

The thermodynamics of ammonium indates

I. The heat capacity of the ammonium pentachloroindate monohydrate salt $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ from 8.5 to 349 K

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The heat capacity of ammonium pentachloroindate monohydrate $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ was measured from 8.5 to 349 K using adiabatic calorimetry. The curve of molar heat capacity against temperature is continuous, but exhibits a small anomaly at $110 < T/\text{K} < 130$. Values of the standard molar thermodynamic quantities for $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ are presented up to 345 K.

1. Introduction

Ammonium pentachloroindate monohydrate $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ serves as an ideal host lattice for the study of various cations. The host lattice provides a chemically anisotropic environment in which the guest ion is only loosely coupled to the lattice. This host has been used for electron-paramagnetic-resonance studies of vanadyl,

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molybdenyl, and chromium(III) complexes.^(1,2) Pure $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ shows unusual behaviour in its nuclear quadrupole resonance (n.q.r.). Carr *et al.*⁽³⁾ found an anomalous temperature dependence of the n.q.r. frequencies. The ^{35}Cl frequencies change only slightly between 300 and 130 K, but below 130 K two of the four ^{35}Cl lines show an anomalous temperature dependence. In addition, the ^{115}In quadrupole-coupling parameters show an unusually large temperature dependence and undergo a sharp break in slope around 140 K. Further studies of the temperature dependence of n.q.r. frequencies in ammonium indium halides have been reported by Yamada and Weiss.⁽⁴⁾

The crystal structure of $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ has been determined at room temperature by Klug *et al.*⁽⁵⁾ using a single-crystal X-ray diffraction method. The structure is orthorhombic with a , b , c values of (1.410 ± 0.005) , (1.017 ± 0.005) , and (0.716 ± 0.005) nm, respectively, $Z = 4$, and a space group P_{nma} or No 62 D_{2h}^{16} . Revised a , b , and c values⁽⁶⁾ based on our sample from the current Joint Committee for Powder Diffraction Standards (JCPDS) are (1.3967 ± 0.0002) , (1.0122 ± 0.0002) , and (0.7169 ± 0.0001) nm, respectively. Results of structure determinations are not available at other temperatures. Heat-capacity results have been published only by McElearney and Merchant⁽⁷⁾ who investigated $C_{p,m}$ at $4.4 \text{ K} < T < 33 \text{ K}$ as part of a study of the antiferromagnetic behaviour of the two isomorphous iron salts. They found two antiferromagnetic transitions in the $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ at 6.87 and 7.25 K, and only one in the $\text{K}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ at 14.1 K.

As part of our continuing study of ammonium salts, the heat capacity of $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ has been measured from 8.5 to 349 K. These results together with their interpretation are presented in this paper.

2. Experimental

Our $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ sample was prepared by evaporation at room temperature of a solution containing stoichiometric amounts of InCl_3 and NH_4Cl . The X-ray powder diffraction pattern (JCPDS #37-832) was consistent with the published crystal structure.⁽⁵⁾

The calorimetric results were taken in the Mark X cryostat, an improved version (by addition of a guard shield surrounding the adiabatic shield) of the Mark II cryostat described previously.⁽⁸⁾ The acquisition of heat capacities from about 9 to 349 K was computer assisted.^(9,10) 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 difference and 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 re-entrant well for (heater + thermometer) was loaded with $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ within a dry box. After loading, the calorimeter was evacuated and pumping was continued for several hours at room temperature until

successive weighings showed that moisture was no longer freed from the sample. Less than 10 mg of gas was evolved and removed within the first hour of pumping, suggesting removal of adsorbed moisture rather than water of hydration. Helium gas was then added to the vessel to a pressure of about 3 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 ($2.239 \text{ g} \cdot \text{cm}^{-3}$)⁽⁵⁾ derived from the single-crystal X-ray diffraction study on the salt. The mass of the $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ was 14.965556 g, *i.e.* 0.0432309 mol based on its molar mass of $346.1772 \text{ g} \cdot \text{mol}^{-1}$ calculated from the IUPAC recommended molar masses of the elements.

3. Results and discussion

The experimental molar heat capacities of our $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ sample are given in table 1, where the results are presented in order of increasing temperature. There was no evidence that the $C_{p,m}$ values depended upon the sample's thermal history. The probable errors in our heat-capacity values of the sample drop from about 1 per cent at 10 K to less than 0.15 per cent at temperatures above 30 K. The heat capacity of our empty vessel amounted to about 20 per cent of the total heat capacity at $T < 20 \text{ K}$ and about 30 per cent above 30 K.

In a comparison of our results in the region of overlap with those of McElearney and Merchant,⁽⁷⁾ substantial differences between the two sets of results are evident. The McElearney and Merchant values lie between 22 and 40 per cent above our smooth curve at $8 < T/\text{K} < 34$, as shown in figure 1. Such large systematic differences are disturbing. Upon investigation of their technique, we found that errors up to 5 per cent were introduced routinely by temperature drifts and, in addition, no corrections were made to the total heat capacity for the contributions

TABLE 1. Experimental molar heat capacity of $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ ($M = 346.177 \text{ g} \cdot \text{mol}^{-1}$; $R = 8.31441 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
8.98	0.296	25.91	3.687	70.48	17.19	144.20	29.41	220.72	33.21	294.70	34.69
10.09	0.429	28.09	4.276	75.28	18.39	150.32	29.93	226.40	33.33	300.39	34.80
11.74	0.647	30.41	4.928	80.11	19.63	156.43	30.29	232.09	33.49	306.05	35.00
12.55	0.762	32.96	5.667	84.85	20.86	162.52	30.66	237.77	33.58	311.74	35.19
13.41	0.902	35.62	6.469	90.07	22.22	168.68	31.08	243.46	33.73	317.41	35.34
14.29	1.057	38.50	7.397	95.91	24.02	174.81	31.46	249.16	33.87	323.10	35.46
15.18	1.220	41.62	8.424	101.78	25.59	180.87	31.69	254.85	33.99	328.80	35.58
16.28	1.437	44.99	9.571	107.65	26.59	186.75	31.98	260.55	34.07	334.50	35.68
17.58	1.710	48.62	10.78	113.68	27.19	192.41	32.20	266.25	34.17	340.20	35.83
18.89	1.995	52.49	12.04	119.85	27.42	198.05	32.47	271.95	34.27	345.91	35.96
20.42	2.345	56.64	13.34	125.95	27.66	203.69	32.70	277.64	34.39		
22.17	2.748	61.05	14.65	132.05	28.35	209.38	32.94	283.33	34.51		
23.92	3.177	65.73	15.93	138.09	28.96	215.07	33.10	289.02	34.58		

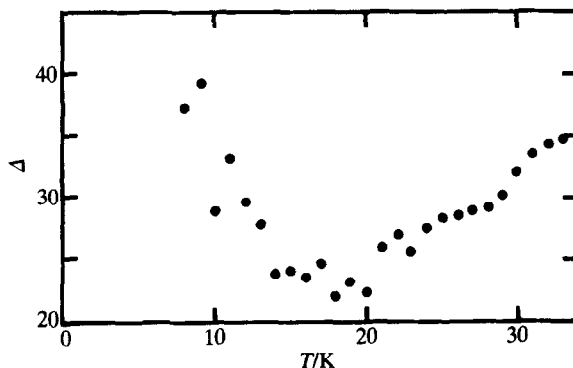


FIGURE 1. A comparison of heat-capacity results for $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ in the range $8 < T/\text{K} < 34$: $\Delta = 100\{C_{p,m}(\text{reference } 5) - C_{p,m}(\text{present work})\}/C_{p,m}(\text{present work})$.

from the thermometer, heater, and other addenda fastened directly to the sample, which was suspended without a sample container.⁽¹¹⁾ McElearney *et al.*⁽¹¹⁾ note for previous heat-capacity work on $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ that the contributions by these addenda were negligible, but they do point out that their technique must lead to heat capacities that are "slightly high". For their runs on $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$,⁽⁷⁾ the scatter in their heat-capacity points amounts to 3 to 6 per cent at $20 < T/\text{K} < 34$

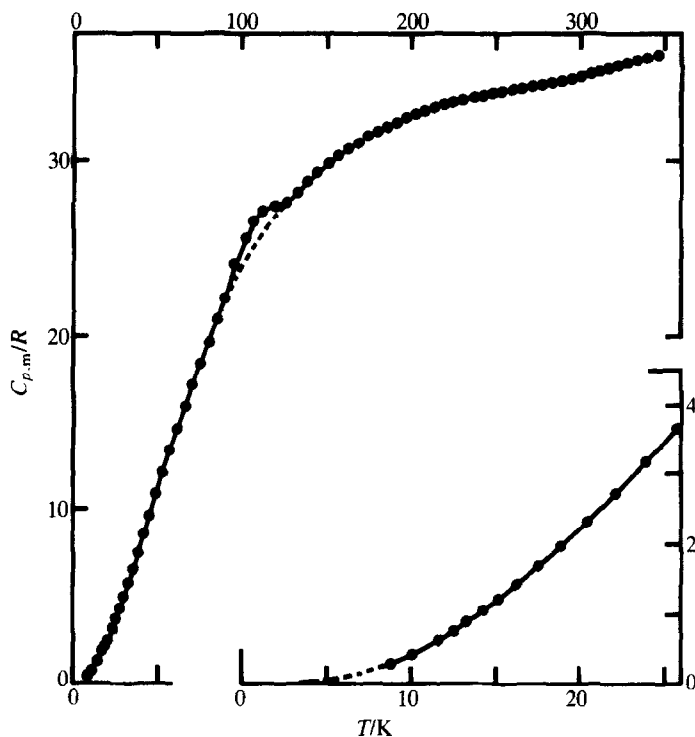


FIGURE 2. Molar heat capacities $C_{p,m}$ of $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$.

and up to 30 per cent at the lowest temperatures. Problems with temperature drift might have caused this large scatter, and the failure to correct for the background heat capacity contributes to their results lying 22 to 40 per cent above ours.

Shown in figure 2 is the $C_{p,m}/R$ curve representing our results for $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ from 9 to 350 K. The experimental points lie within 0.2 per cent of the smooth curve, which is without any signs of a λ -type transition or a hump due to fusion at the (salt + water) eutectic. If a solution were occluded within the crystal, melting would be expected to occur at approximately 270 K. However, an anomaly is present between 90 and 125 K and appears as a shoulder on the background curve. Through the temperature region of this anomaly, the times required for our sample to equilibrate after heating were normal and identical to those observed at other temperatures. The entropy associated with the hump, *i.e.* the area between the experimental continuous line and the background dotted line in figure 3, amounts to $\Delta S_m = 0.31R$ or $2.58 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

The temperature region from 90 to 125 K is also the region where the n.q.r. frequencies undergo significant change. Two of the ^{35}Cl n.q.r. frequencies show discontinuities in slope beginning at 125 K. One of the chlorine atoms whose n.q.r. is normal is that at the lowest frequency, which is the one most probably hydrogen

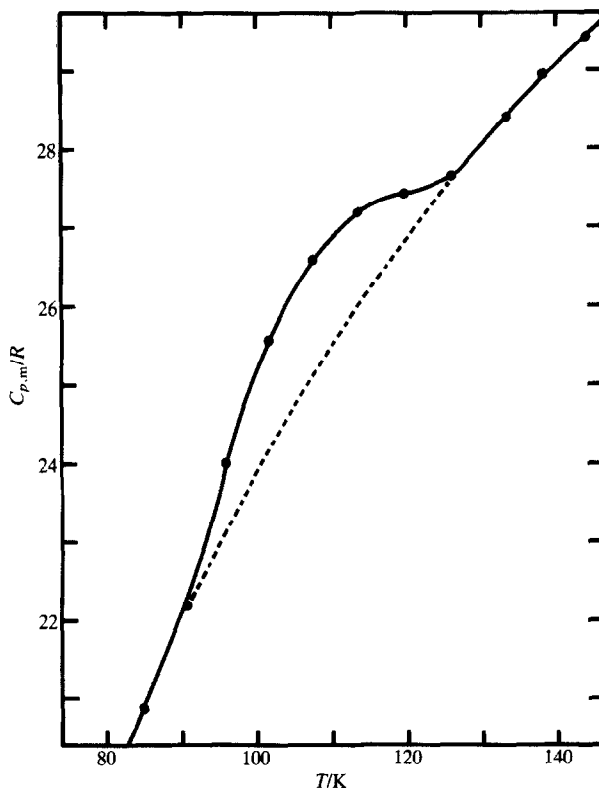


FIGURE 3. Molar heat capacities $C_{p,m}$ of $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ in the vicinity of the anomaly.

bonded⁽⁴⁾ to the H₂O molecules in the anion complex [InCl₅ · H₂O]²⁻. The slope of the quadrupole-coupling parameters with respect to temperature for ¹¹⁵In becomes unusually large and a break occurs at 140 K.⁽³⁾ These changes can be interpreted as signifying a phase transition. Although our heat capacities do not support this interpretation, they do suggest that changes are occurring within the crystal. In a number of ammonium compounds where NH₄⁺ rotation is known to cause peaks in the heat-capacity curve,⁽¹²⁻¹⁸⁾ these peaks are much broader than that noted for our (NH₄)₂InCl₅ · H₂O salt. However, this does not rule out the possibility of NH₄⁺ rotation contributing to the anomaly. In K₂InCl₅ · H₂O, Wignacourt *et al.*⁽¹⁹⁾ confirmed the existence of hydrogen bonding by means of a molecular spectroscopic study. The influence of hydrogen bonding is not known within the (NH₄)₂InCl₅ · H₂O, although Cole and Garrett⁽²⁰⁾ concluded from their e.p.r. study on this salt that the water molecule is bonded to one of the indium d orbitals. This locks it into a specific orientation and does not permit H₂O rotation about the O-In bond at either 300 or 77 K. In a study of CaSnCl₆ · 6H₂O, the anomalous temperature dependence of the ³⁵Cl n.q.r. resonance required an activation energy equal to that for reorientation of the H₂O molecules.⁽²¹⁾ The absence of experimental results for crystal structure at temperatures other than room temperature, thermal expansion, and n.m.r. hamper the interpretation of the

TABLE 2. Standard molar thermodynamic quantities for pure (NH₄)₂InCl₅ · H₂O; $M = 346.177 \text{ g} \cdot \text{mol}^{-1}$; $p^\circ = 101.325 \text{ kPa}$; $\Phi_m^\circ = \Delta_0^T S_m^\circ - \Delta_0^T H_m^\circ / T$; $R = 8.31441 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

T K	$C_{p,m}^\circ$ R	$\Delta_0^T S_m^\circ$ R	$\Delta_0^T H_m^\circ$ R · K	Φ_m° R	T K	$C_{p,m}^\circ$ R	$\Delta_0^T S_m^\circ$ R	$\Delta_0^T H_m^\circ$ R · K	Φ_m° R
5	(0.0571)	(0.0215)	(0.0804)	(0.0054)	130	28.09	25.43	1931.3	10.57
10	0.427	0.148	1.10	0.038	140	29.11	27.55	2217.7	11.71
15	1.197	0.452	4.98	0.120	150	29.90	29.59	2512.7	12.83
20	2.249	0.934	13.49	0.259	160	30.53	31.54	2814.9	13.94
25	3.464	1.561	27.77	0.451	170	31.14	33.41	3123.3	15.03
30	4.823	2.310	48.49	0.693	180	31.65	35.20	3437.3	16.10
35	6.302	3.162	76.30	0.982	190	32.11	36.92	3756.2	17.16
40	7.902	4.106	111.8	1.311	200	32.55	38.58	4079.4	18.19
45	9.598	5.133	155.6	1.676	210	32.95	40.18	4407.0	19.20
50	11.22	6.227	207.6	2.075	220	33.20	41.72	4737.8	20.18
55	12.85	7.372	267.8	2.503	230	33.43	43.20	5070.9	21.15
60	14.36	8.554	335.8	2.957	240	33.63	44.63	5406.3	22.10
65	15.74	9.758	411.0	3.434	250	33.89	46.01	5744.0	23.03
70	17.03	10.97	492.9	3.929	260	34.07	47.34	6083.8	23.94
75	18.34	12.19	581.3	4.439	270	34.24	48.63	6425.4	24.83
80	19.61	13.41	676.2	4.962	280	34.43	49.88	6768.8	25.70
85	20.91	14.64	777.5	5.495	290	34.61	51.09	7114.0	26.56
90	22.22	15.87	885.3	6.037	300	34.79	52.27	7460.9	27.40
95	23.54	17.11	999.7	6.588	310	35.13	53.41	7810.5	28.22
100	25.08	18.36	1121.3	7.145	320	35.40	54.53	8163.2	29.02
105	26.16	19.61	1249.7	7.709	330	35.60	55.62	8518.2	29.81
110	26.90	20.85	1382.4	8.278	340	35.82	56.69	8875.3	30.59
115	27.25	22.05	1517.9	8.851	345	35.96	57.21	9054.7	30.97
120	27.43	23.21	1654.6	9.425	298.15	34.73 ± 0.04	52.05 ± 0.08	7396.6 ± 11.1	27.24 ± 0.04
125	27.62	24.34	1792.2	9.999					

anomaly in $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$. Only a limited number of the expected i.r. and Raman frequencies are available and these have been reported only at room temperature.⁽²²⁻²⁴⁾

Values of the smoothed heat capacities and associated thermodynamic quantities obtained by integration of the smoothed results for $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ are presented at selected temperatures in table 2. The heat capacities below 8 K were obtained by fitting 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 not used because our results do not extend to temperatures low enough to pass below the maximum value of $C_{p,m}/T^3$. It is only below this peak that the curve becomes linear to allow the extrapolation to $T \rightarrow 0$.

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