Thermodynamic Properties of Carbon Nanotubes

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Low-temperature molar heat capacities of the carbon nanotubes (CNTs) including single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs) were measured, respectively, by a precision automated adiabatic calorimeter over the temperature range of (78 to 398) K. The observed results demonstrated that the change in the molar heat capacity with thermodynamic temperature was different for the SWNTs and the MWNTs. Polynomial equations of the molar heat capacities as a function of the temperature were fitted by the least-squares method for SWNTs and MWNTs, respectively. Smoothed heat capacities and the changes in thermodynamic functions of the CNTs, such as $\Delta H = H(T/\mathrm{K}) - H(298.15)$ and $\Delta S = S(T/\mathrm{K}) - S(298.15)$, were calculated on the basis of the fitted polynomials and the relationships of the thermodynamic functions.

Introduction

Carbon nanotubes (CNTs) including single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs) have received great interest since their discovery.[1,2] CNTs constitute a promising material for use in the aerospace, textile, and electronics industries because this material possesses high chemical and thermal stability, mechanical strength, flexibility, and electrical and thermal conductivity as well as low weight.[3−6] In particular, the incorporation of even small amounts of CNTs in other materials can improve the mechanical stabilities and thermal and electrical properties.[7−10] However, heat capacities and other thermodynamic functions of CNTs have not been reported, as we know. Heat capacity is one of the more valuable thermophysical quantities to be considered when studying materials. Accurate heat capacity 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. Heat capacities of C_{60} and C_{70} have been reported.[11,12] Structure changes of C_{60} and C_{70} were investigated on the basis of the heat capacities measured at different experimental temperatures.

The heat capacities of the CNTs including SWNTs and MWNTs were measured with an adiabatic calorimeter, and the thermodynamic properties of the CNTs were derived in this article. The adiabatic calorimeter has been described and used to measure heat capacities of samples in our previous research.[13−15]

Experimental Section

CNTs were purchased from Shenzhen Nanotech Port, were prepared by the method of chemical vapor deposition (VCD), and contained ≥ 90 % SWNTs and ∼ 98 % MWNTs with a length of (1 to 15) μm.

The morphologies of the CNTs were observed by transmission electron microscope (TEM) images, which were taken on a Hitachi model H-800.

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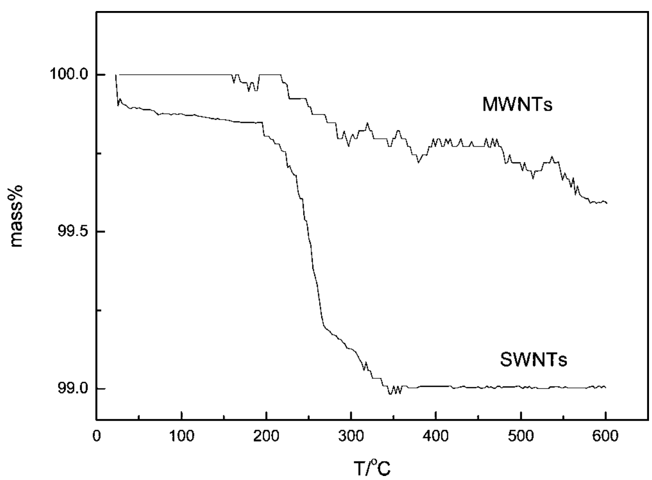

Figure 1. TG curves of the CNTs.

The thermogravimetry (TG) measurements of the samples were carried out by a thermogravimetric analysis system (model: TG 209 F1, NETZSSCH, Germany) under nitrogen with a 10 $\mathrm{K{\cdot}min^{-1}}$ heating rate. The amounts of the samples used for TG analysis were (20.2 and 19.8) mg, respectively, for SWNTs and MWNTs. The flow rate of nitrogen for each of the TG experiments was controlled at 10 $\mathrm{mL{\cdot}min^{-1}}$.

Heat-capacity measurements were carried out in a high-precision automatic adiabatic calorimeter built by Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, described in detail elsewhere.[16] The temperature increment in a heating period was (2 to 4) K and the temperature drift was maintained at about 10^{-3} $\mathrm{K{\cdot}min^{-1}}$ in equilibrium period. All of the data were automatically acquired through a Data Acquisition/Switch Unit (model: 34970A, Aglient) and processed by a computer.

To verify the reliability of the adiabatic calorimeter, we measured the molar heat capacities for the reference standard material α-Al_2O_3. The deviations of our experimental results from the values recommended by the National Bureau of Standards[17] were within ± 0.2 % in the temperature range of (80 to 400) K.

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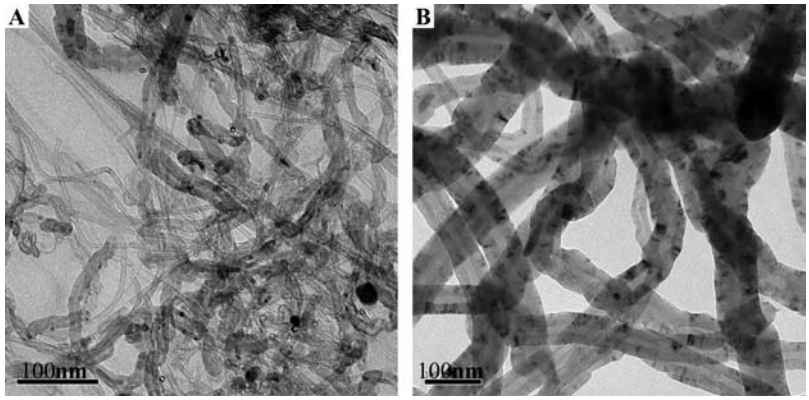

Figure 2. TEM photography of the CNTs: (A) SWNTs and (B) MWNTS.

Table 1. Experimental Molar Heat Capacity of the SWNTs and MWNTs

T/K	$C_{p,m}$/J·K^{-1}·mol^{-1}	T/K	$C_{p,m}$/J·K^{-1}·mol^{-1}	T/K	$C_{p,m}$/J·K^{-1}·mol^{-1}	T/K	$C_{p,m}$/J·K^{-1}·mol^{-1}	T/K	$C_{p,m}$/J·K^{-1}·mol^{-1}	T/K	$C_{p,m}$/J·K^{-1}·mol^{-1}
		SWNTs						MWNTs			
78.13	0.186	191.05	3.801	301.30	6.112	80.88	0.0361	189.98	2.914	295.93	6.247
80.96	0.308	193.73	3.855	304.30	6.149	84.20	0.0712	192.68	3.012	297.37	6.295
84.26	0.428	196.39	3.929	307.29	6.182	87.13	0.134	195.36	3.077	300.04	6.377
87.12	0.532	199.04	3.993	310.30	6.241	90.00	0.175	198.04	3.162	303.06	6.453
89.92	0.633	202.31	4.084	313.31	6.307	92.82	0.224	200.70	3.273	306.09	6.539
92.74	0.741	205.62	4.147	316.31	6.372	95.59	0.286	204.00	3.381	309.11	6.627
95.56	0.81	208.30	4.207	319.31	6.432	98.38	0.339	207.32	3.458	312.12	6.703
98.39	0.88	210.97	4.284	322.31	6.503	101.18	0.41	210.03	3.565	315.13	6.782
101.23	0.985	213.62	4.342	325.30	6.568	105.14	0.491	212.72	3.675	318.13	6.837
105.18	1.138	216.27	4.402	328.29	6.602	109.03	0.591	215.40	3.786	321.13	6.948
109.06	1.282	218.91	4.479	331.27	6.692	111.72	0.639	218.07	3.83	324.12	7.027
111.81	1.366	221.10	4.517	334.25	6.702	114.50	0.713	220.72	3.936	327.40	7.108
114.66	1.44	223.83	4.585	337.22	6.781	117.30	0.791	223.38	4.023	330.38	7.195
117.52	1.565	226.55	4.647	340.19	6.821	120.05	0.891	226.01	4.09	333.36	7.259
120.33	1.65	229.36	4.706	343.15	6.881	122.81	0.943	228.74	4.208	336.33	7.337
123.16	1.724	232.26	4.769	346.10	6.922	125.60	0.995	231.56	4.305	339.30	7.414
126.01	1.817	235.17	4.842	349.05	6.979	128.34	1.102	234.37	4.375	342.25	7.488
128.82	1.938	238.09	4.9	351.99	7.021	131.11	1.146	237.20	4.454	345.21	7.565
131.58	2.012	241.01	4.943	354.92	7.073	133.89	1.222	240.01	4.548	348.15	7.637
134.38	2.111	244.47	5.008	357.83	7.139	136.64	1.279	243.36	4.657	351.09	7.709
137.20	2.175	247.88	5.07	359.37	7.181	139.35	1.347	246.64	4.748	354.03	7.782
139.97	2.263	250.65	5.129	363.69	7.214	142.09	1.422	249.30	4.829	356.96	7.849
142.72	2.35	253.41	5.194	365.17	7.241	144.85	1.499	251.95	4.919	359.90	7.913
145.49	2.445	256.16	5.258	367.40	7.278	147.58	1.594	254.60	5.011	362.82	7.984
148.28	2.543	258.92	5.307	370.03	7.328	150.28	1.661	257.24	5.091	365.74	8.046
151.05	2.579	261.67	5.366	373.29	7.372	153.78	1.757	259.89	5.166	368.66	8.111
154.61	2.749	264.41	5.403	376.75	7.416	157.24	1.861	262.53	5.25	371.58	8.168
158.14	2.842	267.15	5.486	379.60	7.46	159.93	1.957	265.18	5.34	374.50	8.236
160.89	2.883	269.89	5.528	382.15	7.483	162.68	2.031	267.82	5.414	377.41	8.318
163.69	2.997	272.62	5.583	385.97	7.523	165.41	2.096	270.45	5.499	380.31	8.358
166.47	3.107	275.34	5.628	389.19	7.608	168.12	2.211	273.24	5.566	383.22	8.422
169.22	3.191	278.07	5.693	392.23	7.669	170.80	2.293	276.02	5.654	386.13	8.499
171.94	3.269	280.78	5.739	395.25	7.706	173.47	2.379	278.80	5.749	389.03	8.563
174.62	3.347	283.65	5.799	398.26	7.762	176.19	2.467	281.58	5.843	391.93	8.626
177.34	3.422	286.51	5.827			178.99	2.549	284.35	5.901	394.83	8.693
180.12	3.508	289.36	5.899			181.77	2.653	287.26	5.999	397.73	8.751
182.88	3.579	292.33	5.929			184.52	2.745	290.16	6.078		
185.63	3.644	295.31	6.015			187.26	2.829	293.05	6.166		
188.35	3.703	298.30	6.054								

The sample masses of SWNTs and MWNTs used for the calorimetric measurement were 0.67186 and 0.54917 g, respectively, which were equivalent to (0.060000 and 0.045732) mol in terms of the molar mass, $M = 12.0107\ \mathrm{g \cdot mol^{-1}}$.

Results and Discussion

Figure 1 shows the TG curves of the CNTs in the temperature range from (25 to 600) °C. The mass % loss was about 1.0 % and 0.6 % for SWNTs and MWNTs, respectively, when the experimental temperature was $T \leq 600$ °C.

Figure 2 shows TEM photos of the CNTs. Figure 2 demonstrates that the CNTs were dispersed nanotubes and the diameters were about (20 to 40) nm and (30 to 60) nm for SWNTs and MWNTs, respectively.

Low-temperature heat capacities of CNTs were measured by the adiabatic calorimeter. All experimental results were listed in Table 1 and plotted in Figure 3. The obtained results showed that the structure of the CNTs was stable over the temperature range of (78 to 398) K; namely, no phase change, association, or thermal decomposition occurred. These results were agreeable with those obtained by TG curves, as given in Figure 1. The 112 experimental points for the SWNTS and the MWNTs, respectively, in the temperature region of (78 to 398) K were fitted by means of the least-squares method. Polynomial equations of the experimental molar heat capacities ($C_{p,m}$) versus reduced temperature (X), $X = f(T) = (T - ((T_2 + T_1)/2))/((T_2 - T_1)/2)$ were obtained, where T is thermodynamic temperature and T_1 and T_2 are the minimum and the maximum temperatures during the calorimetric experiment, respectively. For the SWNTs

$$C_{p,m}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 0.1376X^4 + 0.3051X^3 - 1.0438X^2 + 3.5028x + 4.890 \quad (1)$$

where $T_1 = 78.13$ K, $T_2 = 398.26$ K, and the standard error of this fit is $\delta = 0.026$ J·K^{-1}·mol^{-1}. The standard δ of the fits was calculated by the following equation

$$\delta = \sqrt{\frac{\sum (C_{p,m}^{\text{fit}} - C_{p,m}^{\text{exptl}})^2}{n-1}} \quad (2)$$

where n is the number of experimental points, and $C_{p,m}^{\text{exptl}}$ and $C_{p,m}^{\text{fit}}$ represent the molar heat capacity obtained by experimental measurement and the corresponding result calculated from eq 1, respectively.

Table 2. Smoothed Heat Capacities and Thermodynamic Functions of the CNTs[a]

T/K	$C_{p,m}$[b]/J·K^{-1}·mol^{-1}	ΔH[b]/J·mol^{-1}	ΔS[b]/J·K^{-1}·mol^{-1}	$C_{p,m}$[c]/J·K^{-1}·mol^{-1}	ΔH[c]/J·mol^{-1}	ΔS[c]/J·K^{-1}·mol^{-1}
80	0.245	−768.3	−4.093	0.019	−647.8	−3.091
85	0.429	−766.6	−4.071	0.099	−647.5	−3.088
90	0.611	−764.0	−4.040	0.187	−646.8	−3.081
95	0.790	−760.5	−4.000	0.281	−645.6	−3.069
100	0.968	−756.1	−3.953	0.382	−644.0	−3.052
105	1.142	−750.8	−3.899	0.488	−641.8	−3.031
110	1.315	−744.7	−3.839	0.601	−639.1	−3.006
115	1.485	−737.7	−3.774	0.719	−635.8	−2.977
120	1.652	−729.9	−3.704	0.842	−631.9	−2.944
125	1.817	−721.2	−3.630	0.969	−627.3	−2.908
130	1.980	−711.7	−3.552	1.101	−622.2	−2.867
135	2.140	−701.4	−3.471	1.237	−616.3	−2.823
140	2.297	−690.3	−3.386	1.377	−609.8	−2.776
145	2.452	−678.4	−3.299	1.520	−602.6	−2.725
150	2.604	−665.8	−3.209	1.667	−594.6	−2.670
155	2.754	−652.4	−3.116	1.816	−585.9	−2.613
160	2.902	−638.2	−3.022	1.967	−576.4	−2.553
165	3.047	−623.4	−2.925	2.121	−566.2	−2.489
170	3.189	−607.8	−2.827	2.277	−555.2	−2.423
175	3.329	−591.5	−2.727	2.435	−543.4	−2.354
180	3.466	−574.5	−2.625	2.594	−530.9	−2.282
185	3.601	−556.8	−2.522	2.755	−517.5	−2.207
190	3.733	−538.5	−2.418	2.916	−503.3	−2.130
195	3.863	−519.5	−2.313	3.079	−488.3	−2.051
200	3.991	−499.9	−2.206	3.242	−472.5	−1.969
205	4.116	−479.6	−2.099	3.405	−455.9	−1.885
210	4.239	−458.7	−1.991	3.569	−438.5	−1.799
215	4.359	−437.2	−1.882	3.732	−420.2	−1.711
220	4.478	−415.1	−1.772	3.895	−401.1	−1.621
225	4.594	−392.4	−1.662	4.058	−381.3	−1.529
230	4.708	−369.2	−1.551	4.221	−360.6	−1.435
235	4.820	−345.4	−1.439	4.383	−339.1	−1.339
240	4.929	−321.0	−1.327	4.543	−316.7	−1.241
245	5.037	−296.1	−1.215	4.703	−293.6	−1.142
250	5.143	−270.6	−1.102	4.862	−269.7	−1.041
255	5.247	−244.7	−0.989	5.020	−245.0	−0.939
260	5.349	−218.2	−0.875	5.176	−219.5	−0.835
265	5.449	−191.2	−0.761	5.331	−193.2	−0.730
270	5.547	−163.7	−0.647	5.484	−166.2	−0.623
275	5.644	−135.7	−0.533	5.636	−138.4	−0.515
280	5.740	−107.2	−0.418	5.786	−109.8	−0.406
285	5.834	−78.30	−0.303	5.934	−80.55	−0.296
290	5.926	−48.90	−0.188	6.080	−50.51	−0.184
295	6.017	−19.04	−0.073	6.224	−19.75	−0.072
300	6.107	11.27	0.043	6.367	11.73	0.042
305	6.196	42.03	0.158	6.507	43.91	0.157
310	6.284	73.23	0.274	6.645	76.80	0.273
315	6.371	104.9	0.390	6.781	110.4	0.389
320	6.458	136.9	0.506	6.915	144.6	0.507
325	6.543	169.4	0.623	7.047	179.5	0.625
330	6.628	202.4	0.739	7.177	215.1	0.745
335	6.713	235.7	0.856	7.305	251.3	0.865
340	6.797	269.5	0.973	7.431	288.1	0.986
345	6.880	303.7	1.090	7.554	325.6	1.108
350	6.964	338.3	1.207	7.676	363.7	1.230
355	7.048	373.3	1.324	7.795	402.3	1.354
360	7.132	408.8	1.442	7.913	441.6	1.478
365	7.216	444.6	1.559	8.029	481.5	1.602
370	7.300	480.9	1.677	8.143	521.9	1.728
375	7.385	517.7	1.796	8.255	562.9	1.854
380	7.471	554.8	1.914	8.366	604.4	1.981
385	7.557	592.4	2.033	8.475	646.5	2.108
390	7.645	630.4	2.152	8.582	689.2	2.237
395	7.733	668.8	2.272	8.689	732.4	2.365
400	7.823	707.7	2.391	8.794	776.1	2.495
298.15	6.074	0	0	6.314	0	0

[a] $\Delta H = H(T/\text{K}) - H(298.15)$. [b] SWNTs. [c] MWNTs.

For the MWNTs

$$C_{p,m}/J{\cdot}K^{-1}{\cdot}mol^{-1} = 0.3477X^4 - 0.7319X^3 - 0.4793X^2 + 5.0884X + 4.521 \quad (3)$$

where $T_1 = 80.88$ K, $T_2 = 397.73$ K, and the standard error of this fit is $\delta = 0.014$ J·K^{-1}·mol^{-1}.

Figure 3 shows that the changes in the molar heat capacity with respect to experimental temperature were different for the SWNTs and MWNTs. The molar heat capacity of the SWNTs is greater than that of the MWNTs when the temperature is smaller than about 275 K. The molar heat capacities of the SWNTs and the MWNTs are equal to about 5.64 J·K^{-1}·mol^{-1} at $T \approx 275$ K, but when the temperature is greater than 275 K, the molar heat capacity of the SWNTs is smaller than that of the MWNTs.

The smoothed molar heat capacities of the CNTs were calculated, respectively, on the basis of the fitted eqs 1 and 3, and the results are listed in Table 2. The changes in the thermodynamic functions of the CNTs, such as ΔH and ΔS, were also calculated, respectively, according to the following thermodynamic equations

$$\Delta H = H(T/K) - H(298.15) = \int_{298.15}^{T} C_{p,m}\, dT \quad (4)$$

$$\Delta S = S(T/K) - S(298.15) = \int_{298.15}^{T} \frac{C_{p,m}}{T}\, dT \quad (5)$$

The calculated changes in the thermodynamic functions of the CNTs, such as ΔH and ΔS, relative to standard to reference temperature, 298.15 K, are given in Table 2 at 5 K intervals.

Conclusions

The thermodynamic properties of the CNTs were investigated in this article. The TG curves of the CNTs showed that the CNTs were stable over the temperature range (25 to 600) °C. The TEM photos of the CNTs demonstrated that the CNTs were dispersed nanotubes (20 to 40) nm and (30 to 60) nm in diameter for the SWNTs and the MWNTs, respectively. The low-temperature heat capacities of the CNTs were measured by adiabatic calorimetry. The molar heat capacity of the SWNTs is greater than that of the MWNTs when the temperature is less than about 275 K. The molar heat capacities of the SWNTs and the MWNTs are equal to about 5.64 J·K^{-1}·mol^{-1} at $T \approx$ 275 K, but when the temperature is greater than 275 K, the molar heat capacity of the SWNTs is smaller than that of the MWNTs. The function of the molar heat capacity with respect to thermodynamic temperature was established for the SWNTs and MWNTs, respectively. The thermodynamic functions were derived on the basis of the established function and the relationships of thermodynamic functions.

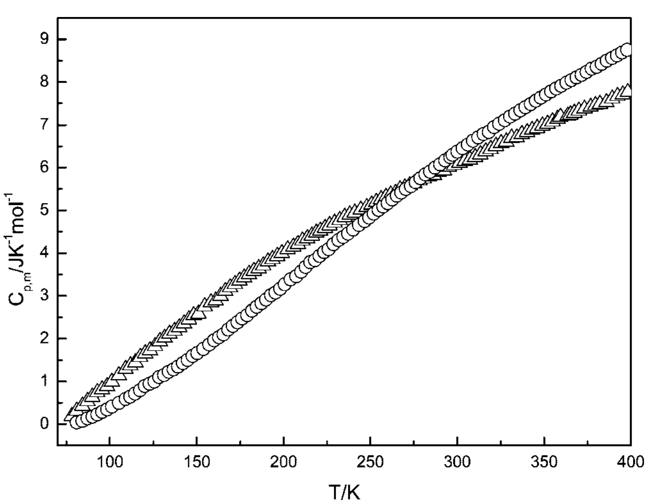

Figure 3. Curves of molar heat capacities of CNTs at different experimental temperatures. △, SWNTs; ○, MWNTs.

Literature Cited

(1) Iijima, S. Helical microtubules of graphitic carbon. *Nature (London, U.K.)* **1991**, *354*, 56–58.
(2) Iijima, S.; Ichihashi, T. Single-shell carbon nanotubes of 1-nm diameter. *Nature (London, U.K.)* **1993**, *363*, 603–605.
(3) Bekyarova, E.; Itkis, M. E.; Cabrera, N.; Zhao, B.; Yu, A.; Gao, J.; Haddon, R. C. Electronic properties of single-walled carbon nanotube networks. *J. Am. Chem. Soc.* **2005**, *127*, 5990–5995.
(4) Coleman, J. N.; Khan, U.; Blau, W. J.; Gunko, Y. K. Small but strong: a review of the mechanical properties of carbon nanotube-polymer composites. *Carbon* **2006**, *44*, 1624–1652.
(5) Artuovic, E.; Kaempgen, M.; Hecht, D. S.; Roth, S.; Gruner, G. Transparent and flexible carbon nanotube transistors. *Nano Lett.* **2005**, *5*, 757–760.
(6) Chen, L.; Xie, H.; Li, Y.; Yu, W. Nanofluids containing carbon nanotubes treated by mechanochemical reaction. *Thermochim. Acta* **2008**, *477*, 21–24.
(7) Saeed, K.; Park, S. Y. Preparation of multiwalled carbon nanotube/nylon-6 nanocomposites by in situ polymerization. *J. Appl. Polym. Sci.* **2007**, *106*, 3729–3735.
(8) Zhang, W. D.; Phang, I. Y.; Liu, T. X. Growth of carbon nanotubes on clay: unique nanostructured filler for high-performance polymer nanocomposites. *Adv. Mater.* **2006**, *18*, 73–77.
(9) Litina, K.; Miriouni, A.; Gournis, D.; Karakassides, M. A.; Georgiou, N.; Klontzas, E.; Avgeropoulos, A. Nanocomposites of polystyrene-*b*-polyisoprene copolymer with layered silicates and carbon nanotubes. *Eur. Polym. J.* **2006**, *42*, 2098–2107.
(10) Liu, L.; Grunlan, J. C. Clay assisted dispersion of carbon nanotubes in conductive epoxy nanocomposites. *Adv. Funct. Mater.* **2007**, *17*, 2343–2348.
(11) Miyazaki, Y.; Sorai, M.; Lin, R.; Dworkin, A.; Szwarc, H.; Godard, J. Heat capacity of a giant single crystal of C_{60}. *Chem. Phys. Lett.* **1999**, *305*, 293–297.
(12) Tanaka, T.; Atake, T. Low temperature heat capacity and lattice dynamics of C_{70}. *J. Phys. Chem. Solids* **1996**, *57*, 277–280.
(13) Nan, Z.; Tan, Z. C. Thermodynamic investigation of the azeotropic binary mixture water + *n*-propanol. *J. Chem. Eng. Data* **2005**, *50*, 6–10.
(14) Nan, Z.; Tan, Z. C. Thermodynamic properties of ethanol and gasoline blended fuel. *Energy Fuels* **2005**, *19*, 2432–2437.
(15) Nan, Z.; Tan, Z. C. Thermodynamic properties of the binary mixture of water and *n*-butanol. *J. Therm. Anal. Calorim.* **2007**, *87*, 539–544.
(16) Tan, Z. C.; Sun, G. Y.; Sun, Y. An adiabatic low-temperature calorimeter for heat capacity measurement of small samples. *J. Therm. Anal.* **1995**, *45*, 59–67.
(17) Ditmars, D. A.; Ishihara, S.; Chang, S. S.; Bernstein, G.; West, E. D. Enthalpy and heat-capacity standard reference material: synthetic sapphire (α-Al2O3) from 10 to 2250 K. *J. Res. Natl. Bur. Stand.* **1982**, *87*, 159–163.

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