

Thermodynamic properties of ammonium halogen stannates

I. Heat capacity and thermodynamic functions of deuterated ammonium hexachlorostannate (ND₄)₂SnCl₆ from 5.9 to 347 K^a

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The heat capacity of deuterated ammonium hexachlorostannate (ND₄)₂SnCl₆ was measured from 5.9 to 347 K by adiabatic calorimetry. The heat capacity is characterized by a λ-shaped anomaly that reaches its maximum $C_{p,m} \approx 53 \cdot R$ ($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) at approximately 244 K. The value of ΔS_m° for the anomaly is $0.48 \cdot R$. Values of the standard thermodynamic quantities are tabulated to 350 K.

1. Introduction

Motion of ammonium ions in ammonium salts has been studied using a variety of techniques which include i.r. spectroscopy, adiabatic calorimetry, n.m.r., and neutron scattering. Much is known about the behaviour of NH₄⁺ in the simple cubic salts and, even in these cases, free rotation of the NH₄⁺ at room temperature is impeded by

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energy barriers arising mainly from the interaction with the neighbouring anions.⁽¹⁾ The ammonium ion may undergo several equilibrium orientations that may or may not be equivalent and are separated by a potential barrier. In ammonium salts with high lattice symmetry, where the anion is not highly charged and is large, Morfee *et al.*⁽²⁾ have suggested that the NH_4^+ motion may approach free rotation at room temperature.

This might be expected to occur in the $(\text{NH}_4)_2\text{MX}_6$ series. In particular, $(\text{NH}_4)_2\text{SnCl}_6$ is well suited for studying molecular rotations and the associated rotational potentials over a wide range of temperature. The heat capacity of this compound does not appear to show any phase transition between room temperature and about 20 K,⁽²⁾ which implies that the rotational potential function is not strongly dependent on temperature. In addition, this substance has a simple highly symmetrical structure with space group $\text{Fm}\bar{3}\text{m}$, four formula units in the face-centred cubic cell, and, at room temperature, a cell constant of $a = 1.0038 \text{ nm}$,⁽³⁾ 1.0044 nm ⁽⁴⁾ or 1.0060 nm .⁽⁵⁾ The NH_4^+ possesses tetrahedral symmetry ($\bar{4}3\text{m}$). The low barrier to rotation of the ammonium ion corresponds to about 600 K.⁽⁶⁻⁸⁾ Smith⁽⁹⁾ has computed the hindered rotational energy levels of NH_4^+ in this molecule by using a potential function of a tetrahedron in a tetrahedral crystalline field. He successfully interpreted the experimental values for $(\text{NH}_4)_2\text{SnCl}_6$ of the librational frequencies,^(7,10) tunnelling frequency,⁽⁷⁾ activation energy,^(6,8) and heat capacity.⁽²⁾ Müller and Hüller⁽¹¹⁾ also calculated a potential to correspond to the experimental findings, but based on the first two librational frequencies and tunnel splitting. These two attempts to obtain the rotational potential from the same experimental values yielded two different sets of potential coefficients.

Recent studies have focussed on the effects of isotopic substitution on rotational motion in $(\text{ND}_4)_2\text{SnCl}_6$. Measurements using thermal neutron scattering with deuterated crystals offer a distinct advantage over the non-deuterated salts. The intense incoherent scattering from the hydrogen atoms is avoided, thereby allowing an investigation of the wavevector dependence of the vibrational and librational modes. The acoustic branches have been measured using inelastic neutron scattering along the three directions of high symmetry, the elastic constants have been derived at 5 K, and no phase transition was detected.⁽¹²⁾ In addition, n.m.r. spectroscopy has been applied to measure the tunnelling frequency at liquid-helium temperatures.⁽¹³⁾ The paucity of experimental results in general and heat capacities in particular for $(\text{ND}_4)_2\text{SnCl}_6$ led us to undertake a study by adiabatic calorimetry as part of our ongoing work on ammonium salts.

2. Experimental

The sample of $(\text{ND}_4)_2\text{SnCl}_6$ was prepared from $(\text{NH}_4)_2\text{SnCl}_6$, a Puratronic reagent certified as 99.9995 mass per cent pure without detectable anionic impurities. About 25 g of $(\text{NH}_4)_2\text{SnCl}_6$ was dissolved completely in D_2O (99.8 moles per cent minimum isotopic purity). The salt dissolved readily at 294 K. A partially deuterated product was obtained on recrystallization. This procedure, carried out in a dry atmosphere,

was repeated three times, and 21.6 g of $(\text{ND}_4)_2\text{SnCl}_6$ was obtained. To remove most of the D_2O trapped in the lattice upon recrystallization, the crystals were placed under an infrared lamp within the dry box and warmed gently for 14 d as the temperature was increased gradually to 369 K. A t.g.a. was done on 10 mg samples removed at intervals. Finally, the sample was held at 383 K for 24 h.

The Guinier–de-Wolff diffraction patterns of our sample were found to be in excellent agreement with the standard pattern for this compound: No. 7–198 as determined by the Joint Committee for Powder Diffraction Standards.⁽¹⁴⁾ Diffraction patterns were obtained for several lots selected from our sample with some showing no scattering due to impurities and others showing only trace levels of NH_4Cl or ND_4Cl , probably the latter, which may have formed during the deuteration process. The structure was found to be face-centred cubic at room temperature with $a = (1.00586 \pm 0.00007)$ nm. In addition, analysis of our sample for Sn content was made by atomic absorption: (31.70 ± 0.10) mass per cent of Sn, and by neutron-activation analysis: (30.0 ± 2.4) mass per cent of Sn, which compare favourably with the theoretical 31.61 mass per cent.

As a check for D_2O trapped within our “dried” sample of $(\text{ND}_4)_2\text{SnCl}_6$, the final t.g.a. was made with 25 mg of the sample which was loaded into the calorimeter. On heating to about 433 K, a mass loss of 0.1 per cent occurred. When the temperature was raised to 473 K, decomposition began slowly, but it was rapid at 573 K. A platinum resistance thermometer was used in the t.g.a. instrument to measure temperature and was calibrated using the ice point and the fixed points of the Curie transition in alumel at 422.5 K, nickel at 631.2 K, and Trafoperm (97 mass per cent of Fe and 3 mass per cent of Si) at 1018.8 K. The estimated precision was ± 2 K and $\pm 1 \times 10^{-6}$ g.

The molar heat capacity $C_{p,m}$ was measured from 5.9 to 347 K by adiabatic calorimetry in the Mark XIII adiabatic cryostat, which is an upgraded version of the Mark II cryostat described previously.⁽¹⁵⁾ The acquisition of heat capacities from about 6 to 350 K was computer assisted.^(16,17) The computer was programmed for a series of determinations. During the drift periods, both the calorimeter temperature and the first and second derivatives of temperature with time were recorded to establish the equilibrium temperature of the calorimeter before and after the energy input. While the calorimeter heater was on, the heater current and potential and the duration of the heating interval were obtained. Also recorded were the apparent heat capacity of the system including the calorimeter, heater, thermometer, and sample.

A gold-plated copper calorimeter (laboratory designation W-139) with four internal vertical vanes and a central entrant well for (heater + thermometer) was loaded with $(\text{ND}_4)_2\text{SnCl}_6$ within a dry box. After loading, the calorimeter was evacuated and pumping was continued for several hours to ensure that no free D_2O remained within the sample. Helium gas was then added to the vessel to a pressure of about 3.4 kPa (at 300 K) so as to facilitate thermal equilibration. The vessel was then sealed by means of an annealed gold gasket tightly pressed on to the stainless-steel knife edge of the calorimeter top using a screw closure about 5 mm in diameter.

Buoyancy corrections were calculated on the basis of a crystallographic density of $2.450 \text{ g} \cdot \text{cm}^{-3}$ derived from the X-ray diffraction of our sample. The mass of the

10 K to less than 0.15 per cent at temperatures above 30 K. The heat capacity of our sample represented about 65 to 85 per cent of the measured total heat capacity.

A plot of $C_{p,m}/R$ against T from 6 to 347 K is shown in figure 1 where a λ -shaped anomaly occurs around 244 K. Four passes were made through the anomalous zone (see the thermal history above), and reproducible heat capacities resulted. The detail of the peak is given in figure 2. The reproducibility of our determinations of the enthalpy and entropy changes through this region is shown in table 2. The agreement between two independent long inputs of electrical energy to obtain the enthalpy associated with the anomaly is 0.06 per cent, and the value obtained from graphical integration lies within 0.01 per cent of the experimental value.

Morphee and Staveley⁽¹⁸⁾ have drawn attention to the unusual phenomenon encountered during their measurements on $(\text{NH}_4)_2\text{SnCl}_6$ and the potassium and rubidium analogues. The heat capacities of these salts were reduced by cooling, and attained reproducible values only after repeated cooling. For the ammonium salt, the effect was noted only above 200 K and the curve through the first values of $C_{p,m}$

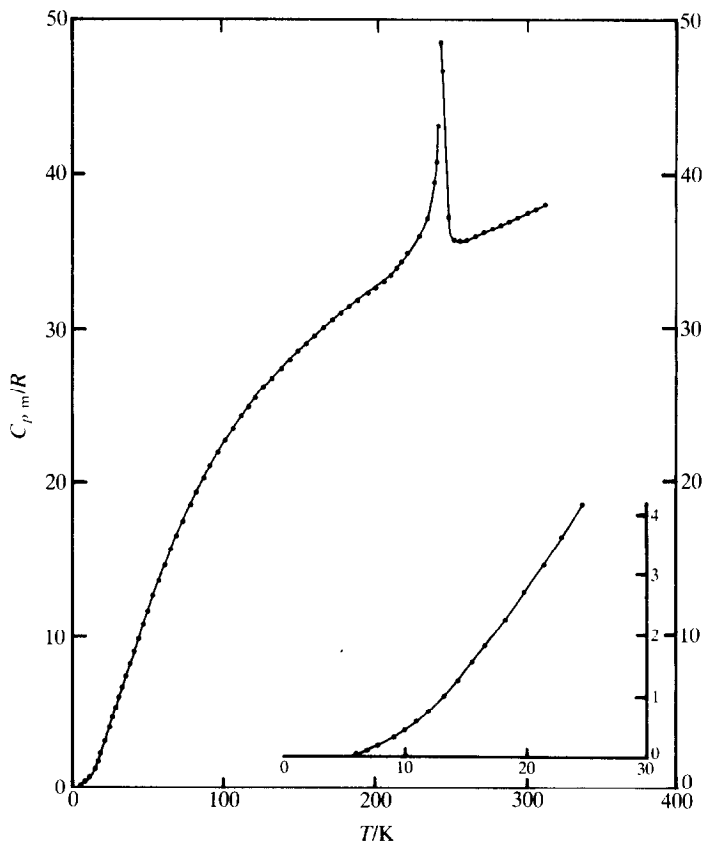


FIGURE 1. Experimental molar heat capacities $C_{p,m}$ at constant pressure plotted against temperature T for $(\text{ND}_4)_2\text{SnCl}_6$. The region below 20 K is enlarged in the lower right-hand corner.

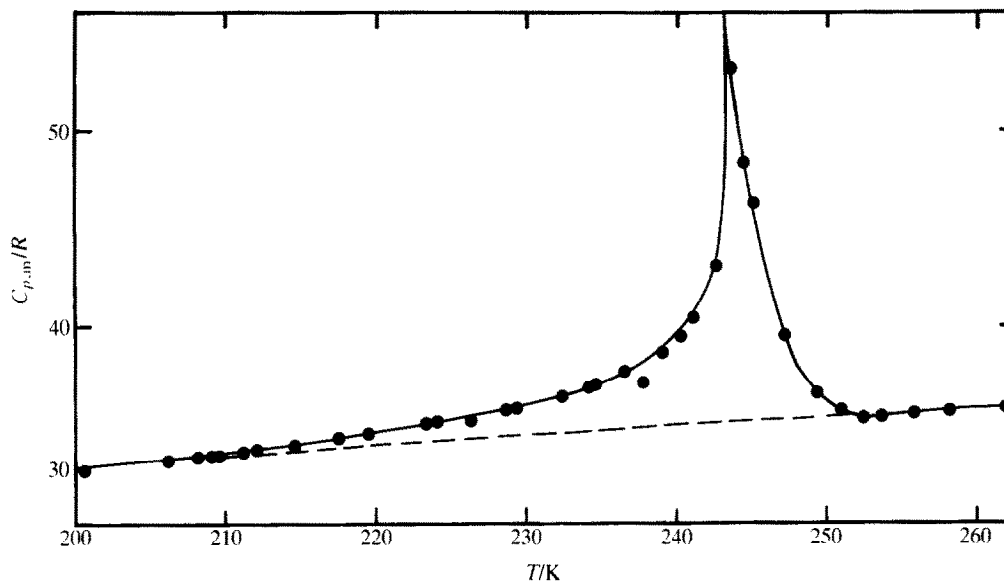


FIGURE 2. Experimental molar heat capacities $C_{p,m}$ of $(\text{ND}_4)_2\text{SnCl}_6$ at constant pressure plotted against temperature T through the anomalous region from 200 to 260 K. ---, The lattice heat capacity.

diverged gradually from the points accepted as the final values, resulting in a 1 per cent lowering of $C_{p,m}$ at 300 K. Cooling the sample below 195 K yielded reproducible values of $C_{p,m}$ above 200 K. The thermal history of our $(\text{ND}_4)_2\text{SnCl}_6$ sample followed that recommended by Morphee and Staveley in order to obtain reproducibility of the heat capacity, and no differences are apparent between the $C_{p,m}$ values in our five series of runs.

Integration of the smoothed values for heat capacity and for the enthalpy and entropy increments through the anomaly yielded the thermodynamic functions.

TABLE 2. Summary of thermophysical quantities through the anomaly for $(\text{ND}_4)_2\text{SnCl}_6$ ($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$). T_1 and T_2 denote the beginning and ending temperatures respectively for the enthalpy determinations through the anomaly

Series	No. of determinations	T_1/K	T_2/K	$\frac{\Delta_{T_1}^{T_2} H_m^\circ}{R \cdot \text{K}}$	$\frac{\Delta_{195\text{K}}^{256\text{K}} H_m^\circ}{R \cdot \text{K}}$	$\frac{\Delta_{195\text{K}}^{256\text{K}} S_m^\circ}{R}$
II	3 ^a	208.091	265.136	2095.4	2196.0	
V	2 ^b	192.723	267.342	2678.7	2198.8	
		Graphical integration:				9.752 ± 0.006
		Mean:			2197.4 ± 1.4	
		Lattice contribution:			2082.1 ± 1.5 ^d	9.270 ± 0.007
		$\Delta_{\text{trs}} H_m^\circ / (R \cdot \text{K})$:			115.3 ± 2.9	
		$\Delta_{\text{trs}} S_m^\circ / R$:				0.482 ± 0.013

^a Including determination A of ΔH . ^b Including determination B of ΔH . ^c Not included in the mean value. ^d Error due to the uncertainty in the position of the lattice-heat-capacity curve through the region of the anomaly.

TABLE 3. Standard molar thermodynamic quantities for $(\text{ND}_4)_2\text{SnCl}_6$; $M = 375.521 \text{ g} \cdot \text{mol}^{-1}$,
 $p^\circ = 101.325 \text{ kPa}$, $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $\Phi_m^\circ = \Delta_0^T S_m^\circ - \Delta_0^T H_m^\circ / T$

T K	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{R \cdot \text{K}}$	$\frac{\Phi_m^\circ}{R}$	T K	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{R \cdot \text{K}}$	$\frac{\Phi_m^\circ}{R}$
5	(0.0535)	(0.0183)	(0.0706)	(0.0042)	200	32.69	38.11	3938.6	18.42
10	0.492	0.151	1.15	0.036		^a (32.67)	(38.11)	(3938.5)	(18.42)
15	1.455	0.512	5.77	0.127	210	33.57	39.72	4269.8	19.39
20	2.769	1.105	16.27	0.292		(33.35)	(39.72)	(4268.6)	(19.39)
25	4.232	1.878	33.75	0.528	220	34.58	41.31	4610.4	20.35
30	5.785	2.787	58.79	0.827		(33.94)	(41.28)	(4605.1)	(20.35)
35	7.298	3.790	91.50	1.176	230	36.01	42.87	4962.7	21.30
40	8.857	4.865	131.9	1.568		(34.47)	(42.81)	(4947.1)	(21.30)
45	10.31	5.991	179.8	1.995	240	39.58	44.47	5337.3	22.23
50	11.75	7.151	234.9	2.452		(34.93)	(44.28)	(5294.1)	(22.23)
55	13.11	8.335	297.1	2.933	250	35.96	46.19	5759.6	23.15
60	14.51	9.535	366.2	3.433		(35.34)	(45.71)	(5645.4)	(23.15)
65	15.70	10.75	441.8	3.949	260	35.72	47.59	6116.1	24.07
70	16.79	11.95	523.0	4.477		(35.72)	(47.11)	(6000.8)	(24.05)
75	17.86	13.14	609.6	5.015	270	36.08	48.95	6475.1	24.96
80	18.93	14.33	701.6	5.561		(36.08)	(48.47)	(6359.8)	(24.94)
85	19.93	15.51	798.8	6.111	280	36.48	50.26	6837.8	25.84
90	20.83	16.67	900.7	6.666		(36.48)	(49.78)	(6722.5)	(25.79)
95	21.64	17.82	1006.9	7.223	290	36.93	51.55	7204.9	26.71
100	22.41	18.95	1117.1	7.781		(36.93)	(51.07)	(7089.6)	(26.64)
105	23.19	20.06	1231.1	8.340	300	37.42	52.81	7576.6	27.56
110	23.92	21.16	1348.9	8.898		(37.42)	(52.33)	(7461.3)	(27.48)
115	24.59	22.24	1470.2	9.454	310	37.78	54.05	7952.6	28.39
120	25.25	23.30	1594.8	10.01		(37.78)	(53.57)	(7837.3)	(28.31)
125	25.90	24.34	1722.7	10.56	320	38.18	55.25	8332.4	29.21
130	26.50	25.37	1853.7	11.11		(38.18)	(54.77)	(8217.1)	(29.11)
135	27.03	26.38	1987.5	11.66	330	38.58	56.43	8716.2	30.02
140	27.56	27.37	2124.0	12.20		(38.58)	(55.95)	(8600.9)	(29.91)
145	28.06	28.35	2263.0	12.74	340	38.99	57.59	9104.0	30.81
150	28.54	29.31	2404.5	13.28		(38.99)	(57.11)	(8988.7)	(30.69)
155	29.00	30.25	2548.3	13.81	350	39.40	58.73	9496.0	31.60
160	29.46	31.18	2694.5	14.34		(39.40)	(58.25)	(9380.7)	(31.47)
170	30.32	32.99	2993.4	15.38	298.15	37.41	52.58	7507.5	27.40
180	31.12	34.75	3300.7	16.41		± 0.04	± 0.07	± 11.2	± 0.04
190	31.89	36.45	3615.7	17.42					

^a Quantities in parentheses represent the values taken on the lattice curve.

Values of $C_{p,m}/R$ and the derived functions are presented at selected temperatures in table 3. The corresponding values for the lattice curve beneath the λ -shaped anomaly, drawn by a smooth extrapolation, are shown in parentheses. The heat capacities of $(\text{NH}_4)_2\text{SnCl}_6$ below 7 K were obtained by fitting our experimental values below 20 K to the limiting form of the Debye equation, using a plot of $C_{p,m}/T$ against T^2 and extrapolating to $T \rightarrow 0$. A plot of $C_{p,m}/T^3$ against T^2 was attempted but an insufficient number of points lay below the maximum value of $C_{p,m}/T^3$. It is the linear portion of the curve below the maximum $C_{p,m}/T^3$ that is needed for the extrapolation to $T \rightarrow 0$.

The finding of a λ -shaped anomaly in $(\text{ND}_4)_2\text{SnCl}_6$ was not anticipated, and contrasts with the neutron-scattering measurements of Powell *et al.*,⁽¹²⁾ who stated that no transition was present, and with the analogous undeuterated ammonium salt. $(\text{NH}_4)_2\text{SnCl}_6$ shows no transition in its heat capacity, although a slight anomaly appears between 235 and 245 K.⁽²⁾ The absence of a phase transition in the undeuterated salt is reinforced by several experiments. In a low-temperature X-ray powder experiment using a Guinier-type diffractometer, no deviations from the cubic symmetry present at room temperature⁽³⁻⁵⁾ were found down to 12 K.^(19,20) Proton relaxation times T_1 and $T_{1,\rho}$ measured from 60 to 500 K show no signs of any anomaly,⁽⁶⁾ nor do the studies on neutron scattering.^(7,8) The conflicting reports of a phase transition in $(\text{NH}_4)_2\text{SnCl}_6$ at approximately 265 K,^(21,22) based on nuclear-quadrupole-resonance studies, have been resolved: no transition is present.⁽²³⁾ Unexpected dielectric relaxation was noted between 23 and 30.5 K in both $(\text{NH}_4)_2\text{SnCl}_6$ and $(\text{ND}_4)_2\text{SnCl}_6$, a phenomenon attributed to hydroxyl impurities.⁽²⁴⁾ However, this relaxation is not evident from the heat-capacity curves in this temperature region. K_2SnCl_6 has a λ -type transition in its heat capacity around 262 K,⁽²⁾ as it changes from a cubic to a tetragonal structure,^(3,12) followed by another transition to a monoclinic phase at 255 K.⁽¹²⁾

For our $(\text{ND}_4)_2\text{SnCl}_6$, an ND_4Cl impurity could induce a λ -type transition depending on the mole fraction, since such a transition is present in pure ND_4Cl at approximately 250 K.⁽²⁵⁾ Assuming ammonium chloride to be responsible for the anomaly, an estimate has been made of the amount needed to produce the required $\Delta_{\text{trs}}H_m^\circ = 115.3 \cdot R \cdot \text{K}$ or $\Delta_{\text{trs}}S_m^\circ = 0.482 \cdot R$ in our sample. Since neither the molar enthalpy nor entropy for ND_4Cl are given by Stephenson *et al.*,⁽²⁵⁾ the value of $\Delta_{\text{trs}}H_m^\circ = 140.5 \cdot R \cdot \text{K}$ for pure NH_4Cl ,⁽²⁶⁾ has been used instead. Our sample would have had to contain about 82 mass per cent of ammonium chloride to account for the peak! However, we have shown experimentally that the impurities consist of 0.1 mass per cent of D_2O and only trace levels of NH_4Cl or ND_4Cl . For the anomaly, the ΔS_m for $(\text{ND}_4)_2\text{SnCl}_6$ amounts to $0.483 \cdot R$ or $0.7 \cdot R \cdot \ln 2$, which is consistent with a change of structure from the cubic above 244 K to one of lower symmetry below 244 K. Careful crystallographic study is now needed to resolve the discrepancy between the results of this work and those from the neutron scattering.

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