

LOW-TEMPERATURE HEAT CAPACITIES AND DERIVED THERMODYNAMIC FUNCTIONS OF CYCLOHEXANE

Z. D. Nan¹ and Z. C. Tan^{2*}

¹Department of Chemistry, Qufu Normal University, Qufu, Shandong 273165, P. R. China

²Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China

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Abstract

The low-temperature heat capacities of cyclohexane were measured in the temperature range from 78 to 350 K by means of an automatic adiabatic calorimeter equipped with a new sample container adapted to measure heat capacities of liquids. The sample container was described in detail. The performance of this calorimetric apparatus was evaluated by heat capacity measurements on water. The deviations of experimental heat capacities from the corresponding smoothed values lie within $\pm 0.3\%$, while the inaccuracy is within $\pm 0.4\%$, compared with the reference data in the whole experimental temperature range. Two kinds of phase transitions were found at 186.065 and 279.684 K corresponding solid–solid and solid–liquid phase transitions, respectively. The entropy and enthalpy of the phase transition, as well as the thermodynamic functions $\{H_{(T)}-H_{298.15\text{ K}}\}$ and $\{S_{(T)}-S_{298.15\text{ K}}\}$, were derived from the heat capacity data. The mass fraction purity of cyclohexane sample used in the present calorimetric study was determined to be 99.9965% by fraction melting approach.

Keywords: adiabatic calorimetry, cyclohexane, heat capacity, sample container, thermodynamic function

Introduction

Heat capacity is one of the more valuable thermophysical quantities to be considered when studying pure liquid and liquid mixtures. Accurate values are needed in many areas of physics, chemistry, and chemical engineering for establishing energy balances, obtaining entropy and enthalpy values, or studying phase transitions. Moreover, ascertainment of the heat capacity of liquids as a function of temperature is a source of important information concerning their molecular structure and is essential for checking the efficiency of estimation models used in industry [1].

The adiabatic calorimeter is the most important and accurate tool for heat capacity determination over a wide range of temperatures. In our previous reports

* Author for correspondence: E-mail: tzc@dicp.ac.cn

[2–7], an adiabatic calorimeter has been described and used to measure heat capacities of solids. However, it is difficult to measure heat capacities of liquids with the adiabatic calorimeter because the adhesive was used to bind the lid and the cell together. Heat capacities of liquids may be affected by the adhesive. In order to determine heat capacities of liquids, on the base of the adiabatic calorimeter mentioned above, a newly constructed sample container was reported in this paper. The heat capacities of cyclohexane in solid and liquid phase have been measured by means of the adiabatic calorimeter.

Experimental

Sample preparation

Commercially available cyclohexane (Shenyang Chemical Agent Factory, normal mass fraction purity, 0.98) was distilled twice in a vacuum. The purified sample was loaded into the calorimeter cell, heated to its boiling point and then the cell was sealed so that the free space of the container was filled with the saturated vapour of cyclohexane instead of air. The mass of samples of cyclohexane was 28.7482 g.

Adiabatic calorimetry

Heat capacity measurements were carried out in an adiabatic calorimeter [2]. The new sample container adapted to measure heat capacities of liquids was used in the calorimeter and described in the following.

A cross sectional view of the calorimeter sample container is shown in Fig. 1. It is made of silver of 99.95% purity, 0.2 mm thick, gold-plated and polished, and has a cylindrical body section and a hemispherical top and bottom. The main body is 31.7 mm in diameter and 60.1 mm high. The mass of the empty container is about 50 g and its

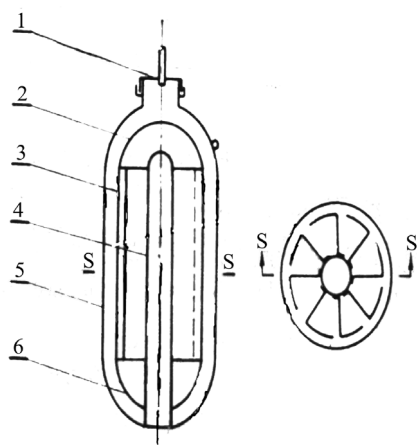


Fig. 1 Sample container. 1 – lid with capillary copper tubing; 2 – upper vanes; 3 – side vanes; 4 – central entrant well; 5 – outer wall of container; 6 – lower vanes

effective capacity around 48 mL. In the center a tapered entrant well is provided for insertion of the thermometer-heater assembly. Onto the well's outer wall eight L-shaped 0.15 mm thick radial silver vanes are brazed one by one by use of silver alloys having different melting points. A space exists between outer edges of the vanes and the cylindrical inside wall and four semi-circular vanes extend into the upper and the lower hemispherical spaces in the container. This arrangement of vanes improves the heat distribution within the container and more reproducible surface temperatures can be achieved between the loaded and empty container measurements. At the top of the container an inlet of 8 mm inner diam. is provided for admitting samples.

The temperature of the cell was alternatively measured. The temperature increment in a heating period was 2–4 K, and temperature drift was maintained at about 10^{-3} K min⁻¹ in equilibrium period. All the data were automatically picked up through a Data Acquisition/Switch Unit (Model: 34970A, Aglient, USA) and processed by a computer.

Results and discussion

Heat capacity of water

In order to verify the reliability of our calorimetric apparatus, we measured the heat capacities of water to calibrate the calorimeter in the temperature 78–370 K. The water used for calorimetric measurements was deionized and distilled twice. The sample was, after being introduced into the container, heated to its boiling point and sealed in by pinching off the capillary tubing, thus both preventing the container from breaking due to the thermal expansion of the sample, and ensuring no air leakage into the free space of the container after the sample cooled down. The mass of sample of water was 42.0317 g.

The plot of molar heat capacities of water as a function of temperature was given in Fig. 2. In order to compare the results of heat capacities of water measured in our laboratory with [8], the data of heat capacities gained from [8] are given in Fig. 2 as well. From Fig. 2, it can be seen that the molar heat capacities reported in this paper are in excellent agreement with the data cited from [8].

The polynomial equations, derived from our experimental data, were fitted by least-squares. The values of the heat capacities of the water were fitted with the following polynomial expressions with a least squares method. For 78–245 K,

$$C_{p,m}=1.2557X^3+0.5800X^2+9.7124X+24.091 \text{ J mol}^{-1} \text{ K}^{-1} \quad (1)$$

where $X=(T-167.95)/87.55$, fitting correlation $R^2=0.9997$.

For 274–320 K,

$$C_{p,m}=75.234\pm 0.212 \text{ J mol}^{-1} \text{ K}^{-1} \quad (2)$$

The smoothed heat capacities of water calculated by use of these equations are listed in Table 1, at intervals of 10 K. In order to evaluate the experimental precision and accuracy, deviations of the heat capacity from the smoothed curves are calculated. The

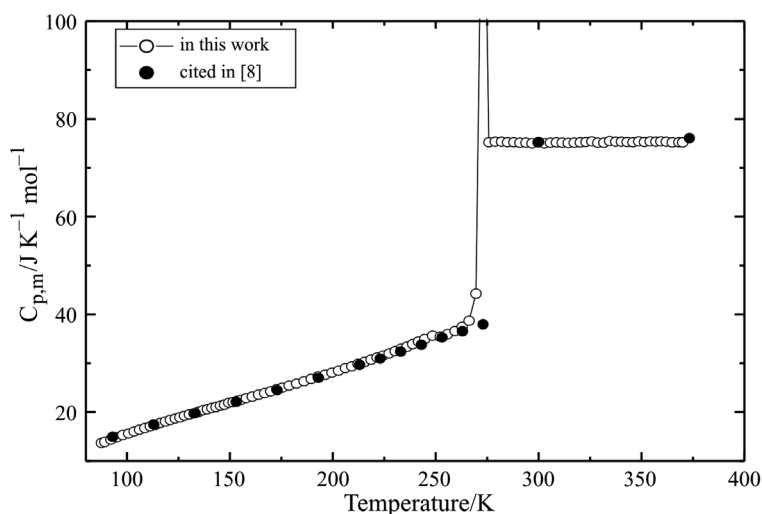


Fig. 2 Molar heat capacities of H₂O as a function of temperature

Table 1 Smoothed heat capacity of water

T/K	$C_{p,m}/J \text{ mol}^{-1}\text{K}^{-1}$	T/K	$C_{p,m}/J \text{ mol}^{-1}\text{K}^{-1}$
80	12.463	220	31.306
90	14.152	230	32.743
100	15.733	240	34.267
110	17.219	280	75.234
120	18.625	290	75.234
130	19.964	300	75.234
140	21.250	310	75.234
150	22.497	320	75.234
160	23.719	330	75.234
170	24.930	340	75.234
180	26.144	350	75.234
190	27.375	360	75.234
200	28.636	370	75.234
210	29.942		

overall measuring precision may be estimated to be $\pm 0.3\%$ by means of the deviations of the experimental data from the smoothed values of the polynomial equations. The precisions have residuals less than $\pm 0.3\%$. By comparing the results of this research with those of other investigation [8], we have assessed the accuracy of the apparatus. Root-mean-square σ of the percentage deviation of the smoothed values from reference results [8] is used. The calculating equation was listed as follows,

$$\sigma = \sqrt{\frac{\sum_{i=1}^n [(C_{p,m}^s - C_{p,m}^f) / C_{p,m}^f]^2}{n-1}} \quad (3)$$

where n is the number of experimental points, and $C_{p,m}^s$ and $C_{p,m}^f$ represent the smoothed heat capacity values and the reference results. The root-mean-square σ was calculated to be 0.4%.

Heat capacity of cyclohexane

The experimental molar heat capacities of cyclohexane are listed in Table 2 in the sequence of the temperature increment and presented graphically in Fig. 3. From the $C_{p,m}$ - T curve, two kinds of phase transitions were observed in the temperature ranges between 182 and 191 K, 273 and 283 K, respectively. The temperatures of the phase transitions were determined to be 186.065 and 279.684 K which were corresponding to the maximum values of $C_{p,m}$, respectively. They were in excellent agreement with the data cited from [9]. The experimental molar heat capacities were fitted to the polynomials by the least-squares fitting. The polynomials obtained from the heat capacities over the temperature ranges 77–182 and 191–273 K for solid and 283–350 K for liquid are as follows:

From 78 to 182 K

$$C_{p,m} = 2.0719X^2 + 21.981X + 70.335 \quad (4)$$

$$\delta = 0.59\%$$

where $\delta = \left\{ \sum_{i=1}^n [(C_{p,m}^e - C_{p,m}^{fit}) / C_{p,m}^{fit}]^2 / (n-1) \right\}^{1/2}$, $C_{p,m}^e$ and $C_{p,m}^{fit}$ represent the experimental heat capacity values and the calculated results from the polynomials. $X = (T-130)/52$.

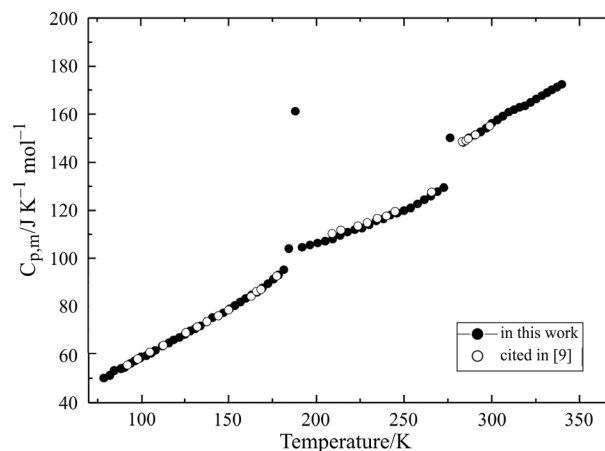


Fig. 3 Molar heat capacities of cyclohexane as a function of temperature

Table 2 Experimental heat capacity of cyclohexane

T/K	$C_{p,m}/J\ mol^{-1}K^{-1}$	T/K	$C_{p,m}/J\ mol^{-1}K^{-1}$	T/K	$C_{p,m}/J\ mol^{-1}K^{-1}$
78.546	50.025	175.459	91.366	265.261	125.942
81.872	51.132	178.462	93.182	268.995	127.795
84.294	53.062	181.422	95.333	272.685	129.414
88.170	53.892	184.298	104.057	276.245	150.147
90.214	54.264	185.783	1325.886	278.530	612.891
93.453	55.947	186.012	5407.175	279.094	1129.478
95.943	57.065	186.034	6616.807	279.174	1895.348
98.947	58.208	186.045	7428.130	279.211	2765.928
100.154	58.987	186.055	7379.455	279.342	3281.931
103.150	59.547	186.065	10841.321	279.486	3807.053
105.871	60.518	186.072	9841.521	279.684	4674.592
108.245	61.732	186.110	8214.996	280.749	243.105
112.234	63.471	186.287	2028.392	283.619	148.405
115.921	64.809	187.974	161.211	286.955	150.166
118.706	66.054	191.953	104.663	290.247	151.203
121.859	67.107	196.352	105.561	293.517	152.603
124.995	68.298	200.711	106.408	296.801	154.210
128.124	69.791	205.034	107.163	299.991	156.245
130.905	70.713	209.314	108.116	303.187	157.699
133.904	71.897	213.562	109.613	306.354	159.156
137.478	73.604	217.768	110.876	309.503	160.906
140.791	75.373	221.931	111.999	312.634	161.933
144.105	76.092	226.052	112.631	315.743	162.833
146.972	77.367	230.115	114.001	318.845	163.534
150.445	78.944	234.158	115.602	322.062	164.941
153.570	80.361	238.148	116.394	325.298	166.335
156.659	81.851	242.089	118.003	328.507	167.712
159.813	83.331	246.021	118.867	331.489	168.925
163.033	84.654	249.944	119.823	334.276	170.147
166.198	85.939	253.824	120.975	337.176	171.328
169.328	87.669	257.672	122.643	339.906	172.407
172.413	89.438	261.484	124.343		

From 191 to 273 K

$$C_{p,m}=2.3249X^2+12.273X+114.480 \quad (5)$$

$$\delta=0.27\%$$

where $X=(T-232)/41$.

From 283 to 350 K

$$C_{p,m}=0.4285T+26.895 \quad (6)$$

$$\delta=0.60\%$$

Thermodynamic functions of cyclohexane

The molar enthalpies ΔH_m and molar entropies ΔS_m of the phase transitions were evaluated to be 6.694 and 2.634 kJ mol⁻¹, 38.98 and 9.44 J mol⁻¹ K⁻¹, respectively, based on the following thermodynamic relationships:

$$\Delta H_m = [Q - n \int_{T_i}^{T_m} C_{p(s)} dT - n \int_{T_m}^{T_f} C_{p(l)} dT - \int_{T_i}^{T_f} C_0 dT] / n \quad (7)$$

$$\Delta S_m = \Delta H_m / T_m \quad (8)$$

in which Q is the total energy introduced into the calorimeter during the course of phase transition, n is the moles of substance of the sample, T_i is a little lower than T_m and T_f a little higher than T_m , C_0 is the heat capacity of the empty calorimeter. The heat capacity polynomials (4), (5) and (6) were used to calculate the smoothed heat capacities, and were numerically integrated to obtain the values of the thermodynamic functions. The results are listed in Table 3.

Adiabatic calorimetry provides one of the most accurate ways of determining melting point and the purity of a substance [10]. The purity of sample can be evaluated from the observed melting-point curve [11, 12]. If the liquid solution formed in the premelting region are ideal, and thus obey Raoult's law, the following expressions can be used to calculate the purity of the sample:

$$X_2 = \frac{\Delta H_m (T_0 - T_1)}{RT_0^2} \quad (9)$$

$$F = q/Q \quad (10)$$

$$T_0 - T = (T_0 - T_1)/F \quad (11)$$

where F is the fraction of sample melted, q is the energy introduced into the calorimeter to melt part of the sample, T_0 is the triple-point temperature of the pure substance, T_1 is the triple-point temperature of the given sample, X_2 is the molar fraction of impurity in liquid solution. The data of T , Q , F and $1/F$ are listed in Table 4. The T_0 is the temperature when $1/F$ equals 0 and T_1 is equivalent to the temperature when $1/F$ is 1. The T_0 and T_1 are found to be 280.630 and 279.761 K based on Eq. (11), respectively. Thus we calculate $X_2=0.0035$ mol%, and the purity of cyclohexane sample used in the calorimetric experiment accounts to $1-X_2=99.9965$ mol%.

Table 3 The thermodynamic functions of cyclohexane

T/K	$C_{p,m}/\text{J mol}^{-1} \text{K}^{-1}$	$[H_T - H_{298.15 \text{ K}}]/\text{kJ mol}^{-1}$	$[S_T - S_{298.15 \text{ K}}]/\text{J mol}^{-1} \text{K}^{-1}$
80	51.33	-31.75	-167.4
90	54.93	-31.22	-161.1
100	58.68	-30.66	-155.2
110	62.60	-30.05	-149.4
120	66.67	-29.40	-143.8
130	70.91	-28.71	-138.3
140	75.30	-27.98	-132.8
150	79.86	-27.21	-127.5
160	84.57	-26.39	-122.2
170	89.45	-25.52	-116.9
180	94.48	-24.60	-111.7
190	104.96	-16.93	-67.44
200	107.00	-15.87	-62.00
210	109.32	-14.79	-56.73
220	111.91	-13.69	-51.58
230	114.79	-12.55	-46.55
240	117.94	-11.39	-41.59
250	121.38	-10.19	-36.71
260	125.10	-8.960	-31.88
270	129.09	-7.689	-27.08
280	Phase transition		
290	151.16	-1.246	-4.238
300	155.45	0.287	0.959
310	159.73	1.863	6.126
320	164.02	3.481	11.26
330	168.30	5.143	16.38
340	172.59	6.847	21.47
350	176.87	8.595	26.53
298.15	154.65	0	0

Conclusions

The low-temperature heat capacity of cyclohexane was determined over the temperature range from 78 to 350 K. A solid–solid phase transition and a solid–liquid phase transition were found between 182 and 191 K, 273 and 283 K, respectively. The

Table 4 The observed equilibrium temperature and fractions melted during the melting process

<i>T/K</i>	<i>Q/J</i>	<i>F</i>	<i>1/F</i>
278.530	371.35	0.4127	2.423
279.094	503.79	0.5599	1.786
279.174	550.32	0.6116	1.635
279.211	558.17	0.6203	1.612
279.342	603.06	0.6702	1.492
279.486	672.98	0.7479	1.337
279.684	825.48	0.9174	1.090

enthalpies and entropies of phase transitions were derived. The purity of the cyclohexane sample was determined to be 99.9965%.

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References

- 1 R. Páramo, M. Zouine and C. Casanova, *J. Chem. Eng. Data*, 47 (2002) 441.
- 2 S. X. Wang, Z. C. Tan, Y. Y. Di, F. Xue, M. H. Wang, L. X. Sun and T. Zhang *J. Therm. Anal. Cal.*, 76 (2004) 335.
- 3 Z. C. Tan, B. Xue, S. W. Lu, S. H. Meng, X. H. Yuan and Y. J. Song, *J. Therm. Anal. Cal.*, 63 (2001) 297.
- 4 Z. C. Tan, G. Y. Sun, Y. Sun and L. X. Zhou, *J. Thermal Anal.*, 45 (1995) 59.
- 5 L. Wang, Z. C. Tan, S. H. Meng, D. B. Liang and Z. K. Hei, *J. Therm. Anal. Cal.*, 66 (2001) 409.
- 6 P. Yu, Z. C. Tan, S. H. Meng, S. W. Lu, X. Z. Lan, L. X. Sun, F. Xu, T. Zhang and S. X. Hu, *J. Therm. Anal. Cal.*, 74 (2003) 867.
- 7 B. P. Liu, Z. C. Tan, Z. D. Nan, P. Liu, L. X. Sun, F. Xu and X. Z. Lan, *J. Therm. Anal. Cal.*, 71 (2003) 623.
- 8 R. L. David, *CRC Handbook of Chemistry and Physics 80th*, CRC Press, Boca Raton London 1999, Chapter 6-6.
- 9 S. P. George, H. M. Huffman and S. B. Thomas, *J. Am. Chem. Soc.*, 52 (1930) 1032.
- 10 E. F. Westrum Jr., G. T. Furukawa and J. P. McCullough, *Experimental Thermodynamics*, Vol. 1. Eds J. P. McCullough and D. W. Scott, Butterworths, London 1968.
- 11 J. P. McCullough and G. Waddington, *Anal. Chim. Acta*, 17 (1957) 80.
- 12 J. H. Badey, *J. Phys. Chem.*, 63 (1959) 1991.