Low-Temperature Heat Capacities and Derived Thermodynamic Functions of 1,4-Dichlorobenzene, 1,4-Dibromobenzene, 1,3,5-Trichlorobenzene, and 1,3,5-Tribromobenzene

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The heat capacities of 1,4-dichlorobenzene, 1,4-dibromobenzene, and 1,3,5-trichlorobenzene from 5 K to 380 K and 1,3,5-tribromobenzene from 5 K to 410 K were measured by adiabatic calorimetry. The experimental data were used to calculate the molar entropy and enthalpy values relative to 0 K. Apart from 1,4-dichlorobenzene, the substances do not show any solid−solid transitions. Molar enthalpies of fusion and melting-point temperatures were determined. The results, given in order, are (17 907 ± 15) J·mol^{-1} and (326.24 ± 0.03) K, (20 387 ± 15) J·mol^{-1} and (360.48 ± 0.03) K, (17 557 ± 35) J·mol^{-1} and (335.92 ± 0.03) K, and (21 721 ± 20) J·mol^{-1} and (394.96 ± 0.07) K.

Introduction

In our ongoing research on molecular mixed crystals, the binary system (1,4-dichlorobenzene + 1,4-dibromobenzene) has become a key system. The end member 1,4-dichlorobenzene is known to occur in three different crystalline forms: γ, α, and β. The low-temperature γ form as well as the α form (stable at room temperature) are monoclinic: space group $P2_1/a$ with two molecules per primitive unit cell (Z).[1] The high-temperature β form is triclinic: $P\bar{1}$ with $Z = 1$.[2] At room temperature, solid 1,4-dibromobenzene is isomorphous with the α form of 1,4-dichlorobenzene: $P2_1/a$, $Z = 2$.[3] The Tx phase diagram of (1,4-dichlorobenzene + 1,4-dibromobenzene), which has a long history and was studied in particular by Campbell and Prodan in 1948,[4] is accurately known and shows a continuous series of mixed crystals at room temperature. Among other things, we have used this phase diagram to find experimental arguments supporting the equal G-curve concept[5,6] and to model the heat capacity versus temperature diagram of the melting process.[7] The latter model was subsequently used to establish the solid−liquid Tx phase diagram of the binary system (1,3,5-trichlorobenzene + 1,3,5-tribromobenzene).[7] The solid phases of the end members of this system are orthorhombic at room temperature: space group $P2_12_12_1$ with four molecules per primitive unit cell.[8,9]

For the determination and analysis of Tx phase diagrams, the thermodynamic properties (heat capacity and temperatures and enthalpies of transition) are of basic importance. In this paper, we report on the heat capacities, determined by adiabatic calorimetry, of the end members of the two binary systems: 1,4-dichlorobenzene, 1,4-dibromobenzene, 1,3,5-trichlorobenzene, and 1,3,5-tribromobenzene.

This work completes our study of the heat capacities and transition properties of the 1,4-disubstituted benzenes with the substituting groups Cl, Br, and I. The data for 1,4-chlorobromobenzene and 1,4-chloroiodobenzene have been published by van Miltenburg et al.[10] The thermodynamic properties of 1,4-bromoiodobenzene and 1,4-diiodobenzene can be found in another paper by the same authors.[11] In view of the level of detail—about the family of materials and the experimental procedures—of the two earlier publications[10,11] and given the fact that detailed information on this work is available in the form of van der Linde's thesis,[12] we prefer to confine ourselves to giving a rather concise account of the results.

This work was carried out in cooperation with our partners from the universities of Bordeaux (France) and Barcelona (Spain) in the scope of the REALM network (Réseau Européen sur les Alliages Moléculaires).

Experimental Section

All four substances were obtained from Aldrich Chemical Co. Inc. with a stated purity of 99 mass % for the chloro-substituted benzenes and 98 mass % for the bromo-substituted compounds. 1,4-Dichlorobenzene and 1,3,5-trichlorobenzene were purified by vacuum sublimation under continuous evacuation at approximately 1 Pa.

1,4-Dibromobenzene (light-brown color) was purified by crystallization from ethanol. The saturated solution was filtered and poured into a large excess of distilled water. The precipitate was isolated by filtration and dried in vacuum (1 Pa). Thereafter, the white substance was sublimated once.

1,3,5-Tribromobenzene (dark-brown color) was sublimated first. Thereafter, the yellow product was dissolved in refluxing ethanol. The saturated solution was then allowed to cool slowly to room temperature; small, white crystals (needles) precipitated. The suspension was centrifuged for 3 min at 2400 rpm. The substance was isolated and washed with a small amount of acetone. Finally, the product was dried in vacuum.

The purity of the substances was checked by means of differential scanning calorimetry using a Setaram DSC 111. Except for 1,3,5-tribromobenzene whose purity was estimated to be 99.9 mol %, the purities were estimated to be ≥99.95 mol %.

The adiabatic calorimeter used for the experiments is CAL V, the original construction of which was described by van Miltenburg et al.[13] Several design improvements,

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Table 1. Experimental Data Series for 1,4-Dichlorobenzene (R = 8.314472 J·K^{-1}·mol^{-1})

T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R
series 1		55.44	5.119	237.27	14.314	358.34	22.070	171.47	11.187
331.52	21.328	57.02	5.229	239.97	14.430	360.89	22.150	174.50	11.333
333.80	21.392	58.55	5.331	242.66	14.559	363.44	22.226	177.53	11.477
336.04	21.450	60.03	5.429	245.34	14.687	365.99	22.296	180.53	11.622
338.28	21.508	63.79	5.682	248.00	14.814	368.54	22.365	183.51	11.768
340.53	21.574	66.94	5.873	250.66	14.921	371.09	22.454	186.47	11.901
342.77	21.638	69.94	6.056	253.30	15.049	373.64	22.508	189.41	12.037
series 2		72.81	6.208	255.92	15.179	376.20	22.580	192.33	12.186
5.11	0.035	series 5		258.54	15.314	series 7		195.23	12.315
7.21	0.100	103.20	7.888	261.14	15.441	82.41	6.799	198.11	12.452
9.58	0.253	107.33	8.096	263.73	15.574	85.29	6.954	200.98	12.586
13.08	0.541	111.35	8.297	266.31	15.703	88.14	7.099	215.03	13.239
15.94	0.939	115.28	8.490	268.87	15.833	91.01	7.253	217.80	13.385
19.00	1.346	119.12	8.680	271.43	15.942	93.90	7.399	220.54	13.515
21.65	1.758	122.89	8.863	282.62	16.544	96.80	7.544	223.28	13.645
25.09	2.239	126.60	9.040	285.11	16.686	99.71	7.690	225.99	13.776
28.53	2.620	130.24	9.217	287.59	16.806	102.62	7.864	228.70	13.902
series 3		133.83	9.389	292.10	16.932	105.55	8.009	231.39	14.030
6.43	0.050	137.36	9.558	series 6		108.49	8.153	234.07	14.156
7.89	0.142	140.85	9.727	293.87	17.009	111.43	8.300	236.73	14.283
11.66	0.387	147.69	10.052	296.42	17.182	114.39	8.444	239.38	14.407
14.50	0.736	151.05	10.209	298.96	17.348	117.35	8.589	242.02	14.528
18.49	1.306	188.91	12.004	301.51	17.522	120.32	8.734	244.65	14.644
20.21	1.559	191.90	12.152	308.59	17.874	123.30	8.879	247.26	14.761
22.92	1.939	194.87	12.295	311.33	18.095	126.28	9.027	249.87	14.879
24.05	2.099	197.82	12.439	314.11	18.222	129.27	9.172	252.46	15.001
26.05	2.365	200.75	12.577	316.65	18.378	132.26	9.320	255.04	15.123
series 4		203.66	12.720	319.20	18.543	135.26	9.466	257.61	15.246
32.77	3.139	206.55	12.858	321.74	18.739	138.27	9.620	260.16	15.367
34.99	3.387	209.43	12.997	332.72	21.349	141.27	9.755	262.71	15.490
36.99	3.597	212.28	13.135	335.40	21.413	144.27	9.902	265.24	15.609
38.82	3.768	215.12	13.281	337.95	21.495	147.28	10.047	267.76	15.737
42.09	4.082	217.94	13.402	340.50	21.559	150.29	10.190	270.28	15.849
44.35	4.289	220.75	13.526	343.05	21.644	153.31	10.334	272.78	15.958
46.46	4.473	223.54	13.662	345.60	21.706	156.33	10.477	281.42	16.394
48.44	4.595	226.32	13.793	348.14	21.778	159.35	10.622	283.88	16.521
50.31	4.759	229.08	13.929	350.69	21.854	162.38	10.764	286.32	16.638
52.09	4.893	231.82	14.058	353.24	21.927	165.40	10.906		
53.80	5.010	234.55	14.187	355.79	22.022	168.43	11.047		

implemented a number of years ago,[14] resulted (among other things) in an extended temperature range (5 K to 420 K) instead of (5 K to 340 K) in the original construction. Below 30 K, the reproducibility of the calorimeter is about 1%, between 30 K and 100 K, 0.05 to 0.1%, and above 100 K, 0.03%. Checking the calorimeter with standard materials (*n*-heptane and synthetic sapphire) showed no deviation larger than 0.2% from the recommended values.[13,14]

For our measurements on 1,4-dichlorobenzene (M = 147.00 g·mol^{-1}), the calorimeter was loaded with 6.5816 g. Because both the α and the β forms can easily be supercooled,[15,16] the sample was (whenever necessary) pretreated by melting, followed by cooling to liquid-nitrogen temperature and controlled heating to 260 K. During the latter step, an exothermic effect was observed indicating relaxation to the γ form. (The heat effect was about as large as the α−γ transition enthalpy.) Heat capacity measurements were made between 5 K and 376 K. Each of the three transitions (γ to α, α to β, and β to liquid) were studied in at least two (separate) series, adapting the energy input, duration of stabilization, and input periods so as to get the best possible results for the temperatures and enthalpies of transition.

Before measurements at low temperatures were made on 1,4-dibromobenzene (M = 235.91 g·mol^{-1}), the sample (10.3975 g) was melted once in the calorimeter (CAL V). Heat capacity measurements were made in the temperature range of 5 K to 381 K. For the determination of the temperature and heat of fusion, three melting experiments were performed.

For 1,3,5-trichlorobenzene (M = 181.45 g·mol^{-1}), two independent data sets were measured: one set in the original CAL V[13] with sample mass 7.3147 g (temperature range 5 K to 340 K) and the other in the reconstructed and improved calorimeter[14] from room temperature to 380 K (sample mass 6.8572 g). The samples were melted once prior to the actual measurements. The temperature and heat of fusion were determined four times, twice in each set.

Before measurements were made between 7 K and 414 K, the sample of 1,3,5-tribromobenzene (7.0982 g) was allowed to anneal for several hours at 360 K.

Results and Discussion

The experimental data series are given in Tables 1 to 4. In these Tables, data collected during the annealing of the sample and data collected for the sole purpose of determining temperatures and enthalpies of transition are left out. Data in transition regions are given in Table 5. In this Table, the enthalpy increment was added because in transition regions the temperature change after a heat input can be very small or even negative.

For each substance, all experimental heat capacity data were combined, and molar heat capacities ($C^{\circ}_{p,m}$) in 1° intervals were calculated from the experimental data using

Table 2. Experimental Data Series for 1,4-Dibromobenzene (R = 8.314472 J·K^{-1}·mol^{-1})

T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R
series 1		series 5		86.22	7.927	172.58	11.955	284.87	16.875
362.85	22.962	10.07	0.614	89.08	8.084	175.60	12.087	287.90	17.013
363.89	22.998	13.60	1.159	91.90	8.226	178.62	12.219	290.93	17.209
366.91	23.082	15.57	1.600	94.65	8.359	181.65	12.351	293.96	17.276
369.93	23.158	17.46	1.928	97.35	8.490	184.69	12.483	296.99	17.414
372.94	23.239	19.73	2.346	100.00	8.624	187.72	12.617	300.02	17.557
374.79	23.281	22.16	2.733	102.59	8.776	190.75	12.750	303.03	17.689
series 2		24.70	3.106	105.15	8.898	193.79	12.880	306.05	17.825
5.27	0.121	27.15	3.432	series 7		196.83	13.013	309.07	17.961
6.45	0.163	29.32	3.704	89.28	8.115	199.86	13.139	312.09	18.097
7.46	0.278	31.27	3.933	92.15	8.259	202.90	13.263	series 8	
8.52	0.441	33.06	4.139	95.04	8.400	205.94	13.400	292.89	17.239
9.52	0.530	series 6		97.94	8.552	208.97	13.535	295.80	17.379
11.80	0.797	23.84	3.016	100.85	8.696	212.01	13.666	298.79	17.525
12.41	0.925	26.55	3.368	103.77	8.853	215.05	13.804	301.84	17.673
series 3		28.82	3.662	106.70	8.983	218.09	13.937	304.88	17.808
6.50	0.166	31.01	3.930	109.64	9.124	221.12	14.069	307.92	17.942
7.71	0.338	33.29	4.188	112.58	9.268	224.16	14.206	310.96	18.069
9.03	0.491	35.63	4.448	115.54	9.408	227.19	14.335	314.00	18.168
10.60	0.701	38.01	4.685	118.50	9.549	230.23	14.470	317.04	18.284
12.47	0.938	40.43	4.895	121.46	9.687	233.27	14.603	320.07	18.419
14.20	1.296	42.90	5.114	124.44	9.827	236.31	14.739	323.10	18.570
15.55	1.599	45.40	5.327	127.42	9.964	239.34	14.876	326.13	18.712
16.68	1.797	47.94	5.531	130.40	10.104	242.38	15.010	329.16	18.854
17.68	1.981	50.51	5.726	133.39	10.240	245.41	15.147	332.19	18.999
18.59	2.140	53.12	5.909	136.39	10.374	248.44	15.290	335.22	19.155
series 4		55.75	6.100	139.39	10.508	251.48	15.421	338.24	19.304
5.80	0.142	58.41	6.281	142.39	10.640	254.52	15.556	341.26	19.461
7.64	0.320	61.09	6.459	145.40	10.773	257.56	15.692	344.28	19.624
8.77	0.465	63.80	6.633	148.41	10.904	260.60	15.825	347.30	19.803
10.26	0.653	66.54	6.802	151.43	11.037	263.64	15.958	350.32	19.999
12.15	0.863	69.30	6.973	154.45	11.166	266.67	16.096	365.71	23.046
14.05	1.284	72.07	7.136	157.47	11.296	269.71	16.229	368.72	23.125
15.90	1.664	74.86	7.303	160.49	11.431	272.74	16.364	371.72	23.201
17.94	2.024	77.68	7.460	163.52	11.562	275.78	16.501	377.70	23.351
20.25	2.436	80.51	7.619	166.54	11.692	278.81	16.625	380.68	23.423
22.64	2.811	83.36	7.778	169.55	11.822	281.84	16.747		

a cubic spline interpolation method. To obtain a starting point for the derivation of the thermodynamic functions, heat capacity data between 5 K and 10 K were subjected to a least-squares fit in terms of the Debye low-temperature limit for the heat capacity:

$$\frac{C_p}{R} = \alpha T^3 \qquad (1)$$

in which R represents the gas constant (R = 8.314472 J·K^{-1}·mol^{-1}). The following values for the parameter α (expressed in K^{-3}) were found: $(25 \pm 4) \times 10^{-5}$ for 1,4-dichlorobenzene, $(47 \pm 6) \times 10^{-5}$ for 1,3,5-trichlorobenzene, and $(84 \pm 5) \times 10^{-5}$ for 1,3,5-tribromobenzene. The observed small discontinuity in the heat capacity of 1,4-dibromobenzene at about 8 K was not taken into account because the inaccuracy of the measurements at temperatures below 10 K for this compound α was found to be $(68 \pm 7) \times 10^{-5}$ K^{-3}. The relative large error margins in the calculated α values are probably caused by not following the Debye low-temperature limit between 5 K and 10 K for these compounds. The contribution of the errors in the calculated α values to the entropy and enthalpy functions is very small. For instance, the maximum error of 16% in α, found for 1,4-dichlorobenzene, contributes an error of 0.06% to the entropy value at 298.15 K.

The thermodynamic functions, entropy ($\Delta_0^T S_m^o$) and enthalpy ($\Delta_0^T H_m^o$) relative to 0 K, at selected temperatures were calculated by numerical integration. The outcome of the calculations is given in Tables 6 to 9.

1,4-Dichlorobenzene. Our experimental molar heat capacity data of 1,4-dichlorobenzene are given in Table 1 and are depicted in Figure 1. Among the publications on the heat capacity of 1,4-dichlorobenzene,[17−21] the work of Dworkin et al.,[20] by adiabatic calorimetry, must be regarded as the most significant. Dworkin et al. took full account of the existence of the different solid forms and the fact that the α and β forms can be supercooled easily.[15,16] However, their calorimeter did not allow mea-

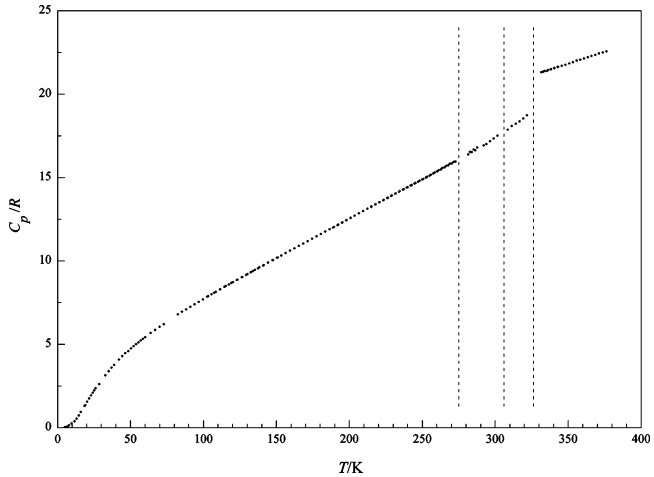

Figure 1. Experimental molar heat capacity of 1,4-dichlorobenzene. (See Table 1.) Dashed lines denote the transition temperatures.

Table 3. Experimental Data Series for 1,3,5-Trichlorobenzene (R = 8.314472 J·K^{-1}·mol^{-1})

T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R
series 1		205.42	14.662	93.56	8.697	37.93	4.318	236.69	16.204
6.76	0.136	207.87	14.784	95.84	8.810	39.58	4.486	239.60	16.341
8.49	0.332	210.30	14.900	98.08	8.954	41.88	4.706	242.50	16.481
9.57	0.399	212.71	15.021	100.29	9.082	44.77	4.984	245.38	16.622
10.48	0.515	215.12	15.146	102.47	9.226	47.40	5.222	248.24	16.759
11.23	0.562	217.51	15.251	104.61	9.319	49.84	5.441	251.09	16.894
series 2		219.88	15.367	106.72	9.449	52.12	5.645	253.93	17.030
6.30	0.088	222.25	15.481	108.81	9.571	54.28	5.826	256.76	17.168
7.61	0.197	224.60	15.594	110.87	9.693	56.33	5.997	259.57	17.294
8.27	0.296	226.94	15.709	114.92	9.927	58.29	6.160	262.36	17.430
series 3		229.27	15.827	116.91	10.048	60.17	6.313	265.15	17.564
7.50	0.226	231.58	15.940	118.88	10.163	61.98	6.456	267.91	17.704
9.54	0.394	236.18	16.162	120.83	10.285	63.73	6.595	270.67	17.821
10.78	0.549	238.46	16.277	124.68	10.497	65.43	6.722	273.41	17.943
11.76	0.610	240.73	16.391	126.58	10.588	67.08	6.854	276.13	18.086
14.33	1.029	242.99	16.498	128.47	10.695	68.68	6.974	278.84	18.211
16.47	1.417	245.24	16.605	130.33	10.808	70.25	7.091	281.54	18.314
18.11	1.689	247.48	16.712	132.19	10.911	71.78	7.201	series 12 (set 2)	
19.49	1.928	249.71	16.818	134.03	11.012	73.27	7.306	306.98	19.432
20.67	2.150	251.93	16.922	135.85	11.113	74.74	7.416	310.04	19.583
21.77	2.306	256.34	17.138	137.66	11.211	76.18	7.519	313.11	19.729
22.76	2.434	258.53	17.243	141.25	11.403	77.59	7.621	338.89	23.886
24.03	2.586	260.71	17.342	series 8		78.98	7.717	341.83	23.949
25.53	2.802	262.88	17.446	80.55	7.872	series 11		344.76	24.016
26.89	3.001	265.05	17.551	82.22	7.991	107.15	9.492	347.69	24.093
28.15	3.191	267.20	17.657	83.86	8.103	111.47	9.734	350.61	24.174
series 5		269.34	17.755	85.47	8.212	115.68	9.993	353.52	24.250
94.95	8.780	271.48	17.854	87.05	8.309	119.79	10.228	356.43	24.328
102.39	9.227	275.71	18.066	88.60	8.419	127.78	10.672	359.34	24.411
105.97	9.413	277.82	18.149	90.14	8.502	131.66	10.904	362.24	24.497
109.46	9.624	279.93	18.267	91.65	8.590	135.48	11.108	365.13	24.578
112.87	9.810	282.02	18.338	93.14	8.683	139.24	11.309	368.02	24.655
119.52	10.193	284.11	18.443	94.61	8.763	142.95	11.507	370.90	24.742
122.75	10.409	286.19	18.510	96.07	8.828	146.61	11.699	373.78	24.811
125.93	10.551	288.26	18.611	97.51	8.916	150.22	11.886	376.65	24.892
129.07	10.727	290.32	18.696	98.92	9.003	153.79	12.069	379.51	24.958
135.22	11.068	292.38	18.784	101.72	9.185	157.32	12.251	series 13 (set 2)	
138.23	11.236	294.42	18.883	103.09	9.246	160.81	12.429	311.61	19.646
141.21	11.396	296.46	18.957	104.45	9.324	164.27	12.608	314.66	19.819
144.16	11.551	300.52	19.154	105.80	9.403	167.69	12.782	317.72	19.988
147.08	11.707	series 6		107.13	9.489	171.08	12.955	320.77	20.145
149.97	11.862	295.88	18.933	108.46	9.561	174.44	13.122	323.83	20.344
152.83	12.012	298.44	19.045	109.77	9.643	177.76	13.293	326.88	20.591
155.66	12.160	300.98	19.181	111.07	9.711	181.06	13.461	341.91	23.967
158.47	12.304	303.51	19.277	112.36	9.783	184.34	13.624	344.94	24.041
161.25	12.447	306.03	19.393	113.65	9.860	187.58	13.787	347.97	24.127
164.01	12.589	308.54	19.512	114.92	9.943	190.81	13.949	350.99	24.194
166.74	12.728	311.04	19.643	116.19	10.008	194.01	14.108	354.00	24.280
169.46	12.867	313.53	19.763	series 9		197.19	14.264	357.01	24.370
172.15	13.003	316.00	19.903	12.18	0.682	200.35	14.426	360.01	24.444
174.82	13.137	318.47	20.048	13.16	0.891	203.48	14.584	363.01	24.517
177.47	13.272	320.93	20.175	14.68	1.094	206.60	14.732	366.00	24.610
180.10	13.404	323.38	20.319	16.54	1.426	209.70	14.884	368.98	24.716
182.71	13.533	325.82	20.483	18.46	1.745	212.77	15.039	371.95	24.776
185.30	13.663	328.25	20.632	20.47	2.091	215.83	15.180	374.93	24.858
187.87	13.791	series 7		series 10		218.86	15.331	377.90	24.939
190.43	13.925	81.45	7.930	26.99	3.017	221.88	15.479	380.86	25.012
192.97	14.050	83.98	8.105	29.75	3.407	224.87	15.622		
195.49	14.172	86.45	8.271	32.12	3.688	227.85	15.769		
198.00	14.296	88.86	8.431	34.24	3.936	230.81	15.915		
202.96	14.543	91.23	8.560	36.16	4.115	233.76	16.054		

surements above 330 K (about 4 K above the temperature of fusion of 1,4-dichlorobenzene). Hence, our main reason for repeating Dworkin's measurements was to extend the number of heat capacity data for the liquid state.

The heat capacity data by Dworkin et al. are systematically higher than ours: 1.2% on average for the γ form and 2.8% on average for the α and β forms (Figure 2). Apart from the deviations in the heat capacity of the liquid phase (probably caused by a lack of thermal equilibrium during Dworkin's measurements), a reasonable explanation for the differences cannot be given. The recent heat capacity data by Roháč et al.,[21] who used a heat conduction calorimeter, are also systematically higher than ours: for (probably) the α phase, their results are about 1% higher, whereas their data for the liquid are 0.6% higher on average (Figure 2).

1,4-Dibromobenzene. When compared with the results of earlier studies,[17−19] our heat capacity data are quite different. There is reasonable agreement between our data

Table 4. Experimental Data Series for 1,3,5-Tribromobenzene (R = 8.314472 J·K^{-1}·mol^{-1})

T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R
series 1		series 5		89.49	9.750	190.00	14.772	315.12	20.098
7.15	0.308	7.61	0.377	92.36	9.893	193.05	14.903	series 8	
9.98	0.809	10.76	0.911	95.25	10.048	196.11	15.043	306.85	19.761
12.40	1.199	13.52	1.438	98.15	10.224	199.17	15.174	310.25	19.896
14.41	1.722	15.97	2.064	101.04	10.400	202.22	15.294	313.63	20.028
series 2		18.13	2.532	series 7		205.28	15.432	317.00	20.166
6.52	0.207	20.32	2.939	84.19	9.386	208.34	15.563	320.37	20.339
7.91	0.470	22.85	3.374	87.47	9.592	211.40	15.707	323.72	20.424
9.26	0.673	25.43	3.789	90.65	9.791	214.46	15.851	327.06	20.548
11.09	0.978	28.08	4.178	93.74	9.972	217.52	15.970	330.40	20.743
13.02	1.337	30.83	4.547	96.75	10.132	220.58	16.105	333.72	20.861
14.86	1.851	33.45	4.879	99.69	10.301	223.64	16.240	337.03	20.999
16.42	2.191	35.86	5.140	102.61	10.519	226.70	16.375	340.34	21.136
17.75	2.433	series 6		105.54	10.698	229.77	16.508	343.63	21.254
18.91	2.695	21.28	3.125	108.48	10.851	232.83	16.635	346.92	21.430
19.96	2.900	23.50	3.489	111.43	11.006	235.89	16.775	350.20	21.524
20.91	3.069	25.52	3.804	114.39	11.162	238.95	16.913	353.46	21.698
series 3		27.61	4.122	117.36	11.324	242.01	17.048	356.72	21.769
6.95	0.263	29.80	4.409	120.34	11.484	245.07	17.183	359.97	21.949
8.43	0.547	32.02	4.718	123.32	11.636	248.12	17.317	363.22	22.075
9.48	0.729	34.29	4.990	126.31	11.791	251.17	17.451	366.45	22.252
11.43	1.033	36.60	5.242	129.31	11.948	254.22	17.583	369.68	22.319
13.44	1.427	38.95	5.511	132.31	12.100	257.27	17.717	372.90	22.476
15.24	1.943	41.31	5.795	135.32	12.252	260.32	17.849	376.11	22.605
16.81	2.263	43.74	6.056	138.33	12.398	263.36	17.983	379.31	22.759
18.13	2.531	46.20	6.318	141.34	12.547	266.41	18.117	series 9	
19.30	2.747	48.69	6.589	144.36	12.694	269.46	18.259	357.65	21.814
20.36	3.009	51.22	6.806	147.39	12.850	272.51	18.393	360.90	21.964
21.33	3.133	53.78	7.064	150.41	12.976	275.56	18.517	364.15	22.106
22.22	3.292	56.38	7.285	153.44	13.122	278.61	18.653	367.38	22.251
series 4		59.00	7.505	156.48	13.260	281.65	18.754	370.61	22.379
6.88	0.259	61.66	7.728	159.51	13.389	284.69	18.892	373.83	22.509
8.64	0.580	64.34	7.950	162.55	13.529	287.74	19.023	377.04	22.647
10.55	0.890	67.06	8.175	165.60	13.667	290.78	19.140	380.25	22.799
12.20	1.150	69.79	8.389	168.64	13.806	293.81	19.244	399.00	26.715
14.28	1.674	72.55	8.587	171.69	13.947	296.86	19.378	401.94	26.804
16.24	2.138	75.33	8.794	174.73	14.087	299.91	19.518	404.87	26.920
18.35	2.560	78.14	8.985	177.78	14.228	302.95	19.615	407.79	26.980
20.69	3.032	80.95	9.171	180.84	14.359	306.00	19.729	410.72	27.166
23.13	3.447	83.79	9.378	183.89	14.497	309.04	19.848	413.63	27.219
25.66	3.841	86.63	9.572	186.94	14.639	312.08	19.971		

and those by Andrews and Haworth[18] at low temperature (about 100 K). However, Andrews and Haworth's high-temperature C_p data are much higher. (They used a continuous heating method based on the calibrated heat conduction of the equipment.) Narbutt's data[17]—drop calorimetry between 125 K and 350 K—agree well with our result at about 280 K, but the average slope, dC_p/dT, is only 50% of our value (0.37 J·K^{-2}·mol^{-1}).

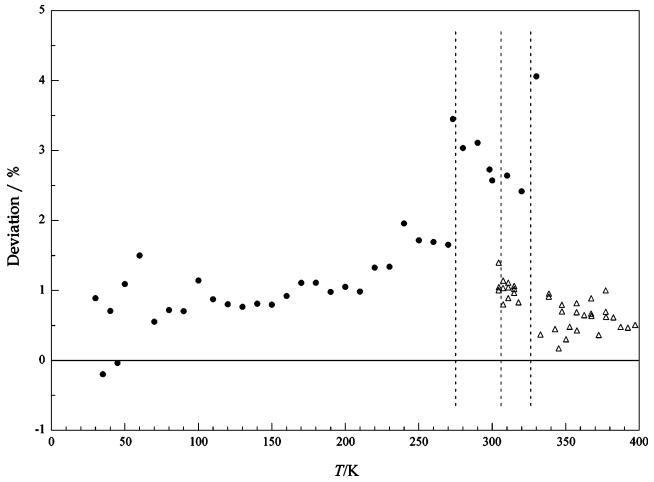

Figure 2. Percentage deviations of the molar heat capacity data of 1,4-dichlorobenzene presented by Dworkin et al.[20] and Roháč et al.[21] with respect to our values. (See Tables 1 and 6.). ●, Dworkin et al.; △, Roháč et al. Dashed lines denote the transition temperatures.

1,3,5-Trichlorobenzene. The data from the two sets were compared and found to be mutually consistent within 0.2%; for further processing, the data were combined. No solid−solid phase transitions were observed. In the literature, the only report on the heat capacity of 1,3,5-trichlorobenzene is by Roháč et al.[21] Their C_p data are in good agreement with, but again systematically higher than, our data. The average difference is 0.5% for the heat capacity of the solid and 1% for the heat capacity of the liquid phase.

1,3,5-Tribromobenzene. Although there was no indication of a solid−solid phase transition, a small anomaly was observed between 90 K and 105 K. The effect (Figure 3) is not related to an enthalpic relaxation (as was observed for metastable 1,4-dichlorobenzene). If so, it could not have been observed in two successive series, the second of which (denoted by the triangles in Figure 3) was measured after cooling from 105 K back to 77 K. In our view, it is a thermal property of the substance. Previous reports on the substance's heat capacity could not be traced.

Phase Transitions. A survey of the temperatures and enthalpies of transition derived from the heat capacity measurements is given in Table 10.

Table 5. Experimental Data in Transition Regions (Mean Temperature, T; Heat Capacity, C_p; Enthalpy Increment, ΔH) for 1,4-Dichlorobenzene, 1,4-Dibromobenzene, 1,3,5-Trichlorobenzene, and 1,3,5-Tribromobenzene (R = 8.314472 J·K^{-1}·mol^{-1})

T / K	C_p/R	$\Delta H/R$·K	T / K	C_p/R	$\Delta H/R$·K	T / K	C_p/R	$\Delta H/R$·K	T / K	C_p/R	$\Delta H/R$·K
1,4-dichlorobenzene (series 5); $\gamma \rightarrow \alpha$ input time: 800 s; stabilization time: 1250 s											
266.31	15.703	0	273.97	15.981	122	277.62	16.393	326	285.11	16.686	450
268.87	15.833	40	275.08	−304.12	192	280.13	16.602	368	287.59	16.806	492
271.43	15.942	81	275.64	43.637	274	282.62	16.544	409			
1,4-dichlorobenzene (series 6); $\alpha \rightarrow \beta$, $\beta \rightarrow$ liquid input time: 900 s; stabilization time: 1500 s											
296.42	17.182	0	319.20	18.543	431	326.24	188 451	1336	326.24	95 614	2368
298.96	17.348	44	321.74	18.739	479	326.24	230 251	1465	326.24	−1 064 551	2497
301.51	17.522	89	324.26	19.373	527	326.24	166 140	1594	326.24	16 452	2626
304.06	17.564	134	325.86	135.79	598	326.24	827 558	1723	327.37	32.730	2727
306.34	28.453	185	326.21	5612.6	701	326.24	269 177	1852	329.91	21.245	2794
308.59	17.874	236	326.22	15 747	821	326.24	−10 925 735	1981	332.72	21.349	2854
311.33	18.095	286	326.23	18 743	950	326.24	−81 213	2110	335.40	21.413	2912
314.11	18.222	337	326.24	41 661	1079	326.24	−40 155	2239	337.95	21.495	2967
316.65	18.378	384	326.24	91 038	1207						
1,4-dichlorobenzene (series 7); $\gamma \rightarrow \alpha$ input time: 800 s; stabilization time: 1250 s											
267.76	15.737	0	274.91	32.840	129	278.97	16.591	327	283.88	16.521	409
270.28	15.849	40	275.58	−276.77	212	281.42	16.394	368	286.32	16.638	449
272.78	15.958	80	276.57	16.921	287						
1,4-dibromobenzene (series 8); solid → liquid input time: 900 s; stabilization time: 1500 s											
344.28	19.624	0	360.42	3795.8	562	360.48	78 581	1578	360.47	−91 904	2595
347.30	19.803	60	360.45	10 739	706	360.48	101 678	1723	360.83	177.29	2732
350.32	19.999	120	360.46	24 163	851	360.48	81 042	1868	362.70	22.951	2830
353.33	20.264	181	360.46	37 007	997	360.48	1 917 038	2014	365.71	23.046	2900
356.33	20.864	243	360.47	42 762	1142	360.48	367 990	2159	368.72	23.125	2969
359.00	33.911	315	360.47	38 706	1287	360.48	−59 284	2304	371.72	23.201	3039
360.29	581.09	422	360.48	54 414	1432	360.48	−35 702	2450			
1,3,5-trichlorobenzene (series 12); solid → liquid input time: 900 s; stabilization time: 1500 s											
306.98	19.432	0	328.38	20.497	430	335.89	68 416	1293	335.90	−262 893	2386
310.04	19.583	60	331.44	20.712	493	335.89	87 344	1449	335.90	−215 994	2542
313.11	19.729	121	334.35	26.028	561	335.89	99 801	1605	336.66	73.415	2676
316.16	19.871	182	335.80	1119.2	672	335.89	86 477	1761	338.89	23.886	2767
319.22	20.030	243	335.87	16 424	825	335.90	60 277	1917	341.83	23.949	2838
322.27	20.180	305	335.88	29 661	981	335.90	315 429	2073	344.76	24.016	2909
325.32	20.336	367	335.88	40 471	1137	335.90	401 386	2230			
1,3,5-trichlorobenzene (series 13); solid → liquid input time: 900 s; stabilization time: 1500 s											
320.77	20.145	0	335.80	1080.8	481	335.90	124 449	1447	336.62	81.776	2394
323.83	20.344	62	335.88	10 642	640	335.90	98 780	1608	338.87	23.900	2490
326.88	20.591	125	335.89	27 973	801	335.90	214 391	1769	341.91	23.967	2564
329.92	21.016	189	335.89	85 947	962	335.90	524 112	1931	344.94	24.041	2637
332.90	23.081	255	335.89	101 498	1124	335.90	−70 438	2092	347.97	24.127	2710
335.05	84.098	346	335.90	109 354	1285	335.90	−154 259	2254			
1,3,5-tribromobenzene (series 9); solid → liquid input time: 900 s; stabilization time: 1500 s											
373.83	22.509	0	388.29	24.547	333	394.80	4904.0	1249	394.98	13163	2792
377.04	22.647	73	391.19	28.177	405	394.85	8291.2	1556	396.26	42.905	3102
380.25	22.799	147	393.48	101.68	486	394.89	9165.8	1865	399.00	26.715	3211
382.37	23.240	194	394.49	947.00	660	394.92	9469.5	2174	401.94	26.804	3289
385.34	23.623	263	394.70	2274.2	948	394.95	11043	2483	404.87	26.920	3368

For 1,4-dichlorobenzene, the systematic deviation between our C_p data and those by Dworkin et al.,[20] as discussed earlier, is also reflected by the transition enthalpies from γ to α (1.5%), α to β (18%), and β to liquid (1.5%). As for the $\gamma-\alpha$ and $\alpha-\beta$ transition temperatures, the data obtained by Dworkin et al. (271.77 K and 304.35 K, respectively) are significantly lower than ours (275 K and 306 K). It is known that both solid−solid phase transitions are rather sluggish[16,22−24]—largely controlled by kinetic factors, crystal size, and crystal imperfections[25]—and, as a result, are easily superheated. In fact, in both of our measuring series in which the $\gamma-\alpha$ transition was studied, slight superheating was observed; for the $\alpha-\beta$ transition, no superheating could be observed at all because in both series the transition was passed in just two heating periods. Taking everything into account, we have the impression that Dworkin's transition temperatures, compared to ours, are closer to the thermodynamically correct ones. In this context, van Miltenburg and van den Berg have described a noteworthy experiment.[26] They studied the $\alpha-\beta$ transition in a differential scanning calorimeter specifically designed for small heat effects. A typical result on a slightly

Table 6. Thermodynamic Properties at Selected Temperatures for 1,4-Dichlorobenzene (M = 147.00 g·mol^{-1}; R = 8.314472 J·K^{-1}·mol^{-1}; $\Phi_m^o = \Delta_0^T S_m^o - \Delta_0^T H_m^o/T$)

T	$C_{p,m}^o$	$\Delta_0^T H_m^o$	$\Delta_0^T S_m^o$	Φ_m^o	T	$C_{p,m}^o$	$\Delta_0^T H_m^o$	$\Delta_0^T S_m^o$	Φ_m^o	T	$C_{p,m}^o$	$\Delta_0^T H_m^o$	$\Delta_0^T S_m^o$	Φ_m^o
K	R	R·K	R	R	K	R	R·K	R	R	K	R	R·K	R	R
10	0.280	0.63	0.084	0.021	150	10.178	872	11.264	5.454	290	16.812	2909	20.459	10.429
15	0.806	3.1	0.279	0.071	160	10.653	976	11.936	5.838	298.15	17.293	3048	20.931	10.710
20	1.526	9	0.608	0.162	170	11.119	1085	12.596	6.216	300	17.415	3080	21.039	10.773
25	2.227	18	1.024	0.292	180	11.596	1198	13.245	6.588	306[b]	17.770	3185	21.338	10.977
30	2.799	31	1.481	0.452	190	12.067	1316	13.885	6.956	306[c]	17.784	3207	21.459	10.977
40	3.881	65	2.444	0.829	200	12.542	1440	14.516	7.318	310	17.975	3279	21.691	11.115
50	4.734	108	3.406	1.248	210	13.024	1567	15.139	7.676	320	18.608	3461	22.271	11.454
60	5.428	159	4.332	1.686	220	13.489	1700	15.756	8.029	326.24[c]	19.003	3579	22.634	11.665
70	6.059	216	5.217	2.128	230	13.971	1837	16.366	8.378	326.24[d]	21.166	5733	29.236	11.665
80	6.656	280	6.064	2.567	240	14.431	1979	16.971	8.724	330	21.272	5812	29.480	11.866
90	7.199	349	6.880	3.001	250	14.886	2126	17.569	9.065	340	21.556	6026	30.119	12.394
100	7.705	424	7.665	3.429	260	15.361	2277	18.162	9.404	350	21.840	6243	30.748	12.909
110	8.229	503	8.425	3.848	270	15.834	2433	18.751	9.739	360	22.124	6463	31.367	13.413
120	8.719	588	9.162	4.261	275.0[a]	16.070	2513	19.044	9.906	370	22.407	6686	31.977	13.907
130	9.206	678	9.879	4.665	275.0[b]	16.171	2662	19.585	9.906	380	22.691	6911	32.578	14.390
140	9.689	772	10.579	5.063	280	16.350	2743	19.878	10.081					

[a] γ form. [b] α form. [c] β form. [d] Liquid phase.

Table 7. Thermodynamic Properties at Selected Temperatures for 1,4-Dibromobenzene (M = 235.91 g·mol^{-1}; R = 8.314472 J·K^{-1}·mol^{-1}; $\Phi_m^o = \Delta_0^T S_m^o - \Delta_0^T H_m^o/T$)

T	$C_{p,m}^o$	$\Delta_0^T H_m^o$	$\Delta_0^T S_m^o$	Φ_m^o	T	$C_{p,m}^o$	$\Delta_0^T H_m^o$	$\Delta_0^T S_m^o$	Φ_m^o	T	$C_{p,m}^o$	$\Delta_0^T H_m^o$	$\Delta_0^T S_m^o$	Φ_m^o
K	R	R·K	R	R	K	R	R·K	R	R	K	R	R·K	R	R
10	0.603	1.72	0.229	0.057	140	10.535	892	12.973	6.604	280	16.673	2795	22.152	12.170
15	1.483	6.6	0.614	0.173	150	10.975	999	13.715	7.053	290	17.107	2964	22.745	12.525
20	2.394	16	1.167	0.350	160	11.409	1111	14.437	7.492	298.15	17.480	3105	23.224	12.811
25	3.147	30	1.786	0.575	170	11.842	1227	15.141	7.922	300	17.556	3137	23.333	12.875
30	3.794	48	2.419	0.829	180	12.279	1348	15.831	8.342	310	18.016	3315	23.916	13.222
40	4.857	91	3.665	1.383	190	12.717	1473	16.506	8.754	320	18.416	3497	24.494	13.565
50	5.689	144	4.841	1.959	200	13.145	1602	17.169	9.158	330	18.894	3684	25.068	13.905
60	6.387	205	5.940	2.532	210	13.580	1736	17.821	9.555	340	19.396	3875	25.640	14.242
70	7.016	272	6.973	3.093	220	14.020	1874	18.463	9.946	350	19.971	4072	26.210	14.576
80	7.590	345	7.948	3.639	230	14.459	2016	19.096	10.330	360	20.618	4275	26.781	14.907
90	8.158	423	8.873	4.170	240	14.906	2163	19.721	10.708	360.48[a]	20.651	4285	26.809	14.923
100	8.624	507	9.757	4.685	250	15.357	2314	20.338	11.081	360.48[b]	22.898	6737	33.611	14.923
110	9.141	596	10.604	5.185	260	15.799	2470	20.949	11.449	370	23.161	6956	34.211	15.411
120	9.619	690	11.420	5.671	270	16.242	2630	21.554	11.812	380	23.406	7189	34.832	15.914
130	10.085	789	12.209	6.143										

[a] Solid. [b] Liquid.

Table 8. Thermodynamic Properties at Selected Temperatures for 1,3,5-Trichlorobenzene (M = 181.45 g·mol^{-1}; R = 8.314472 J·K^{-1}·mol^{-1}; $\Phi_m^o = \Delta_0^T S_m^o - \Delta_0^T H_m^o/T$)

T	$C_{p,m}^o$	$\Delta_0^T H_m^o$	$\Delta_0^T S_m^o$	Φ_m^o	T	$C_{p,m}^o$	$\Delta_0^T H_m^o$	$\Delta_0^T S_m^o$	Φ_m^o	T	$C_{p,m}^o$	$\Delta_0^T H_m^o$	$\Delta_0^T S_m^o$	Φ_m^o
K	R	R·K	R	R	K	R	R·K	R	R	K	R	R·K	R	R
10	0.455	1.17	0.156	0.039	140	11.345	909	12.652	6.160	280	18.270	2990	22.679	12.002
15	1.152	5.0	0.459	0.124	150	11.865	1025	13.452	6.620	290	18.683	3174	23.327	12.381
20	2.013	13	0.910	0.262	160	12.387	1146	14.234	7.072	298.15	19.042	3328	23.850	12.688
25	2.725	25	1.440	0.444	170	12.896	1272	15.000	7.515	300	19.126	3363	23.968	12.757
30	3.437	40	2.001	0.656	180	13.399	1404	15.752	7.952	310	19.582	3557	24.602	13.129
40	4.527	80	3.144	1.136	190	13.900	1540	16.490	8.382	320	20.123	3755	25.232	13.497
50	5.455	130	4.256	1.649	200	14.407	1682	17.216	8.806	330	20.741	3960	25.861	13.862
60	6.299	189	5.326	2.174	210	14.894	1828	17.930	9.223	335.92[a]	21.141	4083	26.233	14.077
70	7.073	256	6.356	2.698	220	15.373	1980	18.634	9.635	335.92[b]	23.799	6195	32.519	14.077
80	7.819	330	7.348	3.218	230	15.870	2136	19.328	10.042	340	23.905	6292	32.807	14.300
90	8.494	412	8.310	3.730	240	16.359	2297	20.014	10.443	350	24.168	6533	33.504	14.839
100	9.065	500	9.234	4.235	250	16.833	2463	20.692	10.839	360	24.437	6776	34.189	15.367
110	9.655	594	10.126	4.730	260	17.313	2634	21.361	11.231	370	24.711	7022	34.862	15.885
120	10.241	693	10.990	5.216	270	17.788	2809	22.024	11.619	380	24.991	7270	35.525	16.393
130	10.786	798	11.832	5.693										

[a] Solid. [b] Liquid.

powdered sample showed four sharp peaks, of about the same height, between 307.5 K and 313.5 K, the heating rate being 0.1 K·min^{-1}. A sample consisting of just one piece of material that was prepared by slow solidification from the melt showed one sharp peak at 309.2 K. These results also point to the sluggishness of the transition.

Neither fractional melting experiment on 1,4-dichlorobenzene could be used to calculate the purity of the sample

Table 9. Thermodynamic Properties at Selected Temperatures for 1,3,5-Tribromobenzene (M = 314.80 g·mol^{-1}; R = 8.314472 J·K^{-1}·mol^{-1}; $\Phi_m^o = \Delta_0^T S_m^o - \Delta_0^T H_m^o/T$)

T	$C_{p,m}^o$	$\Delta_0^T H_m^o$	$\Delta_0^T S_m^o$	Φ_m^o	T	$C_{p,m}^o$	$\Delta_0^T H_m^o$	$\Delta_0^T S_m^o$	Φ_m^o	T	$C_{p,m}^o$	$\Delta_0^T H_m^o$	$\Delta_0^T S_m^o$	Φ_m^o
K	R	R·K	R	R	K	R	R·K	R	R	K	R	R·K	R	R
10	0.812	2.11	0.282	0.070	150	12.958	1189	16.356	8.426	298.15	19.432	3597	27.265	15.201
15	1.887	8.5	0.783	0.218	160	13.412	1321	17.207	8.949	300	19.522	3633	27.386	15.276
20	2.906	20	1.465	0.443	170	13.869	1458	18.034	9.459	310	19.887	3830	28.032	15.677
25	3.720	37	2.204	0.721	180	14.323	1599	18.840	9.958	320	20.324	4031	28.670	16.073
30	4.436	58	2.949	1.030	190	14.772	1744	19.626	10.446	330	20.726	4236	29.301	16.465
40	5.638	108	4.395	1.692	200	15.208	1894	20.395	10.924	340	21.122	4445	29.925	16.851
50	6.701	170	5.772	2.372	210	15.641	2048	21.147	11.393	350	21.531	4658	30.543	17.234
60	7.589	242	7.074	3.048	220	16.080	2207	21.885	11.853	360	21.950	4876	31.155	17.612
70	8.405	322	8.306	3.712	230	16.518	2370	22.610	12.305	370	22.353	5097	31.762	17.986
80	9.108	409	9.475	4.360	240	16.959	2537	23.322	12.750	380	22.775	5323	32.364	18.357
90	9.768	504	10.588	4.991	250	17.400	2709	24.023	13.187	390	23.196	5553	32.961	18.723
100	10.323	604	11.645	5.604	260	17.836	2885	24.714	13.617	394.96[a]	23.405	5668	33.255	18.904
110	10.931	711	12.660	6.199	270	18.283	3066	25.396	14.040	394.96[b]	26.561	8281	39.870	18.904
120	11.466	823	13.634	6.778	280	18.699	3251	26.068	14.458	400	26.741	8415	40.208	19.170
130	11.983	940	14.572	7.342	290	19.111	3440	26.731	14.870	410	27.099	8684	40.872	19.692
140	12.481	1062	15.478	7.891										

[a] Solid. [b] Liquid.

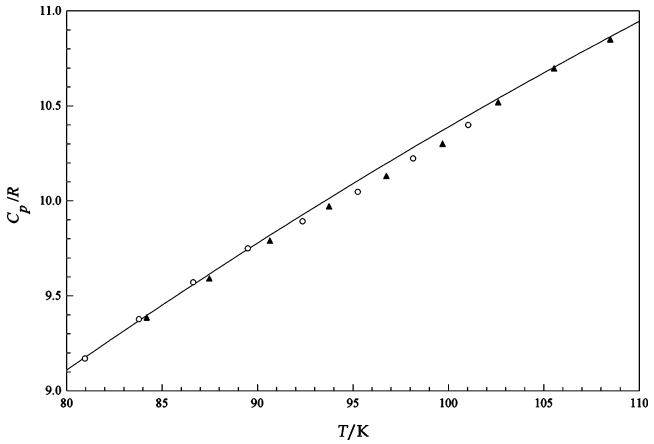

Figure 3. Molar heat capacity of 1,3,5-tribromobenzene between 80 K and 110 K: ○, series 6 (Table 4); ▲, series 7 (Table 4). The solid line represents a fit through the points outside the region of the anomaly in the heat capacity between 90 K and 105 K.

Table 10. Temperatures and Enthalpies of Transition

substance	transition	T/K	ΔH_m^o/J·mol^{-1}
1,4-dichlorobenzene	$\gamma \rightarrow \alpha$	275.0 ± 0.2	1238 ± 7
	$\alpha \rightarrow \beta$	306 ± 1	181 ± 6
	$\beta \rightarrow$ liquid	326.24 ± 0.03	17 907 ± 15
1,4-dibromobenzene	solid → liquid	360.48 ± 0.03	20 387 ± 15
1,3,5-trichlorobenzene	solid → liquid	335.92 ± 0.03	17 557 ± 35
1,3,5-tribromobenzene	solid → liquid	394.96 ± 0.07	21 721 ± 20

because of superheating near the end of the fusion process. The same effect was observed for 1,4-dibromobenzene, 1,3,5-trichlorobenzene, and 1,4-diiodobenzene;[10] see also the discussions by van Miltenburg et al.[10] and van der Linde.[12]

During our measurements on 1,4-dibromobenzene, and in accordance with most of the other reports on the thermal properties of the substance, we did not find any evidence for the solid−solid phase transition at 281.6 K as reported by Beck and Ebbinghaus[27] and Deffet.[28] Also, for 1,3,5-trichlorobenzene and 1,3,5-tribromobenzene we did not find any indication of solid−solid phase transitions. In contrast to that the other substances, the purity level of 1,3,5-tribromobenzene could be determined. The eutectic model was used; the purity, calculated from a linear fit of the equilibrium temperatures during melting as a function of the reciprocal of the melted fraction,[11] is 99.93 mol %, which is in good agreement with the value found by DSC.

As for the temperatures and enthalpies of fusion of the four substances, a comparison was made with literature values.[6,16,18−20,22,27,29,30] Apart from the work by Dworkin et al.[20] on 1,4-dichlorobenzene, this comparison turned out not to be very significant because most of the data were measured with less-sensitive techniques and/or no experimental errors were given; we refer to the thesis by van der Linde[12] for further details.

Supporting Information Available:

The experimental heat capacities and the relative enthalpy values at the mean temperature of the measuring intervals for the transition regions of the four compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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