056	8.20	0.381	12.89
0.099	12.51	0.534	10.42
0.146	14.22	0.592	9.96
0.284	13.61	0.746	5.79

Table 5 contains the results for organic compounds such as ethanol, 1-propanol, 2-propanol, *n*-heptane and cyclohexane at a test temperature of 298.76 K. Again deviations from literature values are below 1%.

Tables 4 and 5 indicate that the method is applicable to solids and liquids equally well and is independent of the thermal conductivity of the specimen.

The excess heat capacity c_p^E of the ethanol–water system was determined in a further series of tests. Several measurements were carried out in the concentration interval of the mole fractions between $x_{\text{ethanol}} = 0.05$ and $x_{\text{ethanol}} = 0.75$. Fig. 5 shows the experimental results of c_p^E in comparison to the measurements of Grolier et al. [7] and Table 6 lists the values. Good agreement is achieved between the literature and the experimental data of this work. At mole fractions near $x_{\text{ethanol}} = 0$ and $x_{\text{ethanol}} = 1$, the accuracy of the method is not sufficient.

5. Conclusion

The proposed method enables the determination of the specific heat capacity of solids and liquids in an LKB 2277 microcalorimeter TAM with an accuracy of below 1%. Even the measurement of excess heat capacities of binary mixtures is possible, as shown for the ethanol–water system as an example.

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