Thermochimica Acta, 109 (1986) 1–10
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A CALORIMETRIC CONTRIBUTION TO THE STUDY OF POLYMORPHISM IN TETRAMETHYLAMMONIUM CHLORIDE *

L.A.K. STAVELEY and R.D. WORSWICK

The Inorganic Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QR (Gt. Britain)

(Received 23 June 1986)

ABSTRACT

The heat capacity of tetramethylammonium chloride has been measured from 115 to 498 K, both for the thermodynamically stable modifications and for the form II, which is metastable below 407 K. The entropy gains at the IV → III λ-transition and at the III → II first-order transition are estimated to be 1.19 J K^{-1} mol^{-1} and 4.16 J K^{-1} mol^{-1}, respectively. At 125 K, the entropy of the metastable phase II exceeds that of the stable modification IV by only 1.76 J K^{-1} mol^{-1}. If, as has been suggested, each cation in phase II has two possible orientations, it would seem that at 125 K this disorder in phase II is largely, if not wholly, suppressed, without the appearance of any transition or thermal anomaly.

Results are also recorded of test measurements of the heat capacity of the NBS sample of synthetic sapphire (α-Al_2O_3) from 138 to 515 K.

INTRODUCTION

The salt tetramethylammonium chloride ($(CH_3)_4NCl$, now indexed in Chemical Abstracts as methanaminium *N*,*N*,*N*-trimethyl chloride, and to which we shall refer as TMAC) exhibits a remarkable polymorphism. At ordinary pressures it exists in five modifications [1]. Form V, which is the stable phase at the lowest temperatures, passes at a first-order transition at 75.76 K into IV, which is tetragonal. IV becomes III, which is also tetragonal, at a λ-type transition, which culminates at 184.45 K. III is the stable phase up to 407 K, when it passes at a first-order transition into a rhombohedral modification II. Finally, II gives place to a face-centered cubic modification I at 537 K.

The study of the polymorphism of TMAC is complicated by the fact that the phase behaviour of this compound is much influenced by the presence of impurities, and also very possibly by its thermal history. TMAC is a

---

* Dedicated to Professor Syûzô Seki in honour of his contribution to Calorimetry and Thermal Analysis.

0040-6031/86/$03.50

hygroscopic substance which is usually purified by recrystallization from anhydrous methanol. There is no doubt that small amounts of occluded methanol or water can have a remarkable effect, notably on whether or not phase II changes into phase III on cooling. Indeed, Dufourcq et al. [2] went so far as to suggest that phase III is really a hydrated form of TMAC, and that II is the stable form of the compound at ambient temperatures. This view can no longer be upheld, but it has been said that II will not revert to III in the absence of traces of solvent [3].

In the cubic modification I, the cations are orientationally disordered, but ordered in phases V, IV and III. Different views have been expressed about II in this respect. Dufourcq et al. [2] considered that the cations are ordered in this phase while Pistorius and Gibson [3] proposed a structure giving each cation two possible orientations, though they acknowledged that interaction between neighbouring cations might prevent any one ion making full use of these.

A careful study of the heat capacity of TMAC from 5 to 350 K was carried out by Chang and Westrum [4]. The present paper is particularly concerned with phase II, and especially with a comparison of the heat capacity of the stable phases IV and III with that of II over the range 120–407 K, throughout which form II is metastable.

EXPERIMENTAL

Materials

A commercial specimen of TMAC was purified by three successive crystallizations from methanol which had been dried over previously heated calcium oxide. From the evidence in the literature it seems that a specimen so purified must be heated to remove occluded solvent. Gibson and Raab [1] heated their sample for several hours at about 400 K, which is just below the III → II transition. Pistorius and Gibson [3] found that heating TMAC to about 540 K (which is just above the II → I transition) prevented phase II reverting to III on cooling, and concluded that this treatment had removed all traces of solvent. While we were concerned to reduce the quantity of occluded solvent to a level at which it could no longer in itself contribute significantly to the overall heat capacity, having in mind the purpose of our investigation, as mentioned above, we adopted a middle course as regards the thermal treatment. The recrystallized sample was kept at 423 K for several hours. Thereafter precautions were taken to ensure that all moisture was excluded from it. Before being loaded into the calorimeter, the TMAC was reheated under evacuation to 423 K for 2 h, and then allowed to cool slowly. Our sample had therefore been twice converted into phase II, but as our results will show, it was in phase III at the start of the heat capacity measurements. The mass of the sample used was 29.1165 g.

The calorimeter

Except for one feature, the calorimeter was virtually identical with that described by Andrews et al. [5]. This calorimeter had been designed to permit the accurate measurement of heat capacities from 300 to 550 K. We are most grateful to Professor Edgar Westrum and Dr. John Andrews for making available to us the details of their calorimeter and for the advice they gave us about its construction. The one change made by us was to incorporate a reservoir for liquid nitrogen so that measurements could also be made at sub-ambient temperatures. Temperatures were measured on IPTS-68.

RESULTS AND DISCUSSION

Before presenting our results for TMAC, we record in Table 1 our values for the heat capacity of the NBS standard synthetic sapphire (α-Al_2O_3) between 138 and 515 K. These measurements were made to test the performance of the calorimeter, especially at higher temperatures. The percentage difference between our values of the molar heat capacity $C_{p,m}$ and the values interpolated for the same temperatures from the data of Ditmars et al. [6] are also given in Table 1. The average value of this numerical percentage difference is 0.13%. As regards the performance of the calorimeter at lower temperatures, we have already published the results for potassium nitrite, for which $C_{p,m}$ was measured from 10 to 476 K using both the present calorimeter and another, well-tried, low-temperature calorimeter [7]. In the overlap region between 86 and 117 K, the two sets of results agreed to within 0.15%. Also, $C_{p,m}$ for caesium nitrite from 83 to 429 K was determined with the present calorimeter [8], and subsequently values for the same substance from 14 to 350 K were published by Moriya et al. [9], whose results were obtained in the Thermodynamics Laboratory at Osaka University which was established by Professor Syûzô Seki, to whom this paper is respectfully dedicated. Over the range 90–300 K, the average numerical difference between our results for caesium nitrite and those of the Japanese workers is 0.15%, the maximum difference being 0.5% at 170 K. From 310 to 350 K, the Japanese results are slightly greater, by between 0.25 and 0.43%.

About one hundred heat capacity measurements were carried out on TMAC, in eight runs. The results are given in Table 2, and the overall picture presented by them is shown in Fig. 1. Some measurements in the neighbourhood of the two transitions have been omitted from this figure to avoid congestion. Figures 2 and 3 are larger scale plots showing the temperature dependence of the heat capacity in the region of the IV → III and III → II transitions, respectively. In these two figures, all relevant experimental points have been included.

TABLE 1

Measured values of the heat capacity $C_{p,\mathrm{m}}$ of the NBS standard synthetic sapphire (α-Al_2O_3). $\Delta = 100[C_{p,\mathrm{m}}(\text{this work}) - C_{p,\mathrm{m}}(\text{NBS})]/C_{p,\mathrm{m}}$, where $C_{p,\mathrm{m}}$ (NBS) has been derived from the values tabulated by Ditmars et al. [6].

T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	Δ
138.22	27.30	−0.04
148.93	31.62	+0.28
158.76	35.58	+0.14
167.91	39.18	+0.26
176.52	42.52	+0.24
184.68	45.65	+0.31
193.75	49.07	+0.46
203.54	52.41	+0.10
214.35	56.16	+0.12
224.61	59.56	+0.21
234.45	62.63	+0.20
243.95	65.43	+0.15
253.15	67.94	−0.13
262.09	70.46	+0.14
270.86	72.54	−0.11
278.63	74.56	+0.04
286.98	76.53	+0.02
295.17	78.36	+0.04
303.21	80.15	+0.06
311.11	81.78	+0.05
318.89	83.26	−0.05
326.26	84.92	+0.29
333.82	86.18	+0.15
341.28	87.29	−0.08
350.86	88.93	−0.04
358.13	90.15	0.00
365.31	91.27	+0.01
372.41	92.43	+0.12
379.45	93.31	−0.02
382.94	93.82	0.00
388.47	94.57	0.00
400.41	95.87	−0.27
414.52	97.48	−0.39
421.20	98.49	−0.14
428.67	99.44	−0.03
436.92	100.32	−0.04
437.89	100.47	+0.01
445.13	101.16	−0.05
446.15	101.10	−0.22
453.28	101.91	−0.13
458.38	102.38	−0.15
461.38	102.71	−0.10
467.10	103.16	−0.14
475.12	104.16	−0.11

TABLE 1 (continued)

T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	Δ
483.13	104.51	−0.22
491.03	105.41	0.00
498.92	105.91	−0.12
506.73	106.48	−0.16
514.52	106.82	−0.39

TABLE 2

Measured values of the heat capacity $C_{p,\mathrm{m}}$ of tetramethylammonium chloride

T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})
Series I		*Series III*		*Series VI*	
114.81	85.67	350.00	179.40	237.82	138.39
127.54	92.56	359.17	183.21	295.86	161.99
137.62	97.67	368.21	186.93	305.70	166.34
147.32	102.56	377.13	190.69	315.38	170.28
165.83	111.90	387.14	194.78	324.89	174.51
183.36	121.67	398.20	199.22	334.28	178.25
191.93	118.77	407.04	420.81	343.52	182.01
200.46	121.41	414.98	239.89		
209.30	124.49	428.84	215.85	*Series VII*	
217.56	127.65	439.14	227.06	126.71	91.44
227.29	131.52	449.06	232.48	135.17	95.54
238.44	135.55	458.87	239.64	144.98	100.28
249.36	139.80	468.66	241.93	154.49	104.79
260.08	143.82	478.20	246.91	163.76	108.75
270.61	147.94	487.50	253.35	172.79	112.67
280.96	151.93	497.54	260.47	248.63	142.44
292.23	155.89			259.21	146.96
302.28	160.01	*Series IV*		269.65	151.26
312.14	163.94	396.36	204.69	279.92	155.20
321.85	168.05	404.82	208.51	288.23	158.65
331.41	171.91	413.12	212.71	350.49	184.89
340.82	175.58	421.42	216.55	359.48	188.97
		429.55	220.15	368.40	192.99
Series II				377.19	196.62
172.57	115.34	*Series V*		385.85	200.83
177.02	117.70	398.44	205.58	394.38	204.89
179.37	118.92	409.05	211.12		
181.13	120.37	421.68	216.78	*Series VIII*	
182.87	121.82			390.51	196.81
184.60	124.24	*Series VI*		399.18	200.07
186.33	120.89	176.02	113.80	406.18	403.36
188.07	118.31	184.81	117.35	410.30	311.62
189.83	118.00	192.18	120.31	416.48	216.14
191.58	118.35	193.19	120.89	423.44	221.10
195.33	119.65	203.99	125.02	431.50	222.86
		215.52	129.67	440.59	226.20
		226.79	134.19		

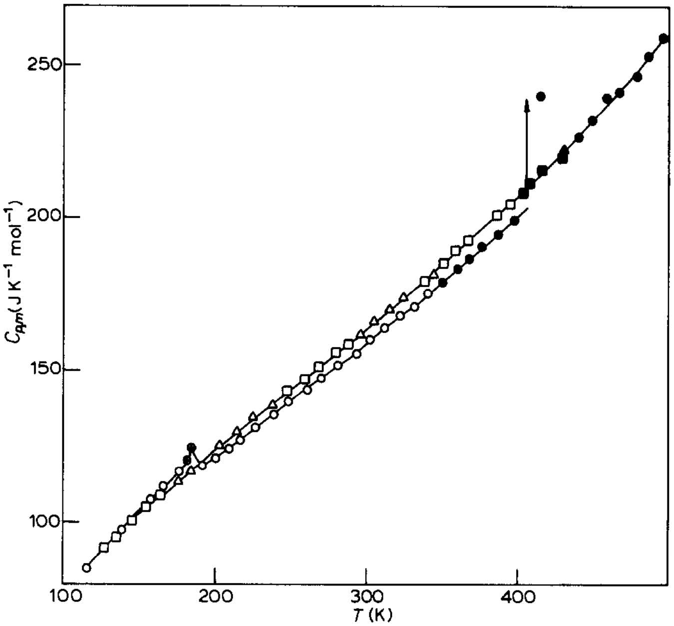

Fig. 1. Temperature dependence of the heat capacity $C_{p,\mathrm{m}}$ of TMAC. (○) Series I; (⊕) Series II; (●) Series III; (■) Series IV and V; (△) Series VI; (□) Series VII; (▲) Series VIII. The vertical arrow indicates the temperature of the III → II transition.

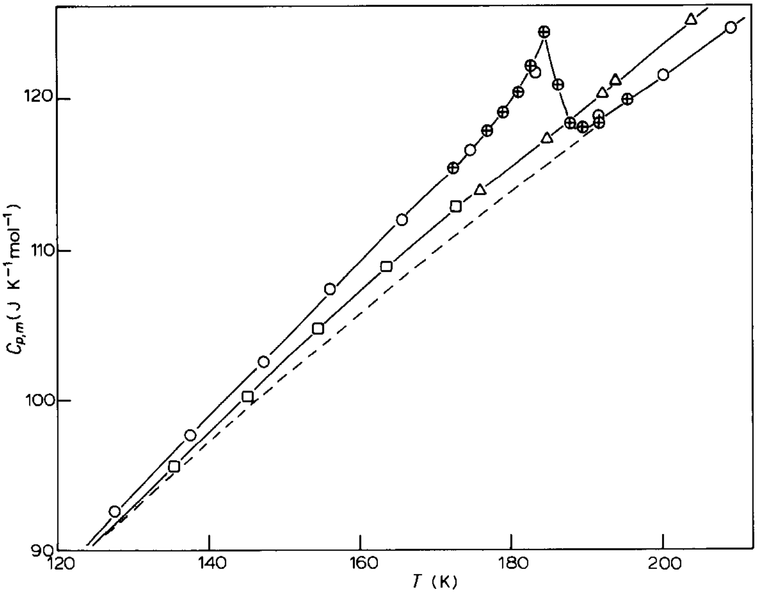

Fig. 2. Temperature dependence of the heat capacity of TMAC in the region of the IV → III transition. Symbols as for Fig. 1.

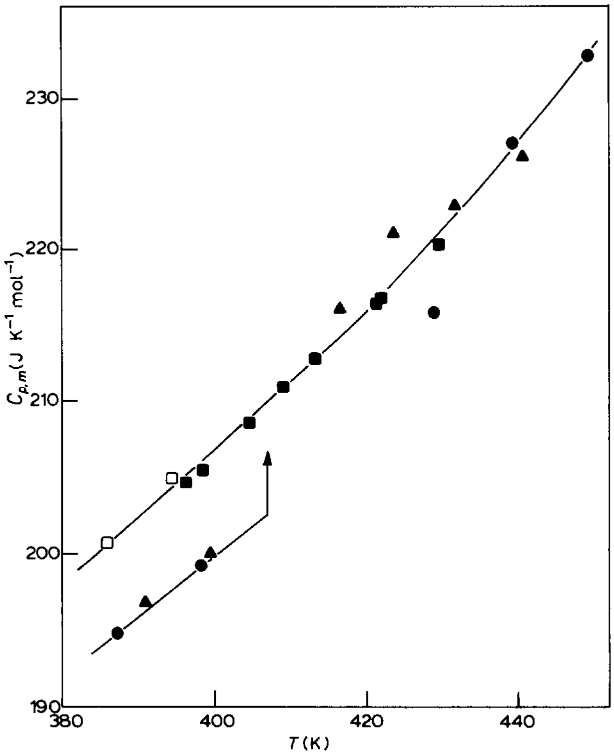

Fig. 3. Temperature dependence of the heat capacity of TMAC in the region of the III → II transition. The vertical arrow indicates the temperature of this transition. Symbols as for Fig. 1.

Series I was preceded by cooling the sample from room temperature to 107 K. This series clearly shows the relatively small λ-transition from form IV to III (Figs. 1 and 2). This run was terminated at 345 K, and the sample cooled to 170 K. Series II was then carried out with smaller temperature intervals through the λ-transition, the run ending at 198 K. The sample was then heated to 346 K, and measurements made from this temperature to 507 K (Series III). This run revealed the expected III → II transition, the maximum value of $C_{p,\mathrm{m}}$ being attained at 407.0 K. The sample, now in phase II, was cooled to 392 K, and the short Series IV carried out, ending at 434 K. Series IV was briefly repeated in Series V, with the same results (Fig. 3). There was no hint at all in these two runs of the III → II transition, so the sample was wholly in form II.

At the conclusion of Series V, the sample was cooled as quickly as possible to room temperature, and then to about 170 K, at which temperature Series VI was commenced. After the measurement made at a mean temperature of 194.43 K, the sample was cooled about 10 K and the run recommenced, ending at 348 K. The TMAC was then cooled to 123 K, and

Series VII carried out. It will be seen from Fig. 2 that the results of Series VI and VII are completely consistent, and show no sign of even slightly "abnormally" high heat capacity values in the region of the IV → III λ-transition, which is of course evidence that in runs VI and VII the sample was wholly in the metastable modification II.

Published work on TMAC indicates that the optimum temperature for the spontaneous conversion of metastable II into the stable III is 380–390 K, and it is interesting to note that although the sample passed through this region in the final stages of Series VII, which ended at 398.6 K, there was no indication of this conversion taking place. Had this happened, it should have been readily apparent by the generation of heat, and even if conversion had occurred to only a small extent it should have been readily detected by giving rise to apparently low values of the heat capacity. There is no sign of this in the last two points of Series VII.

After the completion of run VII, the sample was cooled to 386 K and left overnight before carrying out the final run VIII. Much of the specimen had then been converted into form III, as shown by the high heat capacity at 406.2 K, though, as we shall see, the conversion to III had not been complete.

Our heat capacity results overlap with those of Chang and Westrum [4] from 120 to 350 K. Over the whole of this range, our results for phases IV and III are higher than theirs, by about 1.5% below the IV → III transition, and about 1.2% from 200 to 250 K. Thereafter, the difference decreases to about 0.9% between 280 and 350 K. These differences are perhaps larger than might be expected from the performances of the two calorimeters involved. If, when our sample was thought to be wholly in the stable modification III, it had in fact still contained some metastable II, this would of course have given rise to high heat capacity values, since throughout the range between the two transitions, II has the higher heat capacity. But in this case, the position should have been reversed below the λ-transition, where II has the lower heat capacity. There is no sign of this reversal in the relation between our results and those of Chang and Westrum, so contamination with phase II cannot account for the difference between our results and theirs. It may be associated with the unusual and sensitive dependence of the behaviour of TMAC on occluded impurities and on its thermal history. Chang and Westrum do not mention having heated their sample to remove any occluded solvent, so presumably it was never converted into phase II before being loaded into the calorimeter, or indeed at any stage of their study.

Although the λ-type transition from IV to III is on a relatively minor scale, it appears to be quite extensive, beginning more than 60 K below the temperature at which $C_{p,\mathrm{m}}$ reaches a maximum. To estimate the entropy gain associated with it, a "normal" or "baseline" heat capacity curve is needed. In this case the drawing of such a curve is rather arbitrary. We have used the broken curve in Fig. 2 as the baseline, aided to some extent in drawing this by the curve for the metastable phase II. This procedure gave 1.19 J K^{-1} mol^{-1} for the entropy of transition. This is larger than the estimate of 0.59 J K^{-1} mol^{-1} of Chang and Westrum, which they based on the enthalpy gain over the interval 180–190 K. But however the entropy of this transition is estimated, it is clearly quite small.

For the III → II transition, although circumstances unfortunately prevented us from examining this in greater detail, our observations are consistent with the view that it is a first-order transition. Our estimate of the transition temperature is 407 ± 1 K, a little below the figure of 409.7 K given by Pistorius and Gibson [3]. From the heat capacity results of Series II, we estimate the enthalpy of transition ΔH_t to be 1694 J mol^{-1}, whence the entropy of transition is 4.16 J K^{-1} mol^{-1}. The only value for comparison is that given by Pistorius and Gibson of 3.8 J K^{-1} mol^{-1}, obtained by differential scanning calorimetry. The value of ΔH_t derived from the results of Series VIII is lower, being 1357 J mol^{-1}. This implies that when this run was started, the sample still contained some unchanged phase II, which is also suggested by the fact that the first heat capacity values of this run (which are pre-transition values) are a little higher than would be expected from the results of Series III.

Finally, we will briefly consider the bearing of our results on the question of whether or not phase II is disordered. Pistorius and Gibson noted that their value of the entropy of the III → II transition was about $R \ln 3/2$, and offered the interpretation that the cations are disordered between two orientations in phase II, but become ordered when the transformation to phase III occurs. They suggested that the entropy of transition is less than the $R \ln 2$ which might be expected on this basis because interaction between neighbouring cations prevents full use being made by each cation of its two orientations. They pointed out that if phase II is quenched, either the crystals might become completely ordered without any marked structural change, or that the disorder might be frozen-in.

With the results presented in this paper, it is possible to estimate at any selected temperature at which II is metastable the difference between the entropy of this phase and that of the thermodynamically stable phase at the same temperature. Taking 125 K as this temperature, at which the heat capacities of IV and II have become almost equal, we compare the entropy decreases when, starting with phase II at 420 K, on the one hand this form persists on cooling to 125 K, while on the other hand the transitions II → III and III → IV occur. It is convenient to divide the temperature interval into the ranges 420–400 K, 400–188 K (at which temperature the heat capacities of form III and of metastable II are equal), and 188–125 K. For the first stage, using our value of 4.16 J K^{-1} mol^{-1} for the entropy change at the transition, the entropy of III at 400 K is less than that of II by 4.03 J K^{-1} mol^{-1}. In the second stage, II (having the higher heat capacity) loses more entropy than III, by 3.08 J K^{-1} mol^{-1}. In the final stage, III passes into IV and thereby loses 0.81 J K^{-1} mol^{-1} more than II. (This last entropy difference can of course be estimated much more precisely than the entropy change of the λ-transition, as it depends only on the measured heat capacity values and not on an arbitrary baseline.) The net result is that at 125 K the entropy of II exceeds that of IV by $4.03-3.08+0.81$, $=1.76$ J K^{-1} mol^{-1}. This is considerably less than our estimate of the entropy of the III → II transition. On the model of Pistorius and Gibson [3], the twofold orientational disorder of the cations would have to be largely suppressed at 125 K.

It remains to be seen if metastable II undergoes a structural change on cooling below 120 K. (Phase IV passes to V at 75.76 K with an entropy drop of 1.55 J K^{-1} mol^{-1} [4].) It would be interesting to make heat capacity measurements on two different samples of TMAC from about 10 K to a temperature within the range we have covered, say 150 K. Both samples should be taken from the same batch of purified salt. One sample should be loaded into the calorimeter in the stable form III, while the other should be a rapidly quenched sample of II. The results of such a study, combined with those in this paper, should unambiguously answer the question whether or not TMAC-II at 0 K has a significant residual entropy, and hence some disorder.

REFERENCES

1 A.A.V. Gibson and R.E. Raab, J. Chem. Phys., 57 (1972) 4688.

2 J. Dufourcq, Y. Haget-Bouillaud, N.B. Chanh and B. Lemanceau, Acta Crystallogr., Sect. B, 28 (1972) 1305.

3 C.W.F.T. Pistorius and A.A.V. Gibson, J. Solid State Chem., 8 (1973) 126.

4 S.S. Chang and E.F. Westrum Jr., J. Chem. Phys., 36 (1962) 2420.

5 J.T.S. Andrews, P.A. Norton and E.F. Westrum Jr., J. Chem. Thermodyn., 10 (1978) 949.

6 D.A. Ditmars, S. Ishihara, S.S. Chang, G. Bernstein and E.D. West, J. Res. Natl. Bur. Stand., 87 (1982) 159.

7 S.C. Mraw, R.J. Boak and L.A.K. Staveley, J. Chem. Thermodyn., 10 (1978) 359.

8 S.C. Mraw and L.A.K. Staveley, J. Chem. Thermodyn., 8 (1976) 1001.

9 K. Moriya, T. Matsuo and H. Suga, J. Phys. Chem. Solids, 44 (1983) 1103.