

The thermodynamics of ammonium scheelites

V. Heat capacity of deuterated ammonium metaperiodate ND_4IO_4 from 8 to 329 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 and

*Department of Chemistry and Chemical Engineering, Royal Military College
of Canada, Kingston, Ontario, K7K 5L0, Canada*

EDGAR F. WESTRUM, JR.

*Department of Chemistry, University of Michigan,
Ann Arbor, Michigan 48109, U.S.A.*

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The heat capacity of the scheelite salt: deuterated ammonium metaperiodate, ND_4IO_4 , was measured from 8 to 329 K using adiabatic calorimetry. The heat capacity against temperature curve shows a broad maximum with a peak around 200 K which is typical of other ammonium scheelites. A small peak in the curve around 275 K resulted from fusion of a saturated D_2O salt solution trapped in the lattice. Values of the standard molar thermodynamic quantities for ND_4IO_4 are presented up to 330 K.

1. Introduction

The tetragonal ammonium scheelites ($14_1/a$ or No 88 C_{4b}^6) are well known for their unusual behaviour in nuclear quadrupole resonance (n.q.r.), thermal expansion, Raman spectroscopy, and heat capacity. These scheelites which include ammonium

^a To whom correspondence should be addressed.

perrhenates and periodates are the only known materials to show positive values for the variation $(\partial\nu/\partial T)_p$ of the ^{187}Re and ^{127}I n.q.r. frequency ν with temperature while at the same time having a positive value of the pressure coefficient $(\partial\nu/\partial p)_T$.⁽¹⁻⁴⁾ In all other substances studied, a positive $(\partial\nu/\partial T)_p$ is associated with a negative $(\partial\nu/\partial p)_T$. The pressure coefficients are very large, about ten times greater than in other salts.

The thermal expansivities for the ammonium perrhenates and periodates are also anomalous.^(1,5) Since the coefficient for the *c*-axis is positive and that for the *a*-axis is negative, the volume of the unit cell remains constant to within about 1 per cent from 57 K to room temperature. A highly anisotropic lattice results.

Heat-capacity work shows a large excess molar heat capacity in NH_4ReO_4 , ND_4ReO_4 , and NH_4IO_4 with a maximum around 200 K in each compound,⁽⁶⁻⁸⁾ but none in the heat capacities of KReO_4 ,⁽⁶⁾ and KIO_4 .⁽⁹⁾ This anomalous excess in the heat capacity is due in part to the NH_4^+ ion, but as shown in paper III in our series,⁽¹⁰⁾ a significant portion of the excess results from the contribution of the $(C_{p,m} - C_{v,m})$ correction term for the anisotropic lattice. In the present paper, the experimental heat capacity of ND_4IO_4 is reported from 8 to 329 K. The analysis of these results and of those for KIO_4 and NH_4IO_4 are contained in a separate manuscript to be submitted to this Journal.

2. Experimental

A sample of ND_4IO_4 was prepared in a manner similar to that previously described.⁽¹¹⁾ Ammonium metaperiodate NH_4IO_4 was purchased from Research Organic/Inorganic Chemical Corporation,† Sun Valley, California, and was recrystallized from water before use. These crystals were then dissolved in a solution containing NH_4Cl in D_2O . The D_2O was 99.8 moles per cent minimum isotropic purity. A partially deuterated product was obtained on recrystallization. This procedure, carried out in a dry atmosphere, was repeated several times. The extent of deuteration was measured by solid-state proton n.m.r. using a dilute mixture of NH_4Cl in NaCl as an intensity standard. The fraction of protons was estimated as 0.8 per cent. In addition, no peaks due to species such as ND_3H^+ were seen in the Raman spectrum. SAFETY NOTE: During preparation of a second sample of ND_4IO_4 , hot crystals of product exploded during evaporation of solvent. Drying may be achieved under a stream of dry nitrogen gas at room temperature.

The calorimetric results were determined in the Mark X cryostat, which is an upgraded version of the Mark II cryostat already described.⁽¹²⁾ A guard shield was incorporated to surround the adiabatic shield. A Leeds and Northrup capsule-type platinum resistance thermometer (laboratory designation A-5) was used for temperature measurements. The thermometer was calibrated at the U.S. National Bureau of Standards (N.B.S.) against the IPTS-1948 (as revised in 1960)⁽¹³⁾ for temperatures above 90 K, against the N.B.S. provisional scale from 10 to 90 K, and

† Certain 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.

by the technique of McCracken and Chang⁽¹⁴⁾ below 10 K. These calibrations are judged to reproduce thermodynamic temperatures to within 0.03 K between 10 and 90 K and within 0.04 K above 90 K.⁽¹⁵⁾ Measurements of mass, current, potential difference, and time were based upon calibrations done at N.B.S. The heat capacities from about 8 to 324 K were acquired with the assistance of a computer,^(16,17) programmed for a series of determinations. During the drift periods, both the calorimeter temperature 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 as well as 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.

A gold-plated copper calorimeter (laboratory designation W-99), without internal vanes but with a central re-entrant well for the (heater + thermometer), was loaded with ND_4IO_4 . After loading, the calorimeter was evacuated and pumping was continued for several hours until successive weighings showed that D_2O was no longer evolved from the sample. Less than 10 mg of gas was evolved. 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 4 mm diameter stainless-steel knife edge of the calorimeter top using a screw closure. Buoyancy corrections were calculated on the basis of a crystallographic density of $3.1603 \text{ g}\cdot\text{cm}^{-3}$ derived from the neutron-diffraction studies on the salt.⁽¹⁸⁾ The mass of ND_4IO_4 , before correction for any impurity that might have been present, amounted to 9.7203 g, corresponding to 0.045643 mol, based on its molar mass of $212.965 \text{ g}\cdot\text{mol}^{-1}$ from the 1973 atomic masses recommended by IUPAC.

3. Results and discussion

The experimental heat capacities of our ND_4IO_4 sample are presented in table 1. As there was no evidence that the $C_{p,m}$ values depended on the thermal history of the sample, they are presented in order of increasing temperature. The probable errors are estimated to decrease from about 2 per cent at 8 K to less than 1 per cent at 15 K and to less than 0.15 per cent at higher temperatures. The value of $C_{p,m}$ at 8.14 K, in error due to a lack of thermal equilibrium in the system at the start of the measurements, is presented for completeness.

The curve in figure 1 shows the $C_{p,m}/R$ of our sample from 10 to 329 K. The small peak around 275 K is a result of melting a saturated D_2O salt solution trapped in the lattice. The normal melting temperature of pure D_2O is about 276.97 K.⁽¹⁹⁾ By interpolating the background heat-capacity curve from about 270 to 284 K, the excess enthalpy associated with the anomaly was determined, which led to the calculation of the D_2O impurity of 0.03 mass per cent. The experimental $C_{p,m}/R$ values for our ND_4IO_4 sample shown in table 1 were not adjusted for this impurity.

TABLE 1. Experimental molar heat capacity of ND_4IO_4
 ($M = 212.965 \text{ g} \cdot \text{mol}^{-1}$, $R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

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	$C_{p,m}/R$
8.14	0.8963	23.59	1.292	61.79	5.961	133.84	13.750	212.69	17.538	286.68	18.604
10.49	0.1644	25.18	1.455	69.92	6.904	139.40	14.238	218.38	17.585	292.38	18.731
12.67	0.3192	26.97	1.647	74.78	7.486	144.96	14.774	224.08	17.636	298.03	18.866
13.41	0.3528	28.77	1.845	80.05	8.146	150.56	15.199	229.77	17.685	303.94	19.011
14.31	0.4201	30.81	2.033	85.14	8.791	156.14	15.670	235.46	17.722	310.15	19.147
15.19	0.4918	33.06	2.315	90.13	9.391	161.75	16.053	241.16	17.806	316.35	19.330
16.08	0.5648	35.52	2.611	95.40	9.879	167.37	16.346	246.85	17.852	322.55	19.527
16.98	0.6423	38.21	2.931	100.83	10.444	178.75	16.951	252.55	17.907	328.75	19.684
17.89	0.7225	41.35	3.300	106.31	10.994	184.30	17.154	258.24	18.006		
18.81	0.8102	44.93	3.738	111.76	11.629	189.96	17.301	263.93	18.126		
19.73	0.8981	48.54	4.184	117.23	12.143	195.64	17.352	269.62	18.236		
20.88	1.012	52.62	4.727	122.74	12.697	201.32	17.456	275.27	18.896		
22.24	1.150	57.19	5.302	128.30	13.223	207.01	17.459	280.95	18.587		

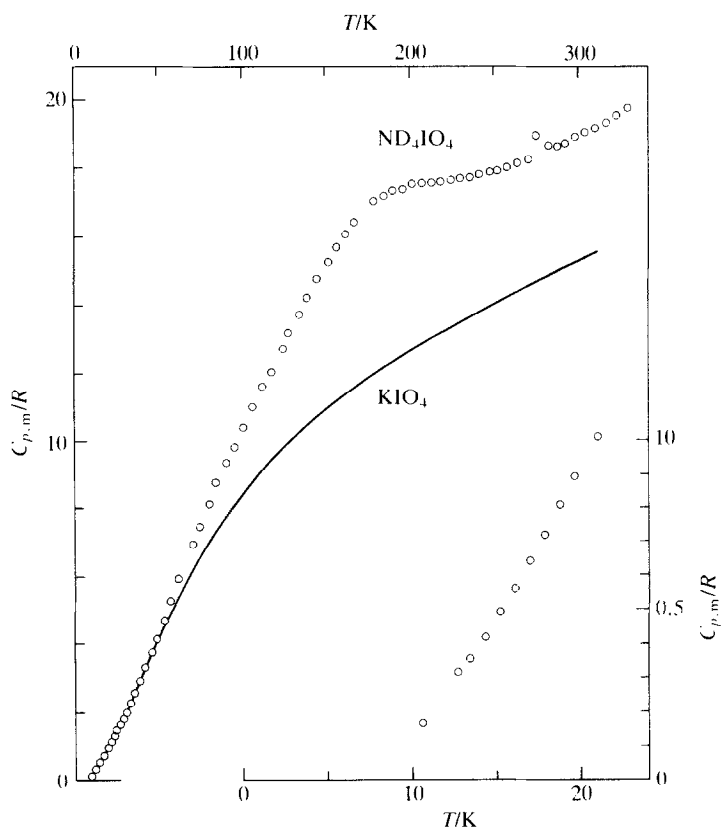


FIGURE 1. Molar heat capacities of ND_4IO_4 (upper curve) and KIO_4 (lower curve).

However, our experimental heat capacities for use in calculating the various thermodynamic properties have been corrected for the 0.03 mass per cent impurity using the $C_{p,m}$ values for solid D_2O given by Long and Kemp.⁽¹⁹⁾ It was assumed that the heat capacities of ND_4IO_4 and D_2O are additive. These corrections lowered our $C_{p,m}$ values by 0.05 per cent up to 190 K, by 0.07 per cent between 190 and 260 K, and by about 0.15 per cent above 260 K. Values of the corrected heat capacities and resulting thermodynamic quantities obtained by integration of the smoothed results for pure ND_4IO_4 are presented at selected temperatures in table 2. The heat capacities below 10 K were obtained by fitting the 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 linear portion of the curve below the maximum $C_{p,m}/T^3$ that is needed for the extrapolation to $T \rightarrow 0$.

Shown for comparison in figure 1 is the $C_{p,m}/R$ for KIO_4 ⁽⁹⁾ which lies well below that for ND_4IO_4 at temperatures above 150 K. This extra heat capacity for ND_4IO_4 is typical of other ammonium scheelites. For NH_4ReO_4 and ND_4ReO_4 , this extra heat capacity is due to both rotational motion by the ND_4^+ ion and a significant contribution caused by anisotropy in the thermal expansivity.⁽¹⁰⁾

TABLE 2. Standard molar thermodynamic quantities for pure ND_4IO_4 .
 $[M = 212.965 \text{ g} \cdot \text{mol}^{-1}; p^\circ = 101.325 \text{ kPa}; R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1};$

$$\Phi_m^{\text{def}} = \Delta_0^T S_m^\circ - \Delta_0^T H_m^\circ / T; \Delta_0^T X(T) = \{X(T) - X(0)\}$$

T/K	$C_{p,m}/R$	$\Delta_0^T S_m^\circ/R$	$\Delta_0^T H_m^\circ/(R \cdot \text{K})$	Φ_m°/R	T/K	$C_{p,m}/R$	$\Delta_0^T S_m^\circ/R$	$\Delta_0^T H_m^\circ/(R \cdot \text{K})$	Φ_m°/R
5	(0.0180)	(0.00625)	(0.0247)	(0.00132)	150	15.130	12.580	1099.8	5.244
10	0.147	0.0492	0.378	0.0115	160	15.924	13.579	1255.0	5.733
15	0.469	0.164	1.86	0.0396	170	16.537	14.565	1417.4	6.224
20	0.922	0.357	5.34	0.0901	180	17.006	15.527	1585.2	6.715
25	1.443	0.617	11.26	0.1666	185	17.163	15.984	1670.6	6.959
30	1.960	0.925	19.76	0.2657	190	17.283	16.453	1756.6	7.202
35	2.543	1.270	31.02	0.3831	195	17.415	16.898	1843.8	7.445
40	3.142	1.648	45.23	0.5166	200	17.427	17.343	1930.4	7.687
45	3.743	2.052	62.45	0.6640	205	17.464	17.776	2017.6	7.928
50	4.371	2.479	82.72	0.8236	210	17.500	18.197	2105.4	8.168
55	5.023	2.925	106.2	0.9939	220	17.584	19.003	2280.4	8.642
60	5.713	3.392	133.0	1.174	230	17.680	19.797	2456.6	9.109
65	6.341	3.873	163.2	1.363	240	17.776	20.542	2634.0	9.570
70	6.910	4.364	196.3	1.560	250	17.872	21.276	2812.0	10.025
75	7.509	4.861	232.4	1.763	260	18.017	21.974	2991.8	10.471
80	8.144	5.365	271.5	1.973	270	18.221	22.659	3172.8	10.910
85	8.764	5.878	313.8	2.187	280	18.414	23.333	3356.2	11.342
90	9.364	6.396	359.0	2.407	290	18.642	23.982	3541.4	11.766
95	9.838	6.914	407.1	2.630	300	18.895	24.620	3729.0	12.184
100	10.359	7.433	457.6	2.858	310	19.123	25.233	3919.1	12.592
110	11.417	8.468	566.4	3.320	320	19.424	25.846	4111.5	13.001
120	12.424	9.505	685.6	3.792	330	19.701	26.448	4306.9	13.398
130	13.362	10.537	814.5	4.272	298.15	18.835	24.499	3693.6	12.111
140	14.276	11.561	952.7	4.756		± 0.024	± 0.036	± 5.4	± 0.024

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R. J. C. Brown, J. E. Callanan, R. D. Weir, and E. F. Westrum, Jr.

In table 2, p. 791, the three values of $S_m^\circ(T)$ at 300, 310, and 320 K, should be 211.9, 217.1, and 222.2 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, in lieu of 220.7, 225.9, and 231.0 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively.

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.; 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. Brown, R. J. C.; Callanan, J. E.; Haslett, T. L.; Weir, R. D.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1987**, 19, 711.
9. Staveley, L. A. K.; Weir, R. D. *J. Chem. Thermodynamics* **1984**, 16, 165.
10. Brown, R. J. C.; Callanan, J. E.; Weir, R. D.; Westrum, E. F., Jr. *J. Chem. Phys.* **1986**, 85, 5963.
11. Shurvell, H. F.; Brown, R. J. C.; Korppi-Tommola, J. *J. Raman Spect.* **1980**, 9, 28.
12. Westrum, E. F., Jr.; Furukawa, G. T.; McCullough, J. P. *Experimental Thermodynamics*. Volume I. McCullough, J. P.; Scott, D. W.: editors. Butterworths: London. **1968**, p. 133.
13. Stimson, H. F. *J. Res. Natl. Bur. Stand.* **1961**, 65A, 139.
14. McCracken, F. L.; Chang, S. S. *Rev. Sci. Instrum.* **1975**, 46, 550.
15. Chirico, R. D.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1980**, 12, 311.
16. Westrum, E. F., Jr. *Proceedings NATO Advanced Study Institute on Thermochemistry at Viana do Castelo, Portugal*. Ribeiro da Silva, M. A. V.: editor. Reidel: New York. **1984**, p. 745.
17. Andrews, J. T. S.; Norton, P. A.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1978**, 10, 949.
18. Brown, R. J. C.; Segel, S. L.; Dolling, G. *Acta Cryst.* **1980**, B36, 2195.
19. Long, E. A.; Kemp, J. D. *J. Am. Chem. Soc.* **1936**, 58, 1829.