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Measurement of Heat Capacities for Nine Organic Substances by Tian−Calvet Calorimetry

Lars Becker, Oliver Aufderhaar, and Jürgen Gmehling*

University Oldenburg, Technische Chemie, Fachbereich 9, Postfach 2503, 26111 Oldenburg,
Federal Republic of Germany

Heat capacities for *n*-heptane, 2-methyl-1-propanol, toluene, and 1-propanol were measured with the “step by step” method and those for 2-methyl-1-propanol, 1-propanol, methylcyclohexane, toluene, 2,4-pentanedione, 1-bromooctane, dibenzyl ether, and benzoic acid with the “three-step” method using a Tian−Calvet batch calorimeter. The measurements of saturated liquid heat capacity have an approximate uncertainty of ±0.5% and cover temperatures within the range 288 K to 363 K.

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1. Introduction

To complete the Dortmund Data Bank, which contains nearly all the world’s available phase equilibrium data and excess properties, work on pure component properties was started in 1992 at the University of Oldenburg. The project was sponsored by the German Federal Ministry for Research and Technology (BMBF). The main objectives are to collect and correlate pure component properties but also to test and to develop estimation methods for pure component properties. Up to the present, the department of industrial chemistry of the University of Oldenburg has amassed the world’s largest factual data bank for pure component properties. Nevertheless, it is often necessary to measure pure component properties for compounds with missing or questionable data or for which data are available only over a limited temperature range. This is especially important for testing or developing estimation methods for pure component properties. Thus, the department of industrial chemistry of the University of Oldenburg has developed several experimental apparatus to measure pure component properties.

The aim of this work is to measure heat capacities with the help of a SETARAM Tian−Calvet calorimeter. Furthermore, two different procedures are tested for measuring heat capacities (Höhne et al., 1996) using differential scanning calorimetry (DSC), namely, the “step by step” method and the “three-step” method.

2. Experimental Section

The measurements reported here were performed using a Tian−Calvet heat flow batch calorimeter from SETARAM, France (model BT2.15), with a temperature range from 77.15 K to 473.15 K. The principle of the measurement method has been described in detail by Calvet and Prat (1963). The calorimeter consists of two thermal flux meters, each constructed by a series of 480 thermocouples surrounding a cylindrical cavity. The flux meters are arranged symmetrically around the two cells in an aluminum block located in the cavity. The signal delivered by the power difference of the two flux meters is proportional to the heat effects occurring in the cells. The temperature of the calorimeter block can be regulated using liquid nitrogen and electrical heating and is monitored using a Pt 100 resistance thermometer located between the two cells. Only the temperature of the calorimeter block is recorded. It is not possible to measure the temperature of the sample directly in the cell. For heat capacity measurements, the temperature of the calorimeter block is varied linearly with time. Thus, there is a temperature difference between the calorimeter block and the sample during the measurement. To account for this temperature delay, a calibration was necessary. Therefore, the melting points of *n*-heptane and benzoic acid were each measured with three different temperature programs with heating rates of 0.15, 0.3, and 0.5 K min^{-1} (in total, six data points).

The parameters of the following equation were fitted to the differences ΔT_m between the measured and published melting temperatures [$T_m = 182.57$ K for *n*-heptane (van Miltenburg et al., 1987) and $T_m = 395.49$ K for benzoic acid (Höhne et al., 1996)] and the corresponding heating rates Z:

$$T_{cor} = b_0 + b_1 \Delta T_m + b_2 Z + b_3 Z^2 \tag{1}$$

where T_{cor} is the corrected temperature. The temperature is computer controlled, and the signals (temperature and heat flux) are automatically recorded.

The cells used (volume 8.5 cm^3) are made of stainless steel with aluminum or Teflon seals. The two cells were placed in the calorimeter: one was charged with the sample while the other cell was empty. A SATORIUS A 200 S balance with an accuracy of ±0.2 mg was used to determine the mass of the samples. As the cells were not totally filled with the sample, the measured heat capacities c^s are measured at saturated pressure. However, it is not necessary to make any distinction below $0.9T_S$ (normal boiling point) between isobaric heat capacities c_P at the saturation curve and c^s, since the differences are less than the uncertainty of the high-precision measurements (Domalski et al., 1996).

For the step by step method the calorimeter was calibrated using special cells with precise resistance heaters (Handa et al., 1984). The temperature program of the step by step method (performed between 25 °C and 70 °C) keeps the temperature of the cells constant for 4 h at 25 °C; then the temperature is increased 5 °C with a heating rate of

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* Corresponding author. E-mail: Gmehling@tech.chem.uni-oldenburg.de.

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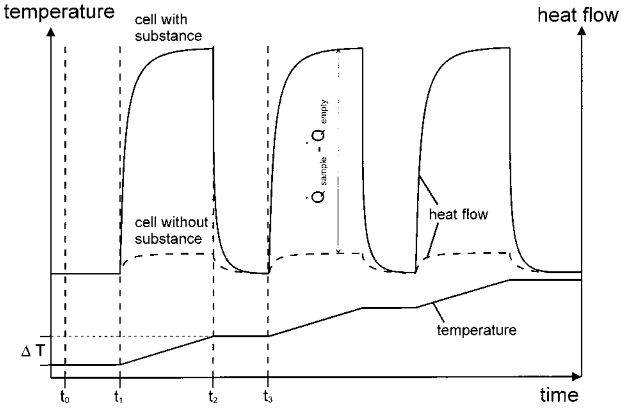

Figure 1. Step by step method for determination of heat capacities (the course of the temperature is not true to scale).

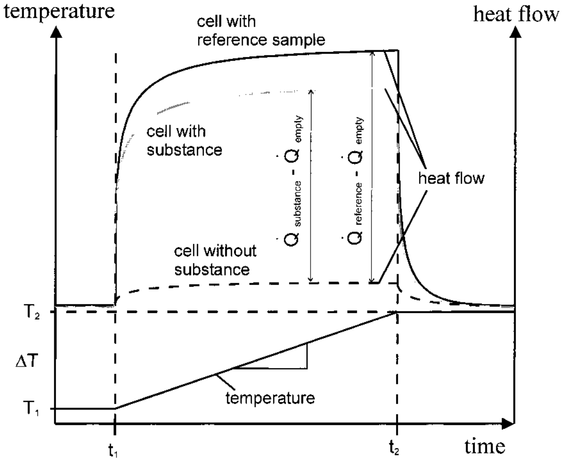

Figure 2. Three-step method for determination of heat capacities (the course of the temperature is not true to scale).

0.15 K min^{-1}, and finally it is kept constant again for 4 h at the final temperature (30 °C). This procedure is repeated several times until the upper temperature of 70 °C is reached. The temperature program has to be repeated with empty cells. Depending on the temperature interval, the procedure corresponds to Figure 1, where the operation must be repeated with empty cells. The average heat capacity of the sample can then be calculated by the following equation (Höhne et al., 1996):

$$c_{avg} = \frac{\int_{t_1}^{t_3} (\dot{Q}_{sample} - \dot{Q}_{empty})\, dt}{(T_2 - T_1)} \tag{2}$$

The average heat capacity is related to the average temperature, $T_{avg} = (T_1 + T_2)/2$. The heat capacity of a liquid always changes with temperature, and c_{true} (the "true" heat capacity at the average temperature) and c_{avg} are identical at T_{avg} only when heat capacity is a linear function of temperature. Usually, it is not necessary to make any distinction between c_{true} and c_{avg} if the interval between T_1 and T_2 is not larger than 10 °C (Domalski et al., 1996).

The temperature program of the three-step method (performed between 10 °C and 95 °C) keeps the temperature of the cells constant for 4 h at 10 °C before the temperature is increased to 95 °C with a heating rate of 0.15 K min^{-1}. This procedure corresponds to Figure 2.

The temperature program has to be repeated not only with empty cells but also with the reference sample (because of the reference sample, no electrical calibration is required). In this work, *n*-heptane was used as reference substance, since a large amount of reliable heat capacity data is available for this compound. The Tian−Calvet calorimeter records 5000 heat-flow data points for each run (temperature, heat flow, time). About 1500 data points can be used for calculating the heat capacities by the following equation (Höhne et al., 1996):

$$c_{probe} = \frac{\dot{Q}_{sample} - \dot{Q}_{empty}}{\dot{Q}_{ref} - \dot{Q}_{empty}} \frac{n_{ref}}{n_{sample}} c_{ref} \tag{3}$$

where n describes the number of moles of sample (n_{sample}) or reference sample (n_{ref}).

Heat capacities for *n*-heptane (C_7H_{16}, 100.2 g/mol, CAS# 142-82-5), 2-methyl-1-propanol ($C_4H_{10}O$, 74.12 g/mol, CAS# 78-83-1), 1-propanol (C_3H_8O, 60.1 g/mol, CAS# 71-23-8), methylcyclohexane (C_7H_{14}, 98.19 g/mol, CAS# 108-87-2), toluene (C_7H_8, 92.14 g/mol, CAS# 108-88-3), 2,4-pentanedione ($C_5H_8O_2$, 100.13 g/mol, CAS# 123-54-6), 1-bromooctane ($C_8H_{17}Br$, 193.13 g/mol, CAS# 111-83-1), dibenzyl ether ($C_{14}H_{14}O$, 198.27 g/mol, CAS# 103-50-4), and benzoic acid ($C_7H_6O_2$, 122.12 g/mol, CAS# 65-85-0) were measured. All chemicals were obtained from Aldrich and stored over 3 Å molecular sieves. All compounds were distilled under vacuum using a Vigreux column with a height of 1.5 m. The purities (determined using gas chromatography) of all compounds were >99.95% by mass. The benzoic acid used in this work has a stated purity >99% by mass; the sample was further purified by sublimation.

3. Results

3.1. Step by Step Method. The results of the heat capacity measurement for the step by step method are listed in Table 1 and shown graphically in Figure 3 together with the published data. As can be seen, the measured values are in good agreement with the recommended heat capacity data of Domalski et al. (1996). The average deviation, given by $100/n_p \sum |(c^s_{lit.} - c^s_{meas})/c^s_{lit.}|$, where n_p is the number of data points, is about 0.22%. The deviations of the measured heat capacities from the recommended heat capacities, given by $100\{c^s_{lit.} - c^s_{meas}\}/c^s_{lit.}$, do not exceed ±0.3%.

3.2. Three-Step Method. The results for the three-step method are listed in Table 2 and presented in Figure 4 together with the published data. One measurement yields about 1500 data points. For clarity, only the values in 5 K steps are given.

The measured heat capacities are in very good agreement with data observed by other authors and the recommended heat capacity data of Domalski et al. (1996). The average deviation is about 0.13%. The deviations of the measured heat capacities from the recommended heat capacities do not exceed ±0.2%. For methylcyclohexane and 2,4-pentanedione, the temperature range in which heat capacities are available was increased. For 1-bromooctane and dibenzyl ether, no heat capacities could be found in the literature. In addition to liquid heat capacities, solid heat capacities were measured for benzoic acid by Tian−Calvet calorimetry. The measured data deviate on average by 0.23% from the values published by Ginnings et al. (1953). The deviations are within ±0.3%.

4. Discussion

While the heat capacity of isolated molecules (ideal gas phase) can be calculated with high precision from the energy levels of the different translation, rotation, oscillation, and so forth degrees of freedom usually available from

Table 1. Experimental Saturated Liquid Heat Capacity Data c^s for *n*-Heptane, 2-Methyl-1-propanol, Toluene, and 1-Propanol Measured Using the Step by Step Method

T/K	c^s/J mol^{-1} K^{-1}	T/K	c^s/J mol^{-1} K^{-1}	T/K	c^s/J mol^{-1} K^{-1}	T/K	c^s/J mol^{-1} K^{-1}
n-Heptane		2-Methyl-1-propanol		Toluene		1-Propanol	
302.05	226.49	307.05	188.77	302.05	157.85	307.05	148.83
307.05	228.52	312.05	193.69	307.05	159.38	312.05	151.80
312.05	230.68	317.05	198.42	312.05	161.01	317.05	155.74
317.05	232.58	322.05	203.36	317.00	162.44	322.05	158.77
322.00	234.17	327.05	207.83	321.95	164.05	326.95	161.77
326.95	236.47	332.00	213.30	326.95	166.29	331.95	165.20
331.95	238.09			331.95	167.12	336.95	169.00
336.95	240.88			336.95	169.00		

Table 2. Experimental Saturated Liquid Heat Capacity Data c^s for 2-Methyl-1-propanol, 1-Propanol, Toluene, Methylcyclohexane, 2,4-Pentadione, 1-Bromooctane, and Dibenzyl Ether and Experimental Saturated Solid Heat Capacity Data for Benzoic Acid Measured Using the Three-Step Method

T/K	c^s/J mol^{-1} K^{-1}	T/K	c^s/J mol^{-1} K^{-1}	T/K	c^s/J mol^{-1} K^{-1}	T/K	c^s/J mol^{-1} K^{-1}
2-Methyl-1-propanol		1-Propanol		Toluene		Methylcyclohexane	
323.16	202.72	330.06	163.73	288.13	154.41	288.21	180.41
328.15	207.89	335.05	167.60	293.15	155.96	293.16	182.76
333.15	213.07	340.13	171.45	298.21	157.42	298.14	184.87
338.15	217.69	345.04	175.37	303.16	158.84	303.17	187.00
343.22	223.04	350.03	179.10	308.20	160.40	308.21	189.18
348.12	227.62	354.92	182.85	313.17	161.92	313.19	191.31
353.20	232.57			318.16	163.49	318.18	193.51
358.19	237.36			323.16	165.07	323.17	195.73
363.18	242.00			328.15	166.42	328.16	197.75
				333.15	168.14	333.16	199.99
				338.14	169.60	338.15	201.97
				343.13	171.06	343.23	204.74
				348.21	172.50	348.13	206.65
				353.20	174.13	353.21	208.98
2,4-Pentanedione		1-Bromooctane		Dibenzyl Ether		Benzoic Acid (Solid)	
300.03	208.77	295.44	280.39	295.56	324.85	288.13	143.62
305.05	210.44	300.16	282.20	300.06	326.91	293.14	145.05
310.04	212.29	305.12	284.12	305.07	328.81	298.21	147.20
315.05	214.55	310.04	285.85	310.07	331.08	303.16	149.24
320.07	216.00	315.05	287.58	315.08	333.47	308.20	151.39
325.08	217.46	320.06	289.25	320.01	335.55	313.17	153.59
330.08	218.92	325.07	291.04	325.01	337.41	318.16	155.86
335.00	220.43	330.07	292.96	330.01	338.98	323.16	158.12
340.08	222.09	335.07	295.13	335.01	340.56	328.16	160.26
345.08	223.53	340.07	297.31			333.15	162.81
350.07	225.66	345.06	299.27			338.14	165.47
355.06	227.10	350.06	301.41			343.22	167.91
360.05	228.56	355.05	304.11			348.21	170.93
		360.05	306.23			353.20	173.96

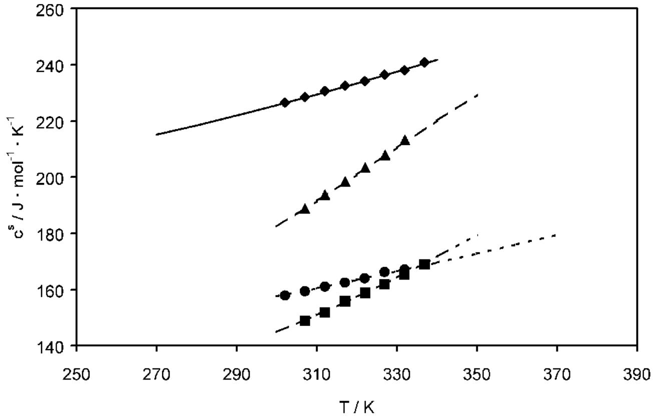

Figure 3. Experimental saturated heat capacity data c^s measured with the step by step method compared with literature data: (◆) heptane, this work; (—) heptane, Domalski et al., 1996; (▲) 2-methyl-1-propanol, this work; (— — —) 2-methyl-1-propanol, Domalski et al., 1996; (●) toluene, this work; (- - -) toluene, Domalski et al., 1996; (■) 1-propanol, this work; (— - - —) 1-propanol, Domalski et al., 1996.

spectroscopic data, theoretical calculations for condensed phases are usually not possible except for the case of the perfect crystal (Born and von Karman theory (Horvath, 1992)). Therefore, liquid heat capacities are either determined experimentally or calculated using the knowledge about the ideal gas heat capacity and the *PVT* behavior of the pure compound.

The heat capacities of the alcohols (2-methyl-1-propanol and 1-propanol) shown in Figures 3 and 4 show a stronger temperature dependence than those for the other substances. This is caused by the strong hydrogen bonds (association) of the alcohols. The association decreases with temperature, and this causes the observed strong temperature dependence of the heat capacities of the alcohols.

The heat capacity data for 1-propanol, 2-methyl-1-propanol, and toluene were measured by the step by step method as well as by the three-step method. To compare the two methods, the deviations of the experimental heat capacities in the overlapping temperature range were investigated. The deviations are within ±0.2%. This agreement shows that Tian−Calvet calorimetry and both procedures are well suited for measuring heat capacities.

Handa et al. (1984) found that the precision of the c^s measurements is ±0.5% above 100 K with a SETARAM Tian−Calvet calorimeter (BT type). This value is based on the reproducibility of results from a series of measurements made on samples of ice and THF hydrate, and also from sensitivity-calibration runs. Repeated heat capacity meas-

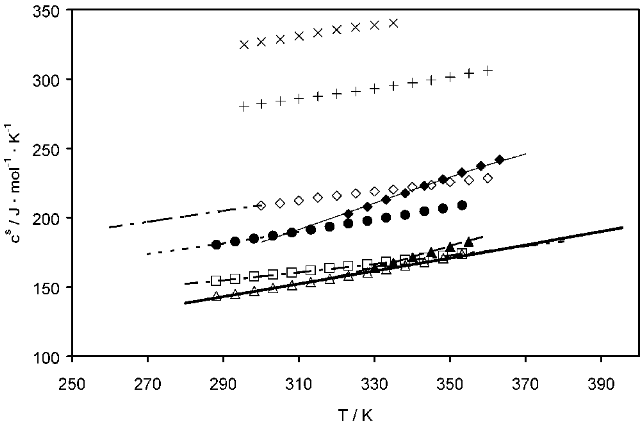

Figure 4. Experimental saturated heat capacity data c^s measured with the three-step method compared with literature data: (◆) 2-methyl-1-propanol, this work; (—) 2-methyl-1-propanol, Domalski et al., 1996; (▲) 1-propanol, this work; (– – –) 1-propanol, Domalski et al., 1996; (●) methylcyclohexane, this work; (- - -) methylcyclohexane, Domalski et al., 1996; (□) toluene, this work; (– - –) toluene, Domalski et al., 1996; (◇) 2,4-pentanedione, this work; (– - - –) 2,4-pentanedione, Domalski et al., 1996; (+) 1-bromooctane, this work; (×) dibenzyl ether, this work; (△) benzoic acid, this work; (—) benzoic acid, Ginnings et al., 1953.

urements and sensitivity-calibrations show the same precision in heat capacity measurements in this work. Comparisons of the measured heat capacity data with recommended values from Domalski et al. (1996) confirm these results (see sections 3.1 and 3.2).

5. Conclusion

The three-step method is a very effective technique for measuring heat capacities of liquids and solids with the help of a Tian–Calvet calorimeter. It allows measurement of about 1500 data points over a large temperature range in a rather short time. A requirement is that reliable heat capacity data for the reference substance are available in the desired temperature range. The step by step method needs no reference values; thus, this method can also be used when no reliable heat capacity data are available. The disadvantage of the step by step method is that it is more time-consuming than the three-step method.

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