Low-Temperature Heat Capacities and Derived Thermodynamic Functions of Para-Substituted Halogen Benzenes. 1. *p*-Chlorobromobenzene and *p*-Chloroiodobenzene

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Heat capacity measurements were made on *p*-chlorobromobenzene and *p*-chloroiodobenzene from 5 K to 360 K. The measurements were used to calculate the entropy and enthalpy relative to 0 K. The enthalpy of melting of *p*-chlorobromobenzene was found to be (18 696 ± 20) J·mol^{-1} and the triplet point temperature (337.93 ± 0.01) K. For *p*-chloroiodobenzene these values were respectively (16 103 ± 20) J·mol^{-1} and (326.72 ± 0.01) K. A very small glass transition was found in *p*-chloroiodobenzene between 270 K and 283 K.

Introduction

The para-substituted benzenes, with the substituting groups −Cl−, −Br−, and −I−, form an interesting family of compounds. The compounds have been used in binary systems to study thermodynamic aspects of mixing in the solid and liquid state. Examples of this work are to be found in the work of Campbell and Prodan[1] and the thesis of van der Linde,[2] which also contains thermodynamic data of the pure compounds *p*-dichlorobenzene and *p*-dibromobenzene. Correlations of the thermochemical and phase-diagram data for the binary systems were discussed by Calvet et al.[3]

The compounds that are the subject of this calorimetric study (*p*-chloroiodobenzene and *p*-chlorobromobenzene) have not been investigated with low-temperature calorimetry. Other data like DSC or microcalorimetry data are very scarce. The enthalpy of fusion of *p*-chlorobromobenzene has been measured;[1,4] however, for *p*-chloroiodobenzene we did not find any data at all. Structural investigations of these compounds are more numerous.[5,6] The two compounds give rise to just one crystalline form, which is the same for both. The space group is $P2_1/a$ with two molecules per unit cell. The crystal structures show orientational disorder in that the positions of the two different halogens cannot be distinguished by X-ray diffraction.[7,8] The issue of orientational disorder has recently been addressed again by Meriles et al.[9] who applied nuclear quadrupole resonance.

The purpose of this work is to obtain reliable thermodynamic data such as entropy and heat capacity values for the six possible para-substituted dihalobenzenes. Fluorine-substituted benzenes were not taken into consideration, because it is very difficult to obtain these compounds.

Experimental Section

The two compounds were purchased from Aldrich, with a stated purity of 99%. Both compounds were vacuum-sublimated before use. In this sublimation procedure, the first and last part (about 10%) of the sublimated compound were rejected. For most compounds, this method gives an improvement in purity. The calorimeter vessel was filled to the maximum, using 8.4 g for *p*-chlorobromobenzene and 9.88 g of *p*-chloroiodobenzene. After being filled, the vessel was evacuated and filled with about 1000 Pa of helium to improve heat conduction. The calorimeter used, laboratory-designation CAL V, has been described before.[10] More recent improvements in design and data handling were described in 1998 by van Miltenburg et al.[11] Measurements were made in the intermittent mode. Stabilization periods from about 600 s to 1000 s were used between the heating periods. Below 30 K, the periods were on the order of 150 s. Below 30 K, the reproducibility of the calorimeter is about 1%, between 30 K and 100 K, 0.05−0.1%, and above 100 K, 0.03%. Checking the calorimeter with standard materials (*n*-heptane and synthetic sapphire) showed no deviations larger than 0.2% from the recommended values.

Results and Discussion

***p*-Chlorobromobenzene.** The experimental data series are given in Table 1. First, the sample was melted (series 1) and then cooled in about 2 h to 80 K and in 1 more hour to 5 K. Series 2 and 3 give the measurements between 5 K and 30 K, and series 4−6 form a continuous set with increasing temperature. In between these series, measurements were stopped for about 12 h. No solid−solid-phase transitions were observed. The measured heat capacity curve is shown in Figure 1. There are a few points that deviate by more than that expected from the reproducibility of the measurements. Inspection of the files did not reveal any irregularity in the measurements.

Melting Behavior. Assuming that a small concentration of impurity in the sample causes a eutectic melting behavior, the impurity can be calculated using the law of van't Hoff for freezing point depression. The impurity is solvable in the liquid phase and the actual concentration in the liquid during the melting process becomes x/F in which x is the molar fraction of the impurity of the sample and F is the melted fraction. The van't Hoff relation then becomes

$$T = T^* - \left(\frac{RT^{*2}}{\Delta^{\mathrm{liq}}_{\mathrm{sol}}H}\right)\frac{x}{F} \qquad (1)$$

A plot of the equilibrium temperature of the melt versus

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10.1021/je990311t CCC: $19.00
Published on Web 06/21/2000

Table 1. Experimental Data Series for *p*-Chlorobromobenzene

T	C_p	T	C_p	T	C_p	T	C_p	T	C_p
K	J·K^{-1}·mol^{-1}	K	J·K^{-1}·mol^{-1}	K	J·K^{-1}·mol^{-1}	K	J·K^{-1}·mol^{-1}	K	J·K^{-1}·mol^{-1}
series 1		15.57	11.15	64.92	52.86	172.99	97.29	282.54	139.82
298.17	145.53	17.72	14.07	67.66	54.15	175.94	98.51	284.29	141.09
300.18	146.25	20.03	17.17	70.42	55.54	178.90	99.64	286.78	143.39
303.19	147.52	22.40	20.34	73.19	56.90	181.86	100.75	289.27	142.99
306.18	148.72	24.57	23.30	75.98	58.15	184.82	101.77	291.76	144.03
309.17	149.95	26.43	25.40	78.78	59.29	187.78	102.92	294.23	145.08
312.17	151.22	28.11	26.46	81.59	60.71	190.74	104.00	296.70	146.24
315.16	152.53	29.64	28.26	84.42	61.91	193.70	105.12	299.15	147.22
318.15	153.80	series 3		87.26	63.11	196.66	106.09	301.60	148.21
321.14	155.09	5.59	0.88	90.11	64.36	199.62	107.32	304.04	149.25
324.12	156.44	6.76	1.49	92.97	65.66	202.58	108.15	306.47	150.20
327.11	157.88	7.83	1.96	95.84	66.86	205.54	110.96	308.89	151.25
330.09	159.45	9.28	3.24	98.72	68.00	208.49	110.80	311.31	152.37
333.08	161.93	10.74	4.84	series 5		211.46	111.91	313.71	153.48
335.97	187.35	12.26	6.76	101.55	69.82	214.43	113.06	316.11	154.56
337.62	2302	14.09	9.15	103.20	70.23	217.40	114.18	318.49	155.75
337.87	39952	16.09	11.90	105.48	71.07	220.37	115.31	320.87	157.00
337.89	122338	18.25	14.89	108.41	72.29	223.34	114.66	323.24	158.36
337.90	158651	20.58	17.88	111.31	73.37	226.31	117.86	325.60	159.92
337.91	326294	22.91	21.01	114.22	74.50	229.26	119.81	327.95	161.87
339.56	182.99	24.99	23.83	117.13	75.71	232.21	118.01	330.28	164.92
342.54	183.79	26.79	25.57	120.05	76.80	235.19	120.81	332.58	171.11
345.51	184.41	28.42	26.82	122.97	77.92	238.15	122.09	334.80	194.05
348.48	185.04	29.90	28.61	125.89	79.21	241.09	126.47	336.62	402.56
351.43	185.74	series 4		128.82	80.42	244.04	124.59	337.54	2179
354.38	186.42	31.05	29.25	131.74	81.56	247.01	125.71	337.79	8602
357.33	187.08	32.02	30.92	134.67	82.67	249.99	126.91	337.86	22965
360.27	187.82	33.77	32.75	137.61	83.79	252.95	127.89	337.89	60299
363.20	188.56	36.34	35.08	140.55	84.86	255.92	128.49	337.90	322975
366.12	189.15	38.81	36.42	143.49	86.23	258.89	129.66	339.73	183.37
369.04	189.88	41.31	38.35	146.45	84.92	261.86	130.87	341.94	183.85
series 2		43.83	40.19	149.41	88.28	264.83	132.10	344.15	184.42
5.57	0.63	46.37	41.88	152.35	89.53	267.79	133.24	346.36	184.90
6.47	1.02	48.94	43.55	155.29	90.63	270.75	134.49	348.56	185.35
7.57	1.68	51.54	45.44	158.24	91.79	273.71	135.85	350.75	185.82
8.89	2.83	54.17	46.97	61.19	92.85	276.68	136.94	352.95	186.37
10.24	4.26	56.83	48.46	164.14	93.93	279.64	138.19	355.14	186.91
11.83	6.24	59.50	49.91	167.09	95.08	series 6		357.32	187.38
13.61	8.51	62.20	51.50	170.04	96.17	281.56	139.06		

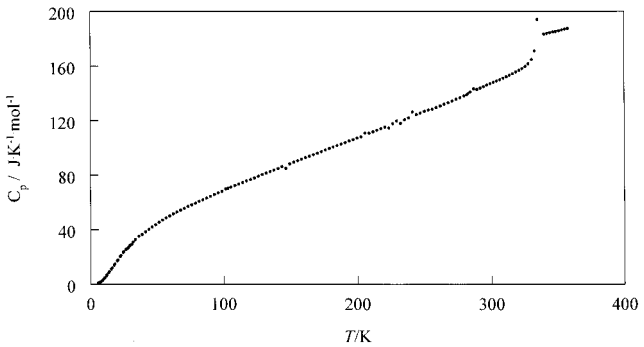

Figure 1. Experimental heat capacity data of *p*-chlorobromobenzene.

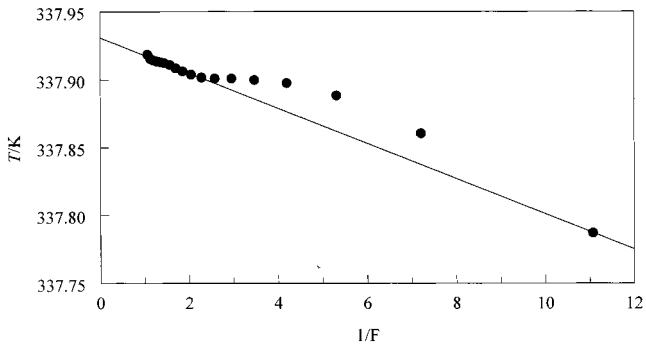

Figure 2. Melting behavior of *p*-chlorobromobenzene. The equilibrium temperature in the melt is plotted versus the reciprocal of the melted fraction.

the reciprocal of the melted fraction ($1/F$) was used to calculate the purity and the triple-point temperature (T^*). The results of the second melting experiment are given in Figure 2. From this curve, a mole fraction of impurity of 0.000 25 was calculated, corresponding to a purity of 99.97%. The triple-point temperature is (337.93 ± 0.01) K. The two melting experiments gave for the enthalpy of melting 18 691 J·mol^{-1} and 18 701 J·mol^{-1}, respectively. No significant difference between the first and second melting experiment was found.

The mean value of the enthalpy of fusion is (18 696 ± 20) J·mol^{-1}. This value corresponds well with the value reported by Cambell and Prodan[1] of 18 761 J·mol^{-1}. They reported a melting temperature of 337.73 K. Adjusting this temperature for the changes in the international temperature scales[12] gives a value of 337.77 K.

The liquid heat capacity data of the two series can be represented by a linear function, $C_{p,l}(T) = \{(106.71 \pm 1.32) + (0.225\ 32 \pm 0.0037)(T/\mathrm{K})\}$ J·K^{-1}·mol^{-1}, and the standard error of this fit is 0.14 J·K^{-1}·mol^{-1}, corresponding to about 0.08%. The low-temperature data were fitted according to the Debye low-temperature limit for the heat capacity curve, $C_p = \alpha T^3$. The value for α was determined to be 0.004 06 J·K^{-4}·mol^{-1}, using this value to calculate the starting values of $S°$ and $H(T) - H(0)$, Table 2 was calculated by numerical integration of the interpolated heat capacity and enthalpy data. In Table 2, the derived

Table 2. Thermodynamic Properties at Selected Temperatures for *p*-Chlorobromobenzene

T	$C^\circ_{p,m}$	ΔS°_m	ΔH°_m	Φ°_m	T	$C^\circ_{p,m}$	ΔS°_m	ΔH°_m	Φ°_m
K	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}	J·mol^{-1}	J·K^{-1}·mol^{-1}	K	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}	J·mol^{-1}	J·K^{-1}·mol^{-1}
10	4.01	1.35	10	0.34	210	111.36	139.92	13895	73.75
20	17.14	8.07	114	2.34	220	115.17	145.18	15027	76.88
30	28.71	17.37	348	5.77	230	119.08	150.39	16200	79.96
40	37.34	26.94	683	9.87	240	122.88	155.54	17408	83.00
50	44.32	36.04	1092	14.20	250	126.91	160.64	18657	86.01
60	50.19	44.67	1566	18.57	260	130.11	165.67	19941	88.97
70	55.33	52.8	2094	22.88	270	134.16	170.66	21263	91.91
80	59.9	60.5	2671	27.11	280	138.34	175.61	22626	94.81
90	64.31	67.81	3292	31.23	290	143.29	180.58	24040	97.68
100	68.82	74.81	3957	35.24	298.15	146.82	184.60	25222	100.00
110	72.88	81.57	4667	39.15	300	147.56	185.51	25494	100.53
120	76.78	88.08	5415	42.95	310	151.83	190.42	26991	103.35
130	80.89	94.39	6203	46.67	320	156.09	195.30	28531	106.15
140	84.66	100.52	7031	50.30	330	160.36	200.17	30113	108.92
150	88.53	106.5	7898	53.85	337.92[a]	163.73	204.01	31396	111.11
160	92.42	112.34	8803	57.32	337.92[b]	182.85	259.39	50110	111.11
170	96.16	118.06	9746	60.73	340	183.32	260.52	50490	112.02
180	100.05	123.66	10727	64.07	350	185.57	265.86	52335	116.34
190	103.73	129.17	11746	67.35	360	187.83	271.12	54202	120.56
200	107.45	134.58	12802	70.58	370	190.08	276.30	56092	124.70

[a] Solid. [b] Liquid phase.

Table 3. Experimental Data Series for *p*-Chloroiodobenzene

T	C_p	T	C_p	T	C_p	T	C_p	T	C_p
K	J·K^{-1}·mol^{-1}	K	J·K^{-1}·mol^{-1}	K	J·K^{-1}·mol^{-1}	K	J·K^{-1}·mol^{-1}	K	J·K^{-1}·mol^{-1}
series 1		244.93	126.36	8.50	4.20	78.92	62.47	244.25	126.05
111.30	76.31	247.90	127.45	9.82	5.89	81.73	63.89	247.85	127.42
113.04	76.95	250.87	128.62	11.28	7.96	84.55	65.10	251.43	128.81
115.37	77.81	253.84	129.32	12.82	10.34	87.39	66.26	254.99	129.48
118.30	78.89	256.82	130.15	14.48	12.81	90.24	67.49	258.54	130.83
121.22	80.00	259.80	131.41	16.28	15.50	93.09	68.74	262.07	132.32
124.14	81.07	262.78	132.63	18.19	18.16	95.95	69.93	265.57	133.84
127.06	82.38	265.75	134.05	20.18	20.82	98.82	71.03	269.05	135.50
129.98	83.47	268.71	135.48	22.25	23.68	series 6		272.50	137.35
132.91	84.51	271.66	137.06	24.37	26.59	101.34	72.69	275.92	138.99
135.84	85.62	274.62	138.58	26.54	28.92	103.00	73.08	279.32	140.74
138.78	86.70	277.30	138.32	28.79	30.80	105.77	74.13	282.70	142.38
141.71	87.76	series 2		31.10	33.28	109.63	75.60	286.07	144.03
144.65	88.84	297.28	147.75	series 4		113.46	77.03	289.41	145.34
147.59	89.93	299.37	148.91	6.83	2.38	117.29	78.49	292.74	146.74
150.53	91.08	302.38	150.14	8.89	4.68	121.13	79.94	296.06	148.06
153.47	92.27	305.35	151.47	10.17	6.42	124.98	81.42	299.35	149.11
156.42	93.30	308.32	152.80	11.57	8.53	128.85	83.02	series 7	
159.36	94.37	311.28	154.20	13.27	11.03	132.72	84.43	296.38	148.47
162.30	95.41	314.24	155.53	15.05	13.63	136.59	85.88	297.49	149.10
165.24	96.57	317.20	157.30	16.92	16.38	140.47	87.31	299.55	149.79
168.19	97.54	320.13	164.67	18.90	19.20	144.35	88.75	302.53	151.00
171.13	98.63	322.87	220.57	20.96	21.90	148.24	90.43	305.51	152.52
174.08	99.71	324.82	688	23.07	24.87	152.13	91.67	308.49	153.91
177.04	100.86	325.73	2493	25.22	27.65	156.04	92.76	311.45	155.26
179.98	101.98	326.08	6499	27.42	29.47	159.93	93.73	314.42	156.48
182.93	103.01	326.24	12505	29.70	31.87	163.84	95.97	317.38	158.19
185.88	104.08	326.33	18082	32.02	34.33	167.75	97.36	320.32	165.99
188.83	105.15	326.39	29339	series 5		171.66	98.80	323.06	223.26
191.78	106.23	327.42	562	33.57	36.08	175.58	100.35	324.97	754
194.73	107.29	329.83	185.43	34.69	37.12	179.51	101.83	326.60	46405
197.69	108.35	332.95	185.99	36.54	38.47	183.43	103.28	326.63	50215
200.64	109.53	335.99	186.59	39.11	39.86	187.35	104.69	327.65	431
203.59	110.58	338.96	187.40	41.61	41.78	191.28	106.19	330.22	185.53
206.54	111.71	341.92	188.13	44.10	43.54	195.21	107.56	333.35	186.23
209.50	112.75	344.89	188.59	46.63	45.29	199.14	108.98	336.41	186.89
212.44	113.95	347.86	189.05	49.19	46.84	203.05	110.45	339.40	187.60
215.39	115.00	350.82	189.64	51.78	48.73	206.93	111.93	342.38	188.19
218.34	116.03	353.79	190.33	54.39	50.20	210.78	113.29	345.36	188.83
221.28	117.21	356.76	190.91	57.03	51.80	214.60	114.73	348.35	189.32
224.23	118.36	359.72	191.61	59.70	53.21	218.40	116.15	351.33	190.12
227.17	119.56	362.68	192.21	62.39	54.79	222.17	117.55	354.32	190.57
230.12	120.61	365.64	192.91	65.10	56.12	225.91	118.96	357.31	191.31
233.07	121.43	368.61	193.45	67.83	57.39	229.62	120.46	360.30	192.07
236.04	122.90	series 3		70.58	58.79	233.31	121.88		
239.00	124.01	5.86	1.62	73.34	60.13	236.98	123.27		
241.96	125.15	7.28	3.03	76.13	61.36	240.63	124.66		

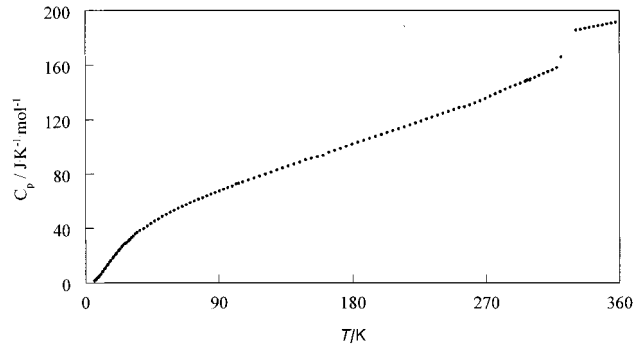

Figure 3. Experimental heat capacities of *p*-chloroiodobenzene.

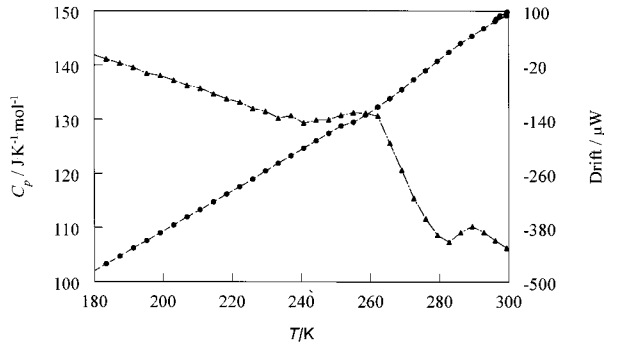

Figure 4. Heat capacity values (●) and drift (▲) for *p*-chloroiodobenzene around the solid glass transition. The drift (see text) is plotted on the right axis.

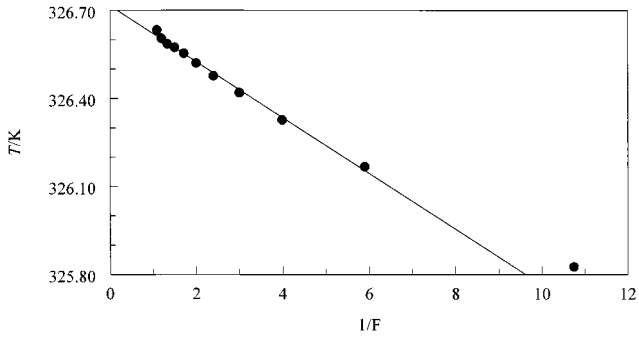

Figure 5. Melting behavior of *p*-chloroiodobenzene. The equilibrium temperature in the melt versus the reciprocal of the melted fraction is given.

thermodynamic properties $S(T)$, $H(T) - H(0)$, and $-\{H(T) - H(0) - T{\cdot}S\}/T$ are given.

***p*-Chloroiodobenzene.** The method of measurement and the thermal history of this compound are identical to the description for *p*-chlorobromobenzene. The experimental data are given in Table 3 and are plotted in Figure 3. In Figure 4 the heat capacity data between 160 K and 300 K are shown, together with the observed temperature drift multiplied by the total heat capacity of the vessel and its contents in the stabilization periods. The latter value is called drift and is plotted in microwatts. The combination of these curves gives a strong indication that a small glass transition in the solid phase took place. When approaching the glass transition, the drift increases because of relaxation of the glass. Both at and after the glass transition, the drift decreases when the relaxed energy is recovered. A glass transition in the solid is not uncommon in the 1,4-disubstituted benzenes and the chloro-, bromo-, and iodotoluenes all show this behavior.[13] For *p*-chloroiodobenzene, the transition takes place between 270 K and 283 K; we estimate the heat capacity jump to be 2.8 J·K^{-1}·mol^{-1}

Table 4. Thermodynamic Properties at Selected Temperatures for *p*-Chloroiodobenzene

(M = 238.45 g·mol^{-1}, $\Phi_m^\circ \overset{\text{def}}{=} \Delta_0^T S_m^\circ - \Delta_0^T H_m^\circ/T$)

T	$C_{p,m}^\circ$	ΔS_m°	ΔH_m°	Φ_m°
K	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}	J·mol^{-1}	J·K^{-1}·mol^{-1}
10	6.15	2.41	17	0.65
20	20.57	11.20	152	3.56
30	32.18	21.94	421	7.89
40	40.53	32.50	790	12.74
50	47.43	42.31	1 232	17.68
60	53.38	51.51	1 737	22.56
70	58.50	60.14	2 297	27.32
80	63.01	68.25	2 906	31.93
90	67.39	75.93	3 558	36.40
100	71.80	83.26	4 253	40.72
110	75.74	90.29	4 992	44.91
120	79.51	97.04	5 768	48.98
130	83.44	103.56	6 583	52.93
140	87.13	109.88	7 436	56.77
150	91.03	116.02	8 326	60.52
160	93.75	121.99	9 251	64.17
170	98.19	127.82	10 213	67.75
180	102.02	133.54	11 214	71.24
190	105.71	139.16	12 253	74.67
200	109.30	144.67	13 327	78.03
210	113.00	150.09	14 439	81.34
220	116.75	155.44	15 588	84.58
230	120.61	160.71	16 775	87.78
240	124.42	165.92	18 000	90.93
250	128.26	171.08	19 263	94.03
260	131.45	176.17	20 560	97.09
270	136.00	181.21	21 896	100.11
280	141.07	186.25	23 282	103.10
290	145.59	191.28	24 716	106.05
298.15	149.15	195.37	25 917	108.44
300	150.00	196.29	26 194	108.98
310	154.60	201.28	27 716	111.87
320	159.26	206.23	29 285	114.72
326.71[a]	162.39	209.55	30 364	116.61
326.71[b]	184.80	258.82	46 461	116.61
330	185.51	260.67	47 071	118.04
340	187.64	266.24	48 936	122.31
350	189.77	271.71	50 823	126.50

[a] Solid. [b] Liquid phase.

Melting Behavior. Two melting experiments were performed. The second experiment was used to calculate the purity. The plot of the equilibrium temperature versus the reciprocal of the melted fraction is shown in Figure 5. The calculated purity is 99.83% and the triple-point temperature is (326.72 ± 0.01) K. The enthalpies of fusion measured were 16 109 J·mol^{-1} and 16 097 J·mol^{-1}. The average value is (16 103 ± 20) J·mol^{-1}.

The derived thermodynamic data are given in Table 4. A fit of the data below 12 K gave the value for $\alpha = 0.0081$ J·K^{-4}·mol^{-1}.

Heat Capacity of the Liquid. The heat capacity data of two series in the liquid phase (25 data points) were fitted to a linear function,

$$C_{p,l}(T) = \{(116.95 \pm 0.78) + (0.2077 \pm 0.0022)(T/\text{K})\}\ \text{J·K}^{-1}\text{·mol}^{-1} \quad (2)$$

The standard error of this fit is 0.12 J·K^{-1}·mol^{-1}, corresponding to 0.06% of the absolute value.

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Received for review December 8, 1999. Accepted April 28, 2000.

JE990311T