The thermodynamics of ammonium scheelites

IV. Heat capacity of ammonium metaperiodate NH$_4$IO$_4$ from 8 to 324 K

R. JULIAN C. BROWN,
Department of Chemistry, Queen's University,
Kingston, Ontario, K7L 3N6, Canada

JANE E. CALLANAN,
Centre for Chemical Engineering, National Bureau of Standards,
Boulder, Colorado 80303, U.S.A.

THOMAS L. HASLETT,
c/o Department of Chemistry, Queen's University,
Kingston, Ontario, K7L 3N6, Canada

RON D. WEIR,[a]
Department of Chemistry and Chemical Engineering,
Royal Military College of Canada,
Kingston, Ontario, K7K 5LO, Canada,

and EDGAR F. WESTRUM, JR.
Department of Chemistry, University of Michigan,
Ann Arbor, Michigan 48109, U.S.A.

The heat capacity of the scheelite salt ammonium metaperiodate, NH$_4$IO$_4$, was measured from 8 to 324 K using adiabatic calorimetry. The heat capacity against temperature curve shows an excess with a maximum around 200 K as is typical of other ammonium scheelites. A small peak in the curve near 270 K resulted from melting a saturated aqueous solution trapped in the lattice. Values of the standard molar thermodynamic quantities for NH$_4$IO$_4$ are presented up to 320 K. Values for $C_{p,m}^\circ(298.15\ \mathrm{K})/R$, $\Delta_0^T S_m^\circ(298.15\ \mathrm{K})/R$, and $\Phi_m^\circ(298.15\ \mathrm{K}, 0)/R$ are (18.58 ± 0.02), (23.03 ± 0.04), and (11.20 ± 0.02), respectively.

1. Introduction

The tetragonal ammonium scheelites [I4$_1$/a or No. 88 C$_{4b}^6$] are well known for exhibiting unusual behaviour in nuclear quadrupole resonance (n.q.r.), thermal expansion, Raman spectroscopy, and heat capacity. These scheelites, including undeuterated ammonium perrhenate and periodate, are the only known substances to show positive values for the variation $(\partial v/\partial T)_p$ of the ^{187}Re and ^{127}I n.q.r.

[a] To whom correspondence should be addressed.

frequency v with respect to temperature as well as of that $(\partial v/\partial p)_T$ with respect to pressure.[1-4] In all other materials that have been studied, a positive $(\partial v/\partial T)_p$ is accompanied by a negative $(\partial v/\partial p)_T$. In addition, the positive pressure coefficients are very large.

The thermal expansivities for the ammonium perrhenates and periodates are also anomalous.[1,5] The large negative coefficients along the a-axis and large positive coefficients along the c-axis result in the volume of the unit cell remaining constant to within 1 per cent from 57 K to room temperature. The lattice is highly anisotropic.

Heat-capacity studies show a large excess molar heat capacity in NH_4ReO_4 and ND_4ReO_4 with a maximum around 200 K in each compound,[6,7] but none in the heat capacities of $KReO_4$,[6] and KIO_4.[8] The anomalous excess heat capacity involves the NH_4^+ ion, but as shown in the previous publication in this series,[9] a significant portion of the excess is the contribution of the $(C_{p,m} - C_{V,m})$ correction term for the anisotropic lattice.

Heat capacities for NH_4IO_4 are useful in assessing molecular motion within its solid phase and since none has been published, their measurement was undertaken. It should be noted that figure 3 in reference 10 depicting the heat capacity against temperature for NH_4IO_4 is actually for H_5IO_6.[11] The objective of this paper is to set out our heat-capacity findings for the interval 8.6 to 324 K.

2. Experimental

The NH_4IO_4 sample was prepared by recrystallization from a solution of periodic acid H_5IO_6 to which NH_3 had been added. The product was characterized by X-ray diffraction and shown to be NH_4IO_4. The periodic acid was supplied by Research Organic/Inorganic Chemical Corp.†

The calorimetric results were obtained in the Mark X cryostat which is an improved version (by addition of a guard shield surrounding the adiabatic shield) of the Mark II cryostat already described.[12] The calibration of the thermometer against the IPTS–48, revised in 1960, above 90 K, against the U.S. National Bureau of Standards (N.B.S.) provisional scale from 10 to 90 K, and below 10 K, have been described previously.[13] Measurements of mass, current, potential, and time were based upon calibrations done at the N.B.S. The acquisition of heat capacities from 8 to 324 K was assisted by computer,[14,15] programmed for a series of determinations. During the drift periods, both the calorimeter temperatures and the first and second derivatives of temperature with respect to 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 duration of the heating interval were determined. Also recorded were the apparent heat capacity of the system including the calorimeter, heater, thermometer, and sample.

† Materials and apparatus are identified in this paper in order to describe adequately the experimental procedure. Such identification does not imply recommendation nor endorsement, nor does it imply that the materials identified are necessarily the best available for the purpose.

A gold-plated copper calorimeter (laboratory designation W–139) with four internal vertical vanes and a central re-entrant well for the (heater + thermometer) was loaded with $\mathrm{NH_4IO_4}$. After loading, the calorimeter was evacuated and pumping was continued for several hours until water was no longer evolved from the sample. Helium gas was then added to the vessel to a pressure of about 3 kPa at 300 K to facilitate thermal equilibration. The vessel was then sealed by means of an annealed gold gasket pressed tightly on to the 5 mm diameter stainless-steel knife edge of the calorimeter top using a screw closure.

Buoyancy corrections were calculated using a crystallographic density of $3.072\ \mathrm{g\cdot cm^{-3}}$ derived from X-ray studies[5] on single crystals of $\mathrm{NH_4IO_4}$. The mass of $\mathrm{NH_4IO_4}$, which was not corrected for impurities, amounted to 25.9396 g, *i.e.* 0.124292 mol based on its molar mass of $208.9406\ \mathrm{g\cdot mol^{-1}}$.

3. Results and discussion

The experimental molar heat capacities of our $\mathrm{NH_4IO_4}$ sample are given in table 1. There was no evidence that the $C_{p,\,\mathrm{m}}$ values depend on the thermal history of the sample so that our results are presented in order of increasing temperature. The probable errors are estimated to drop from about 2 per cent at 7 K to less than 1 per cent at 15 K and to less than 0.15 per cent at higher temperatures.

The upper curve in figure 1 is the $C_{p,\,\mathrm{m}}$ for our $\mathrm{NH_4IO_4}$ from about 8 to 324 K. The peak in the curve with a maximum between 270 and 280 K is the result of melting a saturated aqueous salt solution trapped in the lattice. By interpolating the background heat-capacity curve from about 262 to 284 K, the excess enthalpy associated with the anomaly was determined. The $\mathrm{H_2O}$ impurity amounted to 0.097 mass per cent. The experimental $C_{p,\,\mathrm{m}}$ values for our $\mathrm{NH_4IO_4}$ sample shown in table 1 were not adjusted for this impurity.

However, our experimental heat capacities for use in determining the various thermodynamic quantities have been corrected for the 0.097 mass per cent impurity

TABLE 1. Experimental molar heat capacity of $\mathrm{NH_4IO_4}$
$(M = 208.94\ \mathrm{g\cdot mol^{-1}};\ R = 8.3144\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}})$

| T/K	$C_{p,\,\mathrm{m}}/R$	T/K	$C_{p,\,\mathrm{m}}/R$	T/K	$C_{p,\,\mathrm{m}}/R$	T/K	$C_{p,\,\mathrm{m}}/R$	T/K	$C_{p,\,\mathrm{m}}/R$	T/K	$C_{p,\,\mathrm{m}}/R$
8.62	0.09407	20.83	0.9918	56.76	4.726	122.04	11.67	193.22	16.65	266.98	18.17
9.32	0.1220	22.39	1.145	61.42	5.240	127.53	12.22	198.89	16.78	272.53	19.78
10.13	0.1550	24.17	1.321	62.85	5.401	132.37	12.66	204.56	16.89	278.24	18.68
10.95	0.1938	25.96	1.501	68.38	6.008	137.22	13.12	210.24	16.99	284.18	18.34
11.79	0.2402	27.98	1.708	73.10	6.510	142.77	13.63	215.93	17.08	289.99	18.43
12.63	0.2921	30.23	1.920	77.90	7.042	148.32	14.08	221.62	17.15	295.72	18.53
13.49	0.3517	33.26	2.246	82.73	7.598	153.88	14.54	227.31	17.22	301.42	18.67
14.36	0.4166	36.48	2.577	87.58	8.145	159.46	14.96	233.01	17.30	307.12	18.80
15.25	0.4867	39.18	2.854	92.47	8.674	165.06	15.35	238.70	17.39	312.81	18.92
16.14	0.5616	41.95	3.140	97.39	9.235	170.66	15.70	244.38	17.52	318.50	19.10
17.04	0.6395	45.19	3.481	107.02	10.12	176.28	15.98	250.00	17.61	324.15	19.54
18.17	0.7392	48.87	3.872	110.83	10.48	181.92	16.24	255.62	17.72		
19.50	0.8639	52.57	4.261	116.55	11.13	187.56	16.49	261.30	17.87		
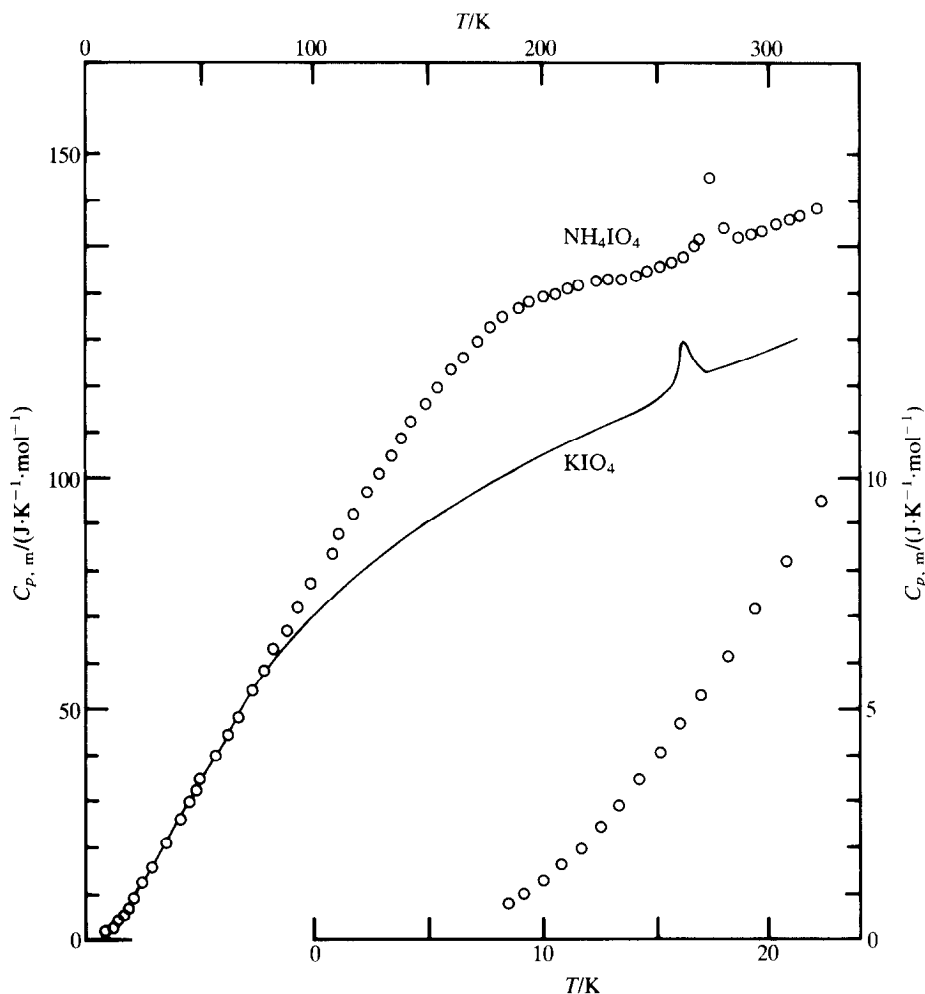
FIGURE 1. Molar heat capacities of NH_4IO_4 (upper curve) and KIO_4 (lower curve).

using the $C_{p,m}$ values for ice given by Giauque and Stout.[14] These corrections lowered our $C_{p,m}$ values for NH_4IO_4 by about 0.15 per cent up to 200 K, by 0.24 per cent between 200 and 260 K, and by about 0.48 per cent above 260 K. Values of the corrected heat capacities and resulting thermodynamic quantities obtained by integration of the smoothed results for pure NH_4IO_4 are presented at selected temperatures in table 2. The heat capacities below 8 K were obtained by fitting our experimental values below 18 K to the limiting form of the Debye equation, using a plot of $C_{p,m}/T$ against T^2 and extrapolating to $T \to 0$. 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 the linear portion of the curve below the maximum $C_{p,m}/T^3$ that is needed for the extrapolation to $T \to 0$.

TABLE 2. Standard molar thermodynamic quantities for pure NH_4IO_4
$\{M = 208.94\ \text{g}\cdot\text{mol}^{-1};\ p^\circ = 101.325\ \text{kPa}:$

$$\Phi_m^\circ(T,0) \overset{\text{def}}{=} -\Delta_0^T H_m^\circ/T + \Delta_0^T S_m^\circ;\quad R = 8.3144\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\}$$

$\dfrac{T}{K}$	$\dfrac{C_{p,m}^\circ}{R}$	$\dfrac{\Delta_0^T S_m^\circ}{R}$	$\dfrac{\Delta_0^T H_m^\circ}{R\cdot K}$	$\dfrac{\Phi_m^\circ(T,0)}{R}$	$\dfrac{T}{K}$	$\dfrac{C_{p,m}^\circ}{R}$	$\dfrac{\Delta_0^T S_m^\circ}{R}$	$\dfrac{\Delta_0^T H_m^\circ}{R\cdot K}$	$\dfrac{\Phi_m^\circ(T,0)}{R}$
5	(0.0192)	(0.00722)	(0.0277)	(0.00168)	140	13.35	10.60	871.3	4.382
10	0.149	0.0511	0.387	0.0124	150	14.20	11.55	1009.1	4.828
15	0.453	0.164	1.84	0.0407	160	14.96	12.50	1154.9	5.278
20	0.904	0.352	5.28	0.0901	170	15.64	13.42	1308.0	5.730
25	1.376	0.603	10.92	0.1650	180	16.19	14.34	1467.3	6.183
30	1.898	0.897	19.10	0.2608	185	16.38	14.78	1548.5	6.409
35	2.427	1.229	29.91	0.3743	190	16.54	15.21	1630.9	6.635
40	2.936	1.586	43.32	0.5029	195	16.66	15.65	1713.9	6.860
45	3.460	1.962	59.32	0.6436	200	16.78	16.07	1797.5	7.087
50	3.991	2.354	77.94	0.7945	205	16.86	16.49	1881.7	7.310
55	4.517	2.758	99.21	0.9545	210	16.96	16.90	1965.9	7.534
60	5.090	3.175	123.3	1.122	220	17.09	17.69	2136.1	7.977
65	5.647	3.605	150.1	1.297	230	17.22	18.45	2308.0	8.417
70	6.168	4.042	179.6	1.477	240	17.38	19.18	2480.6	8.850
75	6.700	4.486	211.8	1.662	250	17.57	19.91	2655.6	9.278
80	7.279	4.937	246.7	1.853	260	17.74	20.59	2832.4	9.700
85	7.847	5.395	284.6	2.047	270	17.98	21.26	3011.0	10.12
90	8.394	5.860	325.1	2.247	280	18.17	21.93	3191.5	10.53
95	8.948	6.328	368.5	2.449	290	18.35	22.56	3374.3	10.93
100	9.457	6.800	414.5	2.654	300	18.56	23.19	3558.9	11.33
110	10.39	7.744	513.8	3.074	310	18.77	23.81	3747.1	11.72
120	11.45	8.695	622.9	3.502	320	18.99	24.42	3937.1	12.11
130	12.42	9.650	742.3	3.939	298.15	18.50 ± 0.02	23.09 ± 0.04	3528.8 ± 5.4	11.26 ± 0.02

The lower curve in figure 1 is $C_{p,m}$ for KIO_4,[8] which lies well below that for NH_4IO_4 at temperatures greater than 150 K. The excess heat capacity for NH_4IO_4 is typical of the ammonium scheelites and may be accounted for by the motion of NH_4^+ and by the anisotropy of the lattice, which is induced when NH_4^+ replaces K^+.

REFERENCES

1. Brown, R. J. C.; Smeltzer, J. G.; Heyding, R. D. *J. Magn. Reson.* **1976**, 24, 269.
2. Segel, S. L.; Brown, R. J. C.; Heyding, R. D. *J. Chem. Phys.* **1978**, 69, 3435.
3. Gillies, G. C.; Brown, R. J. C. *Can. J. Chem.* **1976**, 54, 2266.
4. Segel, S. L.; Brown, R. J. C. *J. Chem. Phys.* **1979**, 70, 3840.
5. Segel, S. L.; Karlsson, H.; Gustavson, T.; Edstrom, K. *J. Chem. Phys.* **1985**, 82, 1611.
6. Weir, R. D.; Staveley, L. A. K. *J. Chem. Phys.* **1980**, 73, 1386.

7. Brown, R. J. C.; Callanan, J. E.; Weir, R. D.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1986**, 18, 787.
8. Staveley, L. A. K.; Weir, R. D. *J. Chem. Thermodynamics* **1984**, 16, 165.
9. Brown, R. J. C.; Callanan, J. E.; Weir, R. D.; Westrum, E. F., Jr. *J. Chem. Phys.* **1986**, 85, 5963.
10. Brown, R. J. C.; Segel, S. L.; Weir, R. D.; Staveley, L. A. K. *Proc. Fifth Intern. Symp. NQR Spectr.* Elsevier: Amsterdam. **1979**.
11. Staveley, L. A. K.; Weir, R. D. *J. Chem. Thermodynamics* **1986**, 18, 477.
12. Westrum, E. F., Jr.; Furukawa, G. T.; McCullough, J. P. *Experimental Thermodynamics*, Vol. 1. McCullough, J. P.; Scott, D. W.: editors. Butterworths: London. **1968**, p. 133.
13. Chirico, R. D.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1980**, 12, 311.
14. Westrum, E. F., Jr. *Proceedings NATO Advanced Study Institute on Thermochemistry at Viana do Castello, Portugal.* Ribeiro da Silva, M. A. V.: editor. Reidel: New York. **1984**, p. 745.
15. Andrews, J. T. S.; Norton, P. A.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1978**, 10, 949.
16. Giauque, W. F.; Stout, J. W. *J. Am. Chem. Soc.* **1936**, 58, 1144.