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Low-Temperature Heat Capacities and Derived Thermodynamic Functions of Para-Substituted Halogen Benzenes. 2. *p*-Bromoiodobenzene and *p*-Diiodobenzene

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Heat capacity measurements were made on *p*-bromoiodobenzene and *p*-diiodobenzene from 5 K to 380 K and from 5 K to 420 K, respectively. The measurements were used to calculate the entropy and enthalpy values relative to 0 K. The enthalpy of melting of *p*-bromoiodobenzene was found to be (19375 ± 20) $J\cdot mol^{-1}$, and the triple-point temperature, (363.52 ± 0.01) K. For *p*-diiodobenzene these values were respectively (22328 ± 50) $J\cdot mol^{-1}$ and (402.40 ± 0.05) K. A small solid−solid transition occurs in *p*-diiodobenzene. The maximum of this transition was measured at 327 K for sublimated material and shifted to 322 K for crystallized material. The enthalpy of transition was found to be (223 ± 10) $J\cdot mol^{-1}$.

Introduction

This is the second article dealing with the thermodynamic properties of the para-substituted benzenes, with the substituting groups Cl^-, Br^-, and I^-. The first article dealt with the thermodynamic properties of *p*-chlorobromobenzene and *p*-chloroiodobenzene between 10 K and 360 K.[1] The family of the para-substituted halobenzenes has been used by our group as a model system for the study of the interactions in molecular mixed crystals.[2,3] The compounds were used in a series of studies on the mixing behavior in the solid and liquid state. The object of this series of publications is to present the thermodynamic properties of the pure compounds. *p*-Bromoiodobenzene and *p*-diiodobenzene did receive very little interest in the literature. Molar heat capacities, measured over a small temperature range, were published.[4,5] The crystal structure of *p*-diiodobenzene was studied by neutron diffraction by Alcobé et al.[6] This compound exists in a low- and a high-temperature crystalline phase, both of which are orthorhombic, with space groups *Pbca* and *Pccn*, respectively. In this respect, *p*-diiodobenzene does form an exception, as it does not occur in the same crystal form ($P2_1/a$) as that for the other *p*-dihalobenzenes.

Experimental Section

The two compounds were purchased from Aldrich. *p*-Bromoiodobenzene had a stated purity of 98%, and *p*-diiodobenzene had one of 99%. Both compounds were vacuum sublimated once before use. In this procedure, the first and last part (about 10%) of the sublimated compound is rejected. For most compounds, this method does give an improvement in purity. The calorimeter vessel was filled to the maximum, using 13.389 g for *p*-bromoiodobenzene (molar mass 282.9062) and 15.73 g of *p*-diiodobenzene (molar mass 329.9067). The molar masses were calculated using the *IUPAC* tables of 1991.[7] After filling, the vessel was evacuated and closed under a helium pressure of about 1000 Pa to improve heat conduction. The calorimeter used, laboratory-design indication CAL V, had been described in 1987.[8] More recent improvements in design and data-handling were described in 1998.[9] The temperature calibration (IPTS-68) of the rhodium−iron thermometer (Oxford Instruments 27 Ohms at 273 K) was corrected to the ITS-90 scale.[10] The resistance of the thermometer was measured with an automatic alternating current bridge (Tinsley type 5840D). The standard deviation of the temperature−time curve in the second half of the stabilization periods was between 25 and 40 μK outside the transition regions. Energy was supplied in a step-shaped protocol; 30%−60%−100% of the maximum power was normally used. This improves the response of the shields to the changing temperature. A constant current supply (Keithley model 220), programmed by the measuring computer, was used. The reproducibility of the heat capacity measurements was estimated from fitting the measurements with polynomial functions and was found to deviate within ±1% between 5 K and 30 K, 0.05−0.1% between 30 K and 100 K, and 0.03% or less above 100 K. The accuracy was checked by measuring standard substances (synthetic sapphire and *n*-heptane). No deviations larger than 0.2% of the recommended values were found. Measurements were made in the intermittent mode. Stabilization periods of about 600 to 1000 s were used between the heating periods. Below 30 K the periods were on the order of 150 s. We did use energy inputs in the heating periods leading to a temperature increment of about 2 K below 100 K and 3 K above this temperature. As the maximum heat input was limited to a value leading to this increment outside the transition region, a relatively large number of heat inputs were used in the fusion process. The total time spent in the melting region is for every melting experiment on the order of 9 h. To equilibrate the samples, they were first melted (series 1), followed by a slow cooling process. In this cooling process, the temperature of the first shield was set 10 K below the temperature of the vessel, resulting in a cooling speed of about 5 $K\cdot h^{-1}$ outside the crystallization region. In the next measurement (series 2) the sample was heated to the beginning of the melting process and left under adiabatic conditions at that temperature overnight.

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

T/K	C_p/J·K^{-1}·mol^{-1}	T/K	C_p/J·K^{-1}·mol^{-1}	T/K	C_p/J·K^{-1}·mol^{-1}	T/K	C_p/J·K^{-1}·mol^{-1}	T/K	C_p/J·K^{-1}·mol^{-1}
series 1		296.21	148.42	14.74	14.59	141.37	90.28	302.61	148.13
299.25	145.57	297.27	145.33	16.61	17.58	145.27	91.74	305.03	149.04
301.29	146.52	299.31	146.50	18.58	20.47	149.17	93.07	307.99	150.11
304.28	147.88	302.30	147.57	20.65	23.44	153.08	94.60	310.96	151.23
307.27	148.94	305.29	148.81	22.77	26.39	156.99	95.94	313.93	152.36
310.25	150.27	308.27	149.84	24.95	29.44	160.90	97.30	316.90	153.47
313.23	151.47	311.25	151.10	27.19	31.49	164.81	98.68	319.86	154.64
316.21	152.62	314.22	152.22	29.51	33.78	168.73	100.07	322.83	155.91
319.19	153.85	317.20	153.21	31.80	36.23	172.66	101.41	325.80	156.97
322.17	155.08	320.17	154.24	series 5		176.58	102.88	328.76	158.13
325.15	156.30	323.14	155.26	33.60	38.12	180.48	104.25	331.73	159.42
328.13	157.52	326.11	156.27	34.76	39.26	184.36	105.57	334.69	160.68
331.11	158.82	329.08	157.31	36.71	40.86	188.21	106.92	337.65	161.90
334.08	160.04	332.06	158.31	39.42	42.34	192.02	108.28	340.61	163.01
337.06	161.25	335.02	159.16	42.04	44.48	195.80	109.47	343.57	164.23
340.03	162.49	337.99	160.09	44.63	46.37	199.54	110.90	346.53	165.31
343.01	163.66	340.96	160.98	47.24	48.09	203.27	112.22	349.49	166.53
345.98	164.86	343.92	162.14	49.87	49.93	206.96	113.55	352.45	167.96
348.95	166.09	346.88	163.40	52.52	51.76	210.62	114.81	355.40	169.65
351.92	167.31	349.84	164.74	55.19	53.42	214.26	116.10	358.35	172.02
354.90	168.58	352.80	166.33	57.89	54.93	217.87	117.33	361.23	186.22
357.88	169.96	355.75	168.03	60.60	56.54	221.46	118.64	363.06	1152
360.85	173.60	358.70	170.51	63.33	58.05	225.02	119.89	363.50	41471
362.90	804	361.57	195.24	66.07	59.39	228.56	121.28	363.52	242726
363.49	55969	363.23	1892	68.84	60.73	232.08	122.58	363.52	774023
363.50	173442	series 3		71.62	62.23	235.58	123.84	363.52	$>10^6$
363.51	274477	6.97	2.53	74.42	63.53	239.05	125.07	363.52	$<-10^6$
363.51	464726	8.10	3.96	77.24	64.81	242.51	126.27	363.52	$>10^6$
363.51	688238	9.19	5.51	80.07	66.04	245.94	127.58	363.52	$>10^6$
363.51	850032	10.57	7.67	82.90	67.40	249.35	128.79	363.52	$>10^6$
363.51	915057	12.06	10.23	85.75	68.59	252.75	129.82	363.52	$>10^6$
363.52	$>10^6$	13.67	12.93	88.61	69.81	256.12	130.52	363.52	$<-10^6$
363.52	896651	15.44	15.73	91.48	71.09	259.48	131.81	363.52	$<-10^6$
363.52	$>10^6$	17.34	18.63	94.35	72.26	262.83	133.05	363.52	$<-10^6$
363.52	$>10^6$	19.35	21.63	97.24	73.37	266.15	134.39	363.52	$>10^6$
363.52	$>10^6$	21.42	24.62	100.13	74.65	269.46	135.65	363.52	$>10^6$
363.52	$>10^6$	23.56	27.57	series 6		272.75	136.94	363.52	$<-10^6$
363.52	$>10^6$	25.75	30.50	103.98	75.49	276.02	138.07	363.67	3827
363.52	$>10^6$	28.01	32.08	107.02	76.53	279.27	139.31	365.19	196.02
364.34	510.82	30.35	34.69	110.46	78.71	282.51	140.56	367.95	196.51
366.60	196.28	series 4		114.30	80.23	285.73	141.87	370.70	197.19
369.46	196.70	6.03	1.80	118.14	81.69	288.94	143.09	373.45	197.69
372.32	197.21	7.58	3.35	121.99	83.10	292.13	144.35	376.19	198.22
375.17	197.78	8.68	4.81	125.85	84.64	295.30	145.48	378.93	198.75
378.01	198.40	9.96	6.69	129.72	86.16	298.46	146.77		
380.85	198.89	11.43	9.21	133.60	87.56	series 7			
series 2		13.01	11.83	137.49	88.91	300.76	147.33		

Results and Discussion

***p*-Bromoiodobenzene.** No phase transitions were found between 10 K and the melting point. The experimental data series are given in Table 1.The temperatures in the table are the mean temperatures of the temperature intervals used; the heat capacity values are mean values over the temperature interval. Each series forms a continuous set of measurements. Very high values for the heat capacity were measured in the melt. When negative values are reported, the equilibrium temperature (see further on) was found to be lower after a heat input. This phenomenon does not influence the calculation of the enthalpy of fusion, as this calculation is based on the enthalpy increment. Also, the effect is so small that the influence on the calculation of the purity was neglected. However, it is a phenomenon which is common to the *p*-substituted halobenzenes. It was also found, but more outspoken, in *p*-diiodobenzene, where it is discussed in more detail. Series 1 and 2 were made for annealing the sample and were not used for the calculation of the derived thermodynamic properties. To obtain a starting value for the calculation of the absolute entropy, the low-temperature data were fitted to $C_p = \alpha T^3$ between 5 K and 10 K. The value of α found was $\alpha = 7.3 \times 10^{-3}$ J·mol^{-1}·K^{-4}. The experimental series, forming a continuous set from 10 K to the liquid phase, were joined together and interpolated at every degree. From this set the derived thermodynamic properties were calculated and are given in Table 2. Close to the melting point, the heat capacity, the enthalpy, and the entropy increment were calculated using a linear fit of the heat capacity for the solid and the liquid. The linear functions used are given further on ($C_{p,s}(T)$ and $C_{p,l}(T)$), together with the temperature interval in which they were calculated. The note “extrapolated” in Tables 2 and 5 indicates these values. The enthalpy of fusion was calculated by an iterative method; the baseline for the enthalpy increment was first calculated using the linear functions for the heat capacity. The following calculations reconstructed this baseline, using the melted fraction (F) to calculate the liquid contribution and the solid fraction ($1 - F$) for the solid contribution. Generally, three iterations were sufficient to obtain a constant value for the enthalpy of fusion. Two melting experiments were performed; the enthalpy of fusion measured was 19 371 and 19 380 J·mol^{-1}. Plotting the recipro-

Table 2. Thermodynamic Properties at Selected Temperatures for *p*-Bromoiodobenzene ($M = 282.9062$ g·mol^{-1}, $\Phi^\circ_m = \Delta_0^T S^\circ_m - \Delta_0^T H^\circ_m/T$)

T K	$C^\circ_{p,m}$ J·K^{-1}·mol^{-1}	ΔS°_m J·K^{-1}·mol^{-1}	ΔH°_m J·mol^{-1}	Φ°_m J·K^{-1}·mol^{-1}
10	7.32	2.442	18.2	0.62
20	22.55	12.14	167.2	3.78
30	34.32	23.72	456.8	8.49
40	42.8	34.91	847.6	13.72
50	50.03	45.26	1 313	19.00
60	56.19	54.95	1 845	24.20
70	61.35	64.01	2 434	29.24
80	66.01	72.52	3 071	34.13
90	70.43	80.55	3 754	38.84
100	74.60	88.19	4 479	43.40
110	78.53	95.48	5 245	47.81
120	82.37	102.48	6 049	52.07
130	86.27	109.23	6 892	56.21
140	89.79	115.75	7 773	60.23
150	93.38	122.07	8 689	64.15
160	96.98	128.22	9 641	67.96
170	100.51	134.20	10 629	71.68
180	104.09	140.05	11 652	75.32
190	107.56	145.77	12 710	78.87
200	111.06	151.37	13 802	82.36
210	114.60	156.88	14 931	85.78
220	118.10	162.29	16 094	89.13
230	121.81	167.62	17 294	92.43
240	125.40	172.88	18 530	95.67
250	129.00	178.07	19 802	98.86
260	132.01	183.19	21 106	102.01
270	135.86	188.24	22 445	105.11
280	139.58	193.25	23 822	108.17
290	143.51	198.21	25 238	111.19
298.15	146.64	202.23	26 420	113.62
300	147.12	203.14	26 692	114.17
310	150.87	208.03	28 182	117.12
320	154.69	212.88	29 709	120.04
330	158.67	217.70	31 276	122.92
340	162.78	222.50	32 884	125.78
350	166.55	227.27	34 528	128.61
360[a]	170.66	232.01	36 215	131.42
363.52[b]	172.11	233.68	36 818	132.40
363.52[c]	195.62	286.98	56 193	132.40
370	196.84	290.45	57 464	135.14

[a] Extrapolated. [b] Solid. [c] Liquid phase.

Table 3. Equilibrium Temperatures and the Reciprocal of the Melted Fraction for *p*-Bromoiodobenzene

$T(1/F)$/K	$1/F$	$T(1/F)$/K	$1/F$
363.502	13.293	363.522	1.800
363.518	7.408	363.523	1.624
363.521	5.127	363.522	1.480
363.522	3.920	363.522	1.359
363.522	3.172	363.522	1.256
363.522	2.664	363.522	1.168
363.522	2.297	363.522	1.092
363.522	2.018	363.666	1.028

cal of the melted fraction against the equilibrium temperature in the melt of the second experiment resulted in a straight line, giving a calculated purity of 99.99% and a triple-point temperature (T*) of 363.52_3 K, using the van't Hoff relation. The equilibrium temperatures in the melt were calculated by an exponentional extrapolation of the measured temperatures in the second half of the stabilization periods. The measured temperatures after 1000 s of stabilization are within 0.002 K of the calculated equilibrium values for $1/F$ values smaller than 3. The equilibrium temperatures and the $1/F$ values for the second melting experiment are given in Table 3 and plotted in Figure 1.

Liquid Phase. Between the melting point and 380 K, 12 data points were obtained in the liquid phase. The heat capacity of the liquid can be given between 365 K and 380 K by

$$C_{p,l}(T) = \{126.30 + 0.1909(T/\mathrm{K})\}\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

The standard error of the fit is 0.11 J·K^{-1}·mol^{-1}; this corresponds to 0.06% of the absolute value.

The heat capacity of the solid can be represented over a large temperature range by a linear fit. Between 100 K and 360 K this function is

$$C_{p,s}(T) = \{38.61 + 0.36248(T/\mathrm{K})\}\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

The standard deviation of this fit is 0.45 J·K^{-1}·mol^{-1}.

For the calculation of the enthalpy of fusion, a linear fit of the heat capacity data between 300 K and 350 K was used. This fit is

$$C_{p,s}(T) = \{22.598 + 0.411298(T/\mathrm{K})\}\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

The standard deviation of this fit is 0.10 J·K^{-1}·mol^{-1}.

p-Diiodobenzene. The experimental data series are given in chronological order in Table 4. The experimental conditions were similar to those described for *p*-bromoiodobenzene.

Derived Thermodynamic Properties. The derived thermodynamic properties are given in Table 5. The heat capacity data between 5 K and 15 K were fitted to calculate the best value at 8 K. From this value and the assumed relation $C_p = \alpha T^3$, α was calculated to be 8.86×10^{-3} J·K^{-4}·mol^{-1}. Using this value to calculate the starting values at 10 K in Table 5, the entropy and enthalpy increments were calculated by numerical integration.

Fusion Process. Two melting experiments were performed. The enthalpy of fusion was found to be 22 309 and 22 347 J·mol^{-1}. The mean value is (22328 ± 50) J·mol^{-1}. The linear fit of the heat capacity of the solid used for the calculation of the enthalpy of fusion was made between 340 K and 390 K:

$$C_{p,s}(T) = \{36.36 + 0.36873(T/\mathrm{K})\}\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

The standard error of this fit is 0.14 J·K^{-1}·mol^{-1}. The fit for the liquid phase is given further on.

The melting process of the second experiment took place in a very narrow temperature interval; from 30% melted to 100% the equilibrium temperature changed only 0.015 K. This does indicate that the compound is very pure. The plot of the reciprocal of the melted fraction against the equilibrium temperature could however not be used to calculate the purity. The equilibrium temperatures (obtained by exponential extrapolation) and the reciprocal of the melted fraction ($1/F$) are given in Table 6. The curve (given in Figure 2) is not straight and could also not be fitted by a model in which solid solution formation is assumed. This also means that the triple point cannot be given with the usual precision. We estimate it to be (402.40 ± 0.05) K. The literature values found are 402 K for the melting point and 22342 J·mol^{-1} and 22361 J·mol^{-1}, respectively.[5,4] The temperature−enthalpy curves for both melting experiments are given in a narrow temperature interval (0.1 K) in Figure 4. The first melting experiment, performed on a sublimated sample, is given by the triangles. The second experiment, after the annealing process, is given by the dots. There is some superheating in both experiments near the end of the fusion process, which can be caused by a solid−solid transition. In previous experiments on *p*-dichlorobenzene, *p*-dibromobenzene, and 1,3,5-

Table 4. Experimental Data Series for *p*-Diiodobenzene

T / K	C_p / J·K^{-1}·mol^{-1}	T / K	C_p / J·K^{-1}·mol^{-1}	T / K	C_p / J·K^{-1}·mol^{-1}	T / K	C_p / J·K^{-1}·mol^{-1}	T / K	C_p / J·K^{-1}·mol^{-1}
series 1		294.78	146.00	332.40	158.69	102.47	76.91	312.61	152.13
93.55	72.99	297.77	147.19	333.36	158.97	103.83	77.51	313.62	152.51
95.59	73.77	300.75	148.07	334.32	159.36	106.47	78.44	314.62	152.95
98.45	74.90	303.73	149.09	335.27	159.85	110.36	79.90	315.62	153.31
101.33	76.12	306.70	150.14	336.22	159.99	114.20	81.33	316.62	153.96
104.21	77.55	309.68	151.22	337.17	160.53	118.04	82.80	317.62	155.54
107.10	78.69	312.65	152.32	338.12	160.83	121.90	84.23	318.62	159.46
109.99	79.80	315.62	153.37	339.07	161.06	125.76	85.76	319.60	166.35
112.89	80.88	318.59	154.61	340.01	161.35	129.64	87.31	320.55	178.79
115.80	81.97	321.55	156.93	series 4		133.50	88.65	321.49	191.75
118.71	83.07	324.42	182.19	9.15	6.75	137.32	90.05	322.40	201.04
121.62	84.15	327.16	200.45	10.06	8.34	141.09	91.35	323.32	191.27
124.54	85.20	329.99	167.48	11.67	11.43	144.81	92.69	324.28	177.69
127.47	86.50	333.01	160.05	13.29	14.50	148.48	93.98	325.26	168.58
130.39	87.53	336.03	160.53	14.71	17.01	152.10	95.84	326.26	163.63
133.32	88.58	339.01	161.48	15.94	18.96	159.32	97.88	327.25	161.05
136.25	89.63	341.98	162.51	17.04	20.69	162.83	99.13	328.25	159.54
139.18	90.67	344.95	163.60	18.04	22.09	166.30	100.33	329.24	158.78
142.12	91.70	347.93	164.67	18.96	23.44	169.75	101.50	330.24	158.46
145.05	92.76	350.90	165.77	19.83	24.51	173.16	102.70	331.24	158.43
147.99	93.78	353.87	166.84	20.65	25.53	176.54	103.96	332.24	158.40
150.93	94.92	356.84	167.94	21.42	26.67	179.90	105.15	333.24	158.71
153.87	96.00	359.81	169.03	22.15	27.51	183.23	106.28	334.24	158.83
156.81	97.00	362.78	170.13	22.85	28.51	186.53	107.47	335.24	159.16
159.76	98.06	365.73	171.19	23.51	29.35	189.81	108.52	336.23	159.38
162.71	99.10	368.67	172.28	24.16	30.09	193.07	109.73	337.23	159.82
165.66	100.12	371.61	173.39	24.77	30.93	196.30	110.76	338.23	160.05
168.61	101.12	374.53	174.44	25.36	31.50	199.52	111.98	339.23	160.46
171.56	102.09	377.45	175.46	25.94	32.13	202.71	113.09	340.23	160.91
174.50	102.94	380.36	176.53	26.49	32.84	205.89	114.25	series 9	
177.45	104.27	383.25	177.76	27.03	33.51	209.04	115.29	341.19	160.58
180.39	105.28	386.14	178.78	27.55	33.94	212.17	116.44	342.09	161.03
183.34	106.32	389.02	179.83	series 5		215.29	117.54	344.03	162.53
186.29	107.28	391.89	180.89	5.73	2.11	218.38	118.61	347.01	163.69
189.23	108.27	394.76	182.17	7.26	3.72	221.46	119.74	349.98	164.74
192.18	109.34	397.61	183.65	8.32	4.91	224.52	120.78	352.96	165.83
195.13	110.32	400.34	222.80	9.37	7.18	227.57	121.95	355.93	166.75
198.08	111.30	401.90	2022	10.74	9.60	230.60	123.04	358.90	168.04
201.03	112.49	402.20	15994	12.23	12.58	233.61	124.08	361.87	168.96
203.97	113.44	402.25	37896	13.90	15.51	236.61	125.18	364.84	170.11
206.92	114.45	402.28	46522	15.71	18.56	239.59	126.27	367.80	171.20
209.86	115.52	402.30	61784	17.64	21.61	242.55	127.30	370.74	172.34
212.81	116.53	402.32	91259	19.70	24.29	245.51	128.42	373.68	173.45
215.76	117.54	402.33	116499	21.84	27.18	248.44	129.44	376.61	174.64
218.70	118.59	402.34	197436	24.02	29.90	251.37	130.49	379.53	175.82
221.64	119.65	402.34	221110	26.25	32.55	254.28	131.00	382.44	176.94
224.58	120.61	402.35	190162	28.52	35.51	257.18	131.83	385.34	178.11
227.53	121.75	402.36	161152	series 6		260.07	132.85	388.23	179.34
230.47	122.78	402.36	186289	33.37	38.32	262.95	133.96	391.11	180.84
233.41	123.90	402.37	198861	35.03	40.12	265.81	135.06	393.97	183.11
236.35	124.94	402.38	181178	37.45	41.53	268.66	136.15	396.81	188.38
239.29	125.98	402.38	353653	39.98	43.14	271.50	137.22	399.52	229.06
242.23	127.06	402.38	$>10^6$	42.51	45.04	274.33	138.30	401.37	819
245.17	128.16	402.38	−452104	45.04	46.84	277.14	139.30	402.07	4349
248.10	129.18	402.38	$>10^6$	47.60	48.58	279.94	140.34	402.24	12479
251.04	130.25	402.45	7950	50.19	50.45	282.73	141.42	402.31	30032
253.98	131.38	403.80	230.85	52.80	52.25	285.51	142.53	402.34	58679
256.91	132.42	406.43	207.77	55.45	53.87	288.28	143.64	402.36	72241
259.84	133.46	409.12	208.18	58.11	55.44	291.03	144.72	402.37	109794
262.77	134.56	series 3		60.79	57.09	293.78	145.60	402.38	218961
265.70	135.68	318.05	152.69	63.50	58.63	296.52	146.68	402.38	$<-10^6$
268.64	136.76	318.78	153.27	66.23	60.03	299.24	147.59	402.38	$>10^6$
271.57	137.90	319.77	153.74	68.98	61.42	series 8		402.38	$>10^6$
274.49	139.00	320.76	154.30	71.74	62.94	301.01	148.49	402.38	$<-10^6$
277.42	140.01	321.74	154.48	74.52	64.28	301.71	148.07	402.38	766197
280.35	141.11	322.72	154.95	77.32	65.58	302.57	148.57	402.38	$<-10^6$
283.27	142.26	323.70	155.37	80.13	66.88	303.58	149.00	402.38	−351603
286.20	143.44	324.67	155.88	82.95	68.24	304.58	149.26	402.38	$>10^6$
289.12	144.53	325.65	156.28	85.78	69.49	305.58	149.62	402.39	98706
292.04	145.65	326.62	156.49	88.62	70.68	306.59	149.90	402.39	−362579
294.96	146.79	327.59	156.89	91.48	72.03	307.59	150.22	402.45	9133
297.87	147.93	328.56	157.20	94.34	73.20	308.60	150.67	403.53	356
series 2		329.52	157.51	97.21	74.36	309.60	150.93	405.89	208.11
289.88	144.60	330.48	158.02	100.09	75.61	310.61	151.38	408.59	208.34
291.77	144.85	331.44	158.25	series 7		311.61	151.78	411.29	208.98

Table 5. Thermodynamic Properties at Selected Temperatures for *p*-Diiodobenzene (M = 329.9067 g·mol^{-1}, $\Phi^\circ_m = \Delta_0^T S^\circ_m - \Delta_0^T H^\circ_m/T$)

T	$C^0_{p,m}$	ΔS^0_m	ΔH^0_m	Φ^0_m
K	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}	J·mol^{-1}	J·K^{-1}·mol^{-1}
10	8.86	2.955	22.28	0.727
20	24.74	14.11	192.78	4.47
30	36.56	26.54	503.46	9.756
40	43.15	37.98	902.78	15.41
50	50.32	48.38	1 371	20.97
60	56.61	58.13	1 906	26.36
70	61.98	67.27	2 500	31.56
80	66.82	75.87	3 144	36.57
90	71.33	84.01	3 836	41.39
100	75.57	91.75	4 570	46.04
110	79.76	99.18	5 351	50.54
120	83.53	106.28	6 167	54.89
130	87.45	113.12	7 022	59.11
140	90.97	119.73	7 914	63.20
150	94.74	126.13	8 842	67.19
160	98.12	132.21	9 783	71.06
170	101.59	138.26	10 782	74.84
180	105.19	144.17	11 816	78.53
190	108.59	149.95	12 885	82.13
200	112.15	155.61	13 989	85.67
210	115.64	161.17	15 128	89.13
220	119.21	166.63	16 302	92.53
230	122.83	172.01	17 512	95.87
240	126.42	177.31	18 758	99.15
250	130.01	182.54	20 040	102.38
260	132.83	187.69	21 353	105.56
270	136.66	192.78	22 701	108.70
280	140.37	197.81	24 086	111.79
290	144.32	202.81	25 509	114.85
298.15	147.24	206.85	26 697	117.31
300	147.96	207.76	26 970	117.86
310	151.11	212.66	28 465	120.84
320	171.35	217.58	30 013	123.79
330	158.49	222.94	31 755	126.71
340	160.81	227.69	33 347	129.61
350	164.75	232.41	34 975	132.48
360	168.38	237.10	36 640	135.32
370	172.05	241.76	38 341	138.14
380[a]	176.47	246.68	40 102	141.15
390[a]	180.16	251.30	41 882	143.91
400[a]	183.85	255.91	43 702	146.65
402.40[b]	184.96	257.01	44 145	147.31
402.40[c]	207.23	312.55	66 492	147.31
410	208.59	316.44	68 072	150.41

[a] Extrapolated. [b] Solid. [c] Liquid phase.

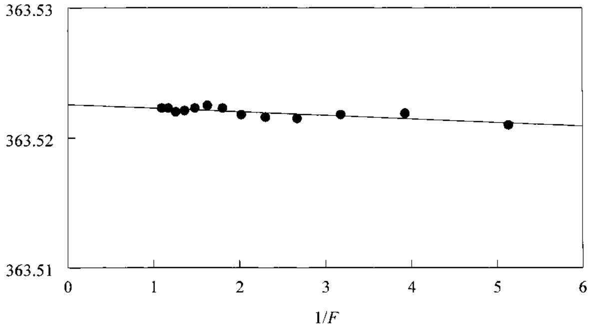

Figure 1. Equilibrium temperatures versus the reciprocal of the melted fraction for the melt of *p*-bromoiodobenzene.

Table 6. Equilibrium Temperatures and the Reciprocal of the Melted Fraction for *p*-Diiodobenzene

$T(1/F)$/K	$1/F$	$T(1/F)$/K	$1/F$
402.243	8.897	402.383	1.697
402.310	6.082	402.384	1.556
402.339	4.605	402.385	1.437
402.358	3.703	402.381	1.335
402.371	3.095	402.379	1.246
402.379	2.658	402.372	1.169
402.382	2.328	402.368	1.100
402.382	2.071	402.370	1.041
402.383	1.866		

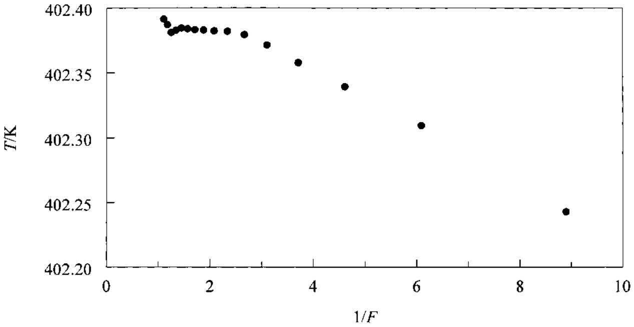

Figure 2. Equilibrium temperatures versus the reciprocal of the melted fraction for the melt of *p*-diiodobenzene.

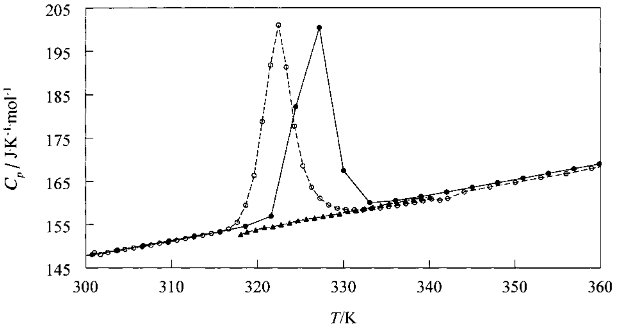

Figure 3. Solid−solid phase transition in *p*-diiodobenzene: (●) vacuum-sublimated material; (○) the same sample after slow crystallization; (▲) undercooled, immediately after cooling from the melt. The lines connecting the experimental points are drawn as a guide for the eye.

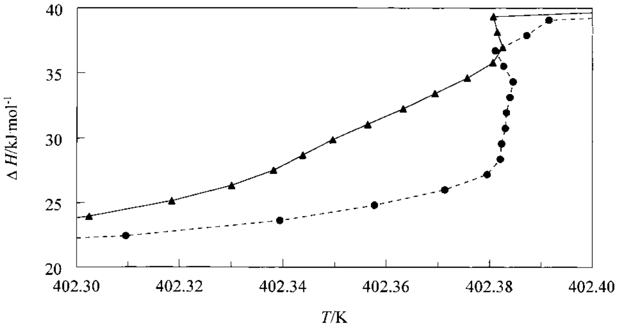

Figure 4. Relative enthalpy increment in the melt of *p*-diiodobenzene: (▲) vacuum-sublimated material; (●) the same sample after melting and annealing. The connecting lines are drawn as a guide for the eye.

trichlorobenzene, a similar effect was observed.[2] For *p*-dibromobenzene the stabilization periods were increased from 1500 s to 3600 s and 7200 s; in the last case the melting experiment took about 35 h. The enthalpy curve changed somewhat, but superheating still occurred. It does seem to be a remarkable coincidence that all these compounds do show a phase transition in the last part of the melting process. We do not have a better explanation at the moment. The melting curve of the sublimated sample is very different. It is probable that after extremely long stabilization the temperature in the melt would increase to the values of the second experiment. No exothermic effect was however observed. The cause of the different behavior may be a different distribution of the impurities or imperfect crystallization during the sublimation process.

Solid−Solid Phase Transition. A small solid−solid phase transition was found around 320 K. In the first measurement (on the vacuum-sublimated material) the maximum in the transition was found at 327 K. After the sample had been melted, this temperature shifted to 322 K. It was also possible to undercool the transition (series 3 in Table 4, given by the closed triangles in Figure 3). The different heat capacity curves are given in Figure 3. The lines connecting the experimental points are drawn as a guide to the eye. The enthalpy of transition was 218 and 226 J·mol^{-1}, respectively. We propose a value of (223 ± 10) J·mol^{-1}. It is not uncommon for small solid−solid phase transitions to occur at different temperatures depending on the way the crystals were prepared. A similar situation was found in *p*-dichlorobenzene.[11] In that case it was shown that the transition temperature was dependent on the crystal size.

Liquid Phase. Only a small number of measurements were made in the liquid phase. The heat capacity of the liquid, using five data points, can be represented between 403 K and 411 K by

$$C_{\mathrm{p,l}}(T) = \{135.51 + 0.1782(T/\mathrm{K})\}\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

The standard error of the fit is 0.25 J·K^{-1}·mol^{-1}, corresponding to 0.12% of the value at 410 K.

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