

Thermodynamic Properties of Fluorine Compounds. Part VII.¹ Heat Capacity and Entropy of Pentafluorochlorobenzene and Pentafluorophenol

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The heat capacities of pure samples of pentafluorochlorobenzene and pentafluorophenol have been measured in the condensed states over the temperature range 12–394°K. The heat of vaporization of pentafluorochlorobenzene in the pressure range $\frac{1}{4}$ –1 atm. and the vapour heat capacity between 383 and 498°K have been determined. Both compounds undergo thermal transitions in the crystalline state. Heats of transition and melting were measured, and thermodynamic properties of crystals and liquid were computed. The entropies at 298·15°K of C₆F₅Cl (l) and C₆F₅OH (c) were found to be 300·7 and 227·1 J deg.⁻¹ mole⁻¹ respectively. Possible molecular changes associated with the thermal transitions in the solid are discussed. A value of 407·6 J deg.⁻¹ mole⁻¹ was found for the entropy of C₆F₅Cl in the ideal-gas state (at 298·15°K and 1 atm. pressure).

MEASUREMENT of heat capacity and entropy of hexafluorobenzene were reported in Part II,² and of pentafluorobenzene in Part VI.¹ The heat capacities of pentafluorochlorobenzene (crystal, liquid, and vapour) and pentafluorophenol (crystal and liquid) have now been measured. Both compounds exhibit transitions in the crystal: pentafluorophenol was found to have a single transition in the temperature range 286–291°K but the thermal transformations of pentafluorochlorobenzene were more complex. Heats of transition and fusion for both compounds, and heats of vaporization for pentafluorochlorobenzene were determined, and thermodynamic properties were calculated for the experimental data.

EXPERIMENTAL

Materials.—Samples of C₆F₅Cl and C₆F₅OH, kindly provided by Imperial Smelting Corporation, were purified by fractional crystallization and zone-melting. The purities of the resulting specimens were determined calorimetrically.

Measurements.—For the measurements on the crystals and liquids, about 0·36 mole of the compound was transferred by vacuum-distillation into a platinum sample container. Before sealing the container, helium (3 cm. Hg pressure) was introduced to promote thermal equilibration. Heat capacities and heats of transition and fusion were

measured by methods described elsewhere.^{3,4} The heat of vaporization and vapour heat capacity of pentafluorochlorobenzene were determined in a vapour-flow calorimeter.⁵

The following values were used: 0°C = 273·15°K; 1 cal. = 4·1840 J; $R = 8·3143$ J deg.⁻¹ mole⁻¹; molecular weight of C₆F₅Cl (202·5119) and C₆F₅OH (184·0663) from 1961 International Table of Atomic Weights.

RESULTS

Phases Changes and Purities of Samples.—Heats of fusion, triple-point temperatures, and purities of the samples were determined in a series of experiments in which melting temperatures were measured as a function of the fraction of sample melted. The results are in Table 1, columns 2–5. The last three columns of Table 1 give experimental values for the transitions in the crystals, which are discussed below.

Heat Capacities of Crystals and Liquids.—Chebyshev polynomials in temperature were fitted to the measured molar heat capacities (Table 2), excluding values in the transition temperature range.⁶ The standard deviation of any experimental point from the calculated curves was $\pm 0·1\%$ above 50°K and $\pm 0·4\%$ below 50°K. The heat-capacity curves were extrapolated from the lowest temperature of the measurements to 0°K by fitting Debye functions to the experimental values below 20°K.⁶ Tables

¹ Part VI, J. F. Counsell, J. L. Hales, and J. F. Martin, *J. Chem. Soc. (A)*, 1968, 2042.

² J. F. Counsell, J. H. S. Green, J. L. Hales, and J. F. Martin, *Trans. Faraday Soc.*, 1965, **61**, 212.

³ J. F. Martin, *Proc. Brit. Ceram. Soc.*, 1967, No. 8, 1.

⁴ R. J. L. Andon, J. F. Counsell, E. B. Lees, J. F. Martin, and C. J. Mash, *Trans. Faraday Soc.*, 1967, **63**, 1115.

⁵ J. L. Hales, J. D. Cox, and E. B. Lees, *Trans. Faraday Soc.*, 1963, **59**, 1544.

⁶ J. F. Counsell, E. B. Lees, and J. F. Martin, *J. Chem. Soc. (A)*, 1968, 1819.

of thermodynamic properties (Table 3) were obtained from heat-capacity values calculated from the polynomials and from the experimental values in the transition regions. Figures 1 and 2 show the heat capacities (calculated values except at transitions) plotted against temperature.

city curve had a small maximum at about 210°K. At about 244°K another transition occurred, and the heat capacity rose to a maximum value of 715 J deg.⁻¹ mole⁻¹. Over a temperature range of 0.5° in the region of 245°K, it was sometimes observed that addition of energy caused a

TABLE 1
Heats and entropies of phase changes; purity of samples

Compound	Melting				Transition		
	Temp. (°K)	Heat (J mole ⁻¹)	Entropy (J deg. ⁻¹ mole ⁻¹)	Purity (mole %)	Temp. (°K)	Heat (J mole ⁻¹)	Entropy (J deg. ⁻¹ mole ⁻¹)
C ₆ F ₅ Cl	257.49 ± 0.01	8355 ± 4	32.45	99.94 ± 0.01	191	3636	17.91
C ₆ F ₅ OH	310.62 ± 0.01	16,410 ± 8	52.83	99.97 ± 0.01	245	983	4.01
					287	1134	3.93

TABLE 2
Experimental molar heat capacity

<i>T</i> (°K)	<i>C_p</i> (J deg. ⁻¹)	<i>T</i> (°K)	<i>C_p</i> (J deg. ⁻¹)	<i>T</i> (°K)	<i>C_p</i> (J deg. ⁻¹)	<i>T</i> (°K)	<i>C_p</i> (J deg. ⁻¹)	<i>T</i> (°K)	<i>C_p</i> (J deg. ⁻¹)	<i>T</i> (°K)	<i>C_p</i> (J deg. ⁻¹)
Pentafluorochlorobenzene											
<i>Crystal</i>		<i>Crystal</i>		<i>Crystal</i>		<i>Crystal</i>		<i>Crystal</i>		<i>Liquid</i>	
11.79	7.376	81.34	75.21	172.98	146.2	203.46	216.1	247.74	309.2	311.33	224.3
12.70	8.770	86.57	79.16	173.31	146.7	206.17	216.4	249.00	185.6	314.03	224.8
13.81	10.61	91.70	83.15	177.58	153.6	207.04	216.4	250.76	187.5	315.39	225.1
15.09	12.64	96.76	86.83	177.85	154.1	210.66	215.5	251.14	187.0	316.44	225.1
16.52	14.74	101.72	90.38	181.10	161.4	211.00	215.9	253.51	189.9	319.27	225.9
18.12	17.07	106.56	93.79	182.51	166.1	214.59	214.3	254.25	197.0	320.29	226.1
19.92	19.46	111.39	97.27	183.87	171.1	216.10	213.0			324.47	227.0
21.94	22.14	115.94	100.5	185.84	181.6	218.90	210.9			329.65	228.2
24.04	24.80	116.34	100.8	187.89	202.0	221.30	209.0	263.00	214.6	334.81	229.3
25.99	27.18	121.25	104.3	188.87	223.9	223.65	207.5	264.93	214.8	339.93	230.3
27.99	29.37	121.26	104.2	189.69	259.8	226.56	205.4	270.18	215.6	345.04	231.6
30.53	32.05	126.41	107.9	190.56	613.5	228.71	204.6	275.30	216.8	350.12	232.8
33.73	35.28	131.55	111.5	190.81	874.6	231.86	203.1	280.40	217.7	355.18	233.8
37.38	38.84	136.77	115.1	191.51	630.3	233.86	202.9	285.47	218.8	360.21	235.0
41.33	42.47	141.94	118.8	191.83	453.6	237.16	202.4	290.52	219.7	365.22	236.0
45.69	46.18	147.11	122.6	192.80	231.0	239.02	202.6	295.54	221.0	370.18	237.1
50.70	50.51	152.37	126.4	193.79	223.4	241.34	202.6	295.85	221.0	375.15	238.4
55.90	55.04	157.57	130.6	194.62	218.9	243.42	203.4	300.54	221.8	380.08	239.6
60.95	59.10	162.77	135.0	196.69	215.6	243.88	203.3	301.04	222.1	385.00	240.7
66.03	63.01	164.38	136.5	197.49	215.0	245.69	664.6	305.51	223.1	389.88	242.1
70.99	66.81	167.95	140.2	200.01	214.7	245.88	714.5	306.20	223.2	394.75	243.2
75.81	70.69	168.90	141.2	201.63	215.2	247.21	329.5	310.46	224.1		
Pentafluorophenol											
<i>Crystal</i>		<i>Crystal</i>		<i>Crystal</i>		<i>Crystal</i>		<i>Crystal</i>		<i>Liquid</i>	
11.73	6.531	55.91	49.71	126.69	100.6	200.59	144.7	281.88	188.7	315.65	279.5
12.78	7.234	60.95	53.52	131.57	103.9	205.63	147.4	285.20	191.2	316.04	279.3
14.05	9.673	61.97	54.26	136.32	107.0	210.66	150.0	286.73	198.9	320.23	279.4
15.51	11.64	65.91	57.07	141.05	109.9	215.68	152.7	288.06	200.8	320.94	279.1
17.17	13.48	66.98	57.85	145.75	113.0	220.50	155.2	289.30	200.8	325.30	279.0
18.96	15.81	71.92	61.43	150.35	115.8	225.43	157.8	290.67	200.8	325.99	278.5
20.78	17.88	76.89	65.26	155.00	118.7	230.42	160.5	292.54	200.8	331.11	278.3
22.68	20.15	81.89	69.12	159.73	121.6	235.61	163.1	295.42	198.2	336.21	277.8
24.74	22.52	86.94	72.73	164.45	124.4	240.99	166.1	295.57	198.8	341.31	277.8
27.11	25.04	92.06	76.65	169.22	127.1	246.29	168.6	299.46	202.5	346.41	277.5
29.89	27.75	98.16	80.87	174.20	130.0	251.52	171.5	299.76	203.2	351.51	277.4
33.19	30.97	104.21	85.12	179.24	132.9	256.69	174.2	300.11	203.2	356.58	277.5
36.99	34.42	106.82	86.87	184.23	135.8	261.79	177.0	303.95	209.7	361.68	277.4
41.23	38.04	111.83	90.39	189.18	138.5	266.75	179.4	304.42	208.0	366.76	277.1
45.92	41.75	116.83	93.87	194.13	141.1	271.77	182.5	304.45	209.7	371.84	277.8
50.89	45.75	121.76	97.24	199.17	143.9	276.83	185.7			376.90	277.8

Pentafluorochlorobenzene showed two major transformations in the crystalline phase, and pentafluorophenol one. The lower-temperature transition in pentafluorochlorobenzene (Figure 1) started at about 150°K, and the heat capacity rose to a maximum of 874 J deg.⁻¹ mole⁻¹ at 191°K. During measurements in the temperature range 193—244°K, it was observed that equilibrium was reached more slowly than usual after each heat input, and the heat capa-

temperature fall. This behaviour was ascribed to the transformation of a metastable form to a stable form. The transition to the stable, higher-temperature form was complete at 249°K and the sample melted at 257.49°K.

A transition in pentafluorophenol occurred in the temperature range 286—291°K (Figure 2), and, as with the chloro-compound, a metastable low-temperature form could exist for about 2° above 286°K before transformation

to the high-temperature form occurred. The heat capacity reached a maximum of $799 \text{ J deg}^{-1} \text{ mole}^{-1}$ at 286.7°K .

The enthalpies and entropies associated with the transitions (Table 1) in pentafluorochlorobenzene were evaluated from the area between the heat capacity in the transition region and a baseline estimated from heat capacities in the temperature ranges above and below the transition region. A quadratic equation in temperature was fitted to the observed heat capacities from 80 to 120°K and from 250 to 254°K . The maximum deviation of the experimental heat capacities from values calculated from the quadratic equation was 0.2% , and the curvature (d^2C_p/dT^2) calculated from the quadratic equation was negative and similar in value to that found experimentally for pentafluorophenol in the temperature range 120 – 250°K . The enthalpy and entropy associated with the combined transitions were 4619 J mole^{-1} and $21.92 \text{ J deg}^{-1} \text{ mole}^{-1}$ respectively. The

TABLE 3

Molar thermodynamic properties

T (°K)	C_p (J deg. ⁻¹)	S (J deg. ⁻¹)	$H - H^\circ_0$ (J)	$(H - H^\circ_0)/T$ (J deg. ⁻¹)	$-(G - H^\circ_0)/T$ (J deg. ⁻¹)
Pentafluorochlorobenzene					
<i>Crystal</i>					
10.00	4.962	1.736	12.94	1.294	0.442
15.00	12.49	5.125	56.01	3.734	1.391
20.00	19.66	9.726	136.8	6.842	2.884
25.00	25.92	14.80	251.1	10.04	4.756
30.00	31.48	20.03	394.9	13.16	6.864
35.00	36.54	25.27	565.1	16.15	9.119
40.00	41.25	30.46	759.7	18.99	11.46
45.00	45.69	35.57	977.1	21.71	13.86
50.00	49.97	40.61	1216	24.33	16.28
60.00	58.22	50.45	1758	29.29	21.16
70.00	66.23	60.03	2380	34.00	26.03
80.00	74.08	69.39	3082	38.52	30.87
90.00	81.72	78.56	3861	42.90	35.66
100.00	89.14	87.55	4715	47.15	40.40
110.00	96.33	96.39	5643	51.30	45.09
120.00	103.4	105.1	6641	55.34	49.73
130.00	110.3	113.6	7710	59.31	54.32
140.00	117.4	122.1	8848	63.20	58.85
150.00	124.7	130.4	10,060	67.06	63.35
160.00	132.6	138.7	11,340	70.90	67.80
170.00	142.5	147.0	12,720	74.81	72.21
180.00	159.0	155.6	14,210	78.97	76.60
190.00	284.5	165.6	16,080	84.64	81.00
200.00	214.7	180.7	19,020	95.08	85.62
210.00	216.1	191.2	21,180	100.8	90.40
220.00	210.0	201.2	23,310	106.0	95.22
230.00	203.6	210.4	25,380	110.3	100.0
240.00	202.6	219.0	27,410	114.2	104.8
250.00	186.9	230.9	30,320	121.3	109.6
257.49	191.1	236.5	31,730	123.2	113.2
<i>Liquid</i>					
257.49	213.3	268.9	40,090	155.7	113.2
260.00	213.8	271.0	40,620	156.2	114.7
270.00	215.8	279.1	42,770	158.4	120.7
273.15	216.4	281.6	43,450	159.1	122.5
280.00	217.8	287.0	44,940	160.5	126.5
290.00	219.8	294.6	47,130	162.5	132.1
298.15	221.4	300.7	48,930	164.1	136.6
300.00	221.8	302.1	49,330	164.4	137.7
310.00	223.9	309.4	51,560	166.3	143.1
320.00	226.0	316.6	53,810	168.2	148.4
330.00	228.2	323.6	56,080	170.0	153.6
340.00	230.4	330.4	58,380	171.7	158.7
350.00	232.6	337.1	60,690	173.4	163.7
360.00	234.9	343.7	63,030	175.1	168.6
370.00	237.2	350.2	65,390	176.7	173.4
380.00	239.6	356.5	67,770	178.4	178.2
390.00	242.0	362.8	70,180	180.0	182.8

TABLE 3 (Continued)

T (°K)	C_p (J deg. ⁻¹)	S (J deg. ⁻¹)	$H - H^\circ_0$ (J)	$(H - H^\circ_0)/T$ (J deg. ⁻¹)	$-(G - H^\circ_0)/T$ (J deg. ⁻¹)
Pentafluorophenol					
<i>Crystal</i>					
10.00	4.272	1.488	11.11	1.111	0.378
15.00	10.76	4.413	48.26	3.217	1.195
20.00	17.06	8.386	118.1	5.904	2.482
25.00	22.74	12.81	217.8	8.713	4.101
30.00	27.90	17.42	344.7	11.49	5.936
35.00	32.62	22.09	496.1	14.18	7.910
40.00	37.00	26.73	670.3	16.76	9.973
45.00	41.12	31.33	865.7	19.24	12.09
50.00	45.08	35.87	1081	21.63	14.24
60.00	52.70	44.76	1570	26.17	18.59
70.00	60.18	53.45	2135	30.50	22.95
80.00	67.61	61.97	2774	34.67	27.30
90.00	74.96	70.36	3487	38.74	31.62
100.00	82.17	78.63	4273	42.73	35.91
110.00	89.21	86.80	5130	46.63	40.16
120.00	96.06	94.85	6056	50.47	44.39
130.00	102.8	102.8	7050	54.23	48.57
140.00	109.3	110.7	8111	57.93	52.73
150.00	115.6	118.4	9235	61.57	56.85
160.00	121.8	126.1	10,420	65.14	60.94
170.00	127.7	133.6	11,670	68.65	64.99
180.00	133.4	141.1	12,980	72.08	69.01
190.00	138.9	148.5	14,340	75.45	73.00
200.00	144.3	155.7	15,750	78.76	76.96
210.00	149.7	162.9	17,220	82.01	80.88
220.00	155.0	170.0	18,750	85.21	84.77
230.00	160.3	177.0	20,320	88.36	88.63
240.00	165.5	183.9	21,950	91.46	92.45
250.00	170.6	190.8	23,630	94.53	96.25
260.00	175.9	197.6	25,360	97.56	100.0
270.00	181.5	204.3	27,150	100.6	103.8
273.15	183.4	206.4	27,730	101.5	104.9
280.00	187.6	211.0	29,000	103.6	107.5
290.00	232.2	221.5	31,990	110.3	111.2
298.15	201.3	227.1	33,650	112.9	114.3
300.00	203.2	228.4	34,020	113.4	115.0
310.00	212.2	235.2	36,100	116.5	118.8
310.62	212.7	235.7	36,230	116.6	119.0
<i>Liquid</i>					
310.62	280.0	288.5	52,640	169.5	119.0
320.00	279.2	296.8	55,270	172.7	124.1
330.00	278.3	305.4	58,050	175.9	129.5
340.00	277.8	313.7	60,830	178.9	134.8
350.00	277.4	321.7	63,610	181.7	140.0
360.00	277.3	329.5	66,380	184.4	145.1
370.00	277.5	337.1	69,160	186.9	150.2
380.00	277.8	344.5	71,930	189.3	155.2

TABLE 4

Molar heat capacities of pentafluorochlorobenzene vapour

P (mm. Hg)	T (°K)	$C_p(\text{obs.})$ (J deg. ⁻¹)	$C_p(\text{calc.})^*$ (J deg. ⁻¹)	$C_p(\text{obs.}) - C_p(\text{calc.})$ (J deg. ⁻¹)
758.6	403.61	193.09	193.18	-0.09
758.8	423.35	195.77	195.97	-0.20
759.7	423.96	196.23	196.06	0.17
759.9	423.98	196.31	196.07	0.24
758.6	448.32	199.87	199.82	0.05
758.8	473.40	203.59	203.77	-0.18
378.5	383.31	186.06	186.07	-0.01
378.8	403.25	189.54	189.63	-0.09
378.5	423.43	193.43	193.36	0.07
379.0	448.35	197.86	197.96	-0.10
378.8	473.66	202.51	202.44	0.07
189.8	383.62	183.84	183.75	0.09
189.9	404.20	188.03	188.08	-0.05
189.6	423.41	191.96	192.06	-0.10
189.6	448.56	197.11	197.07	0.04
189.5	473.68	201.84	201.76	0.08
189.6	498.63	206.06	206.06	0.00

* Calculated from equation (1).

transition at 244–249°K contributed 4.02 J deg.⁻¹ mole⁻¹ to the total entropy of transitions.

The enthalpy and entropy of transition of pentafluorophenol, determined from the area between the heat-capacity curve at the transition and a smooth curve joining the curves

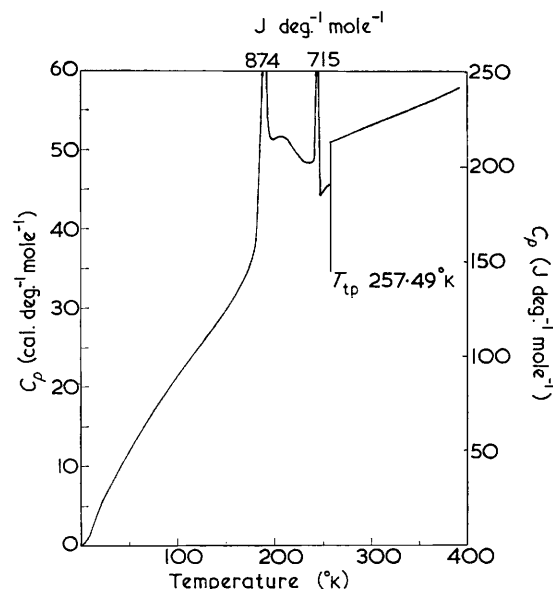


FIGURE 1 Heat capacity of pentafluorochlorobenzene; T_{tp} = triple point

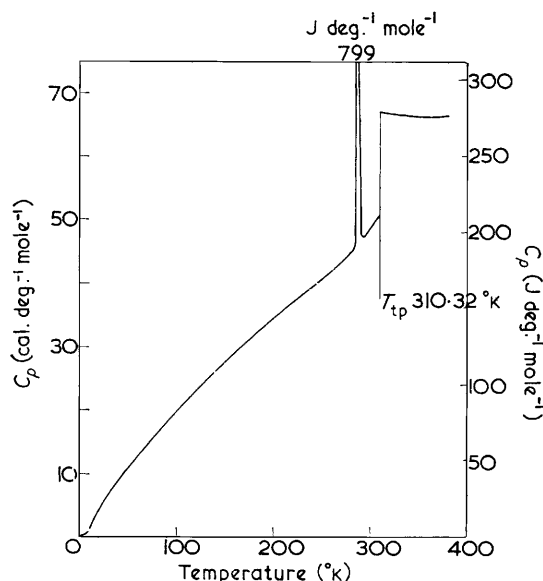


FIGURE 2 Heat capacity of pentafluorophenol

before and after the transition, were found to be 1134 J mole⁻¹ and 3.93 J deg.⁻¹ mole⁻¹ respectively.

Vapour Heat Capacity and Heat of Vaporization of C₆F₅Cl.—The experimental values for the vapour heat capacity (Table 4, columns 1–3) of pentafluorochlorobenzene were correlated by the method described in the previous paper,¹ to give the following equation from which

the calculated heat capacities (Table 4, column 4) were obtained:

$$C_p = 34.756 + 0.51438T - 3.4464 \times 10^{-4}T^2 + 5.975 \times 10^{-3}(2810/T^2 + 1405^2/T^3) \exp(1405/T)P \quad (1)$$

C_p , J deg.⁻¹ mole⁻¹; T , °K; P , mm. Hg. The standard deviation of the experimental from the calculated values (Table 4, column 5) was ± 0.13 J deg.⁻¹ mole⁻¹.

TABLE 5

Molar heats of vaporization and second virial coefficients of pentafluorochlorobenzene

P (mm.)	T (°K)	ΔH_v (J)	$-B^*$ (cm. ³)	$-B^\dagger$ (cm. ³)
760	391.10	34,760 \pm 10	1780	1758
380	368.86	36,370 \pm 10	2131	2136
190	349.41	37,690 \pm 10	2598	2614

* Calculated from equation (2). † Calculated from equation (3).

The experimental values of heats of vaporization (Table 5) and published vapour-pressure data were used to calculate second virial coefficients, B , of pentafluorochlorobenzene vapour from the equation:

$$B = \Delta H_v(TdP/dT)^{-1} - RTP^{-1} + V_l \quad (2)$$

where V_l is the molar volume of the liquid in cm.³. From the values of B and constants of equation (1), the second virial coefficient, B , of pentafluorochlorobenzene vapour can be expressed as:

$$-B = 115 + 44.82 \exp(1405/T) \quad (3)$$

Entropy of C₆F₅Cl in the Ideal-gas State.—The entropy of C₆F₅Cl(g) at 298.15°K and 1 atm. has been calculated by the procedure used in Part VI,¹ as follows:

	$T = 380^\circ\text{K}$	350°K
$S_T(l)$, from Table 3 (J deg. ⁻¹ mole ⁻¹)	356.5	337.1
$\Delta H_v/T$, from Table 5	93.64	107.57
$R \ln P$, from ref. 7	-2.76	-11.34
$S_l - S_T = (dB/dT)P$, from eqn. (3) and ref. 7	1.30	0.75
$S^\circ_T(g)$	448.68	434.08
$(S^\circ_T - S^\circ_{298.15}) = \int_{298.15}^T (C_p^\circ/T) dT$, from eqn. (1)	40.96	26.44
$S^\circ_{298.15}(g)$ (J deg. ⁻¹ mole ⁻¹)	407.7	407.6

In the above calculation, the values of C_p° only have been extrapolated outside the temperature range of the measurements.

DISCUSSION

Notable features of the heat-capacity curves (Figures 1 and 2) are the large lower-temperature transition in pentafluorochlorobenzene and the similarity of the transitions of C₆F₅Cl with a heat-capacity maximum at about 246°K and that of C₆F₅OH with a heat capacity maximum at about 287°K. The heat-capacity curves in the temperature ranges of the higher-temperature transitions in both compounds are similar in appearance, both compounds become metastable before the transitions occur, and the entropies of transition (4.01 and 3.93 J deg.⁻¹ mole⁻¹) are nearly the same. These transitions may be associated with the onset of molecular motion about the axis of the C–Cl or the C–OH bonds.

¹ D. Ambrose, *J. Chem. Soc. (A)*, 1968, 1381.

The occurrence of the transition at 191°K in C₆F₅Cl was reported by us to Dr. I. J. Lawrenson who investigated the n.m.r. spectrum of this compound.⁸ His studies showed that the magnetic properties of the molecule in the crystal were compatible with the onset of rotation of the molecules at the crystal lattice sites about axes perpendicular to the plane of the aromatic ring. Above the transition temperature, molecules occupy randomly any one of six orientations, so the expected entropy of transition would be at least $R \ln 6$ (14.90 J deg.⁻¹ mole⁻¹). If the dividing line between the two major transitions is taken at 244°K, the entropy of the lower-temperature transition is 17.91 J deg.⁻¹ mole⁻¹.

Since completion of these measurements, a paper on the low-temperature heat capacity and entropy of pentafluorochlorobenzene has been published by Paukov and Glukhikh.⁹ These authors only gave their values for C_p in the transition region. Their value for $H_{298} - H_0$, 11,760 cal. mole⁻¹ (49,204 J mole⁻¹), is in good agreement with the value (48,911 J mole⁻¹) in Table 2 but

⁸ I. J. Lawrenson and C. Lewis, *Proc. Phys. Soc.*, 1966, **89**, 923.

there is an appreciable difference in the values for S_{298} : 73.25 cal. deg.⁻¹ mole⁻¹ \equiv 306.5 J deg.⁻¹ mole⁻¹ (ref. 9) and 300.7 J deg.⁻¹ mole⁻¹ (Table 2). The shape of the heat-capacity curve in the region of the transition in ref. 9 is similar to Figure 1 of the present paper but ref. 9 does not record a transition at 244—249°K. The Russian authors' value for the heat of fusion (2007 cal. mole⁻¹ \equiv 8397 J mole⁻¹) is only 0.5% higher than the value in Table 1 but there is a large difference in the two values for the total heats of transition (297.9 cal. mole⁻¹ \equiv 1246 J mole⁻¹, ref. 9, and 4619 J mole⁻¹ for the total transition enthalpy in our work). At least part of this large difference may be accounted for by the choice of the baseline on the heat-capacity curve for the calculation of the entropy of transition. The method used in ref. 9 is not described.

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⁹ I. E. Paukov and L. K. Glukhikh, *Zhur. Vsesoyuz. Khim. obshch. im. D.I. Mendeleeva*, 1967, **12**, 236.