

The thermodynamics of ammonium scheelites

II. Heat capacity of deuterated ammonium perrhenate ND_4ReO_4 from 7.5 to 320 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.*

RON D. WEIR,^a

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

and 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 perrhenate ND_4ReO_4 was measured from 7.5 to 320 K without detection of any phase transition. An anomalous peak found between 270 and 280 K resulted from fusion of a saturated solution of D_2O trapped in the lattice. Values of the standard molar thermodynamic quantities for pure ND_4ReO_4 are presented up to 320 K.

1. Introduction

Ammonium perrhenate NH_4ReO_4 shows unusual behaviour in several of its properties including nuclear quadrupole resonance (n.q.r.), thermal expansion, Raman spectroscopy, and heat capacity. The temperature dependence of the ^{187}Re n.q.r. frequency ν is peculiar. Among substances possessing a positive value of $(\partial\nu/\partial T)_p$,^(1–3) ammonium perrhenate and other ammonium scheelites are the only known materials to have a positive value of the pressure coefficient $(\partial\nu/\partial p)_T$ as well.⁽⁴⁾ In all other materials that have been studied, a positive $(\partial\nu/\partial T)_p$ is associated with a negative $(\partial\nu/\partial p)_T$. For NH_4ReO_4 , $(\partial\nu/\partial T)_p$ is large and positive in the range $100\text{ K} \leq T \leq 400\text{ K}$, although outside this region $(\partial\nu/\partial T)_p$ becomes negative as

^a To whom correspondence should be addressed.

normally expected. Its pressure coefficient $(\partial v/\partial p)_T$ is very large, about ten times greater than in other salts and molecular crystals,^(4,5) and undergoes a sharp change in slope at around 197 K.⁽⁶⁾

The thermal expansivities α_c and α_a of NH_4ReO_4 are large and anomalous in the range 100 to 300 K. The coefficient for the *c*-axis is positive and that for the *a*-axis is negative, and the volume of the tetragonal unit cell is constant to within about 1 per cent.^(2,7) Spectroscopic studies have shown large shifts occurring in the frequency of the Raman lines.⁽⁸⁾ In heat-capacity studies of NH_4ReO_4 , no phase transition was found below 304 K, but a large excess molar heat capacity $\Delta C_{p,m}$ was detected with a peak around 200 K.⁽⁹⁾ This anomalous excess heat capacity involves the NH_4^+ ion, although the various models that were tested accounted for only part of the peak in $\Delta C_{p,m}$. The possibility that hydrogen bonding has some influence cannot be ruled out.⁽¹⁰⁾

To help shed light on the dynamics of the NH_4^+ motions within the lattice, studies have been done on the isotopically substituted compound ND_4ReO_4 . The temperature and pressure dependences of the ^{187}Re n.q.r. frequency in ND_4ReO_4 show behaviour similar to that observed in NH_4ReO_4 . In addition, the temperature dependence of the deuteration shift is similar to that of the pressure coefficient $(\partial v/\partial p)_T$.^(11,12) The deuteration of NH_4ReO_4 to ND_4ReO_4 is approximately equivalent to the application of pressure of 100 MPa over a wide range of temperature.

Since heat capacities have not been published for ND_4ReO_4 and because they are very helpful in determining the nature of molecular motion within the lattice, their measurement was undertaken. The objective of this paper is to report our heat-capacity findings for the range 7.5 to 320 K. Their analysis and interpretation will be published in a subsequent paper.

2. Experimental

A sample of NH_4ReO_4 was supplied by Alfa/Ventron† with minimum purity of 99.9 mass per cent from which the ND_4ReO_4 was prepared by two recrystallizations from D_2O , 99.8 per cent minimum isotopic purity. For each crystallization, the salt was evaporated to dryness in a stream of dry nitrogen gas. All operations were carried out in a dry atmosphere. At no point were the crystals permitted contact with atmospheric moisture nor were they heated to drive off any D_2O trapped within the solid. The Re n.q.r. frequency and the infra-red spectrum of the sample were consistent with >95 per cent deuteration.

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.⁽¹³⁾ The acquisition of heat-capacities from about 7 to 320 K was computer assisted.⁽¹⁴⁾ The computer was programmed for a series of determinations. During the drift periods, both the calorimeter temperature and the

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

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 current and potential of the heater 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 re-entrant well for (heater + thermometer) was loaded with ND_4ReO_4 . After loading, the calorimeter was evacuated and pumping was continued for several hours until D_2O moisture was no longer freed from the sample. Helium gas was then added to the vessel to about 3 kPa (at 100 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 derived from neutron diffraction on the salt ($4.041 \text{ g}\cdot\text{cm}^{-3}$).⁽¹⁵⁾ The mass of ND_4ReO_4 , uncorrected for any impurity that might have been present, amounted to

TABLE 1. Experimental heat capacity of the ND_4ReO_4 sample and the heat capacity of pure ND_4ReO_4

\bar{T} K	$C_{p,m}/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$ sample pure ND_4ReO_4		\bar{T} K	$C_{p,m}/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$ sample pure ND_4ReO_4		\bar{T} K	$C_{p,m}/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$ sample pure ND_4ReO_4	
7.52	1.034	1.030	59.26	49.35	48.88	197.48	155.1	153.5
8.58	1.477	1.471	62.25	51.91	51.41	200.59	155.0	153.4
9.36	1.879	1.870	67.39	56.63	56.09	203.70	154.9	153.2
10.18	2.396	2.385	72.61	61.11	60.52	206.83	154.5	152.7
11.01	2.968	2.953	77.88	65.85	65.23	209.95	153.0	151.3
11.86	3.623	3.604	83.19	70.71	70.05	213.08	152.7	150.9
12.74	4.334	4.310	88.54	75.53	74.83	216.20	152.1	150.2
13.59	5.124	5.095	93.93	79.81	79.07	219.32	151.5	149.6
14.48	6.008	5.972	99.36	84.01	83.22	222.45	151.0	149.1
15.39	6.851	6.806	104.85	88.85	88.00	225.57	150.5	148.5
16.30	7.729	7.663	110.29	92.98	92.08	229.99	150.1	148.1
17.45	8.830	8.752	115.79	97.57	96.62	235.70	150.2	148.1
18.79	10.17	10.07	121.30	102.0	100.9	241.41	150.6	148.4
20.15	11.48	11.37	126.83	106.5	105.4	247.11	150.7	148.5
21.73	13.00	12.87	132.37	110.7	109.6	252.81	151.7	149.4
23.52	14.81	14.67	137.91	115.3	114.1	258.50	153.0	150.7
25.33	16.50	16.33	143.46	120.0	118.8	264.13	159.2	—
27.37	18.50	18.31	149.02	124.6	123.3	269.89	161.1	—
29.63	20.54	20.33	154.58	129.4	128.1	274.96	238.8	—
31.90	22.78	22.55	160.16	134.0	132.7	280.63	176.9	—
34.41	25.26	25.00	165.74	138.7	137.4	287.09	160.3	154.9
37.15	27.81	27.53	171.33	143.3	141.9	292.94	162.1	156.7
40.12	30.62	30.31	176.93	147.2	145.8	298.62	164.0	158.7
43.33	33.68	33.34	182.53	151.1	149.7	302.56	163.8	158.5
46.77	37.15	36.77	188.17	153.6	152.1	308.17	164.1	158.7
50.46	40.98	40.57	191.90	154.4	152.9	313.83	166.1	160.7
54.62	45.32	44.88	194.37	155.0	153.9	319.49	166.6	161.2
56.79	47.13	46.68						

19.7070 g, *i.e.* 0.073809 mol based on its molar mass of $272.268 \text{ g} \cdot \text{mol}^{-1}$ from IUPAC 1973.

3. Results and discussion

The experimental molar heat capacities of our ND_4ReO_4 sample are given in table 1. Since there was no evidence that the $C_{p,m}$ values depend on the thermal history of the sample, the results are presented in order of increasing temperature. The probable errors are estimated to decrease from about 2 per cent at 7 K to 1 per cent at 15 K and to 0.15 per cent at high temperatures.

The upper curve in figure 1 traces the course of the $C_{p,m}$ of our sample from 7 to 320 K. The peak in the curve with a maximum between 270 and 280 K, is probably the result of fusion of a saturated D_2O salt solution trapped in the lattice. The normal melting temperature of pure D_2O is about 276.97 K.⁽¹⁶⁾ By drawing the

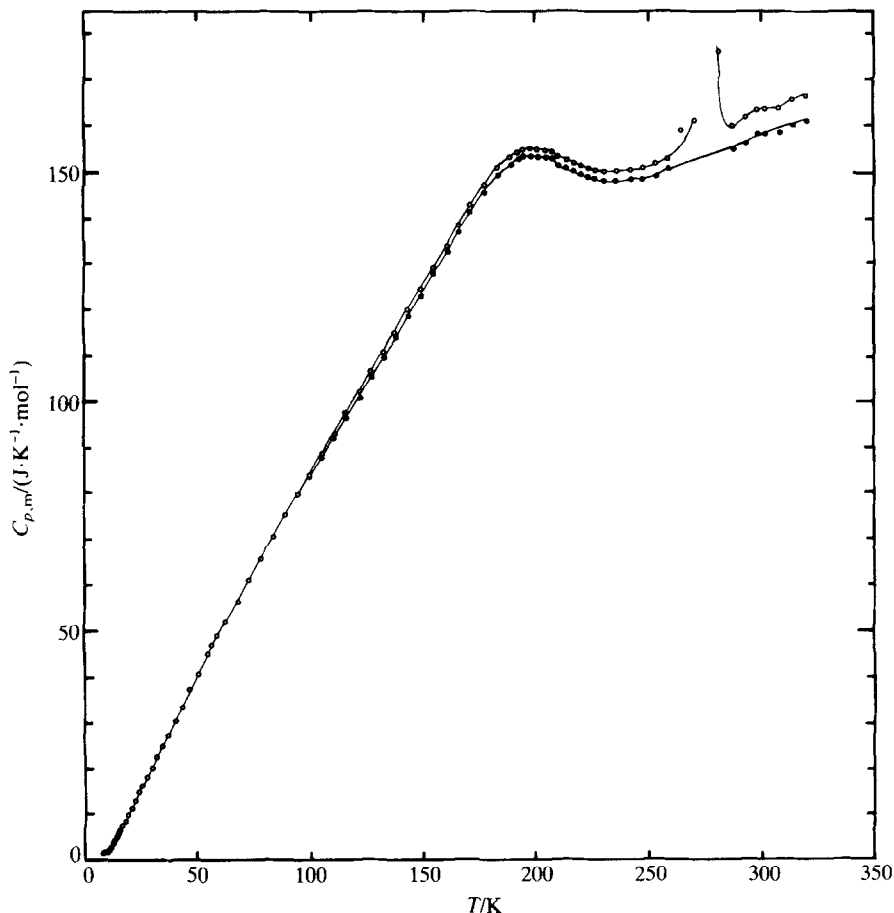


FIGURE 1. Molar heat capacity of ND_4ReO_4 . O. Sample which contained 0.59 mass per cent of trapped D_2O ; ●, corrected curve for pure ND_4ReO_4 .

TABLE 2. Standard molar thermodynamic quantities for pure ND_4ReO_4
 (molar mass: $272.27 \text{ g} \cdot \text{mol}^{-1}$; $p^\circ = 101.325 \text{ kPa}$)

T K	$C_{p,m}$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$S_m^\circ(T)$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$H_m^\circ(T) - H_m^\circ(0)$ $\text{J} \cdot \text{mol}^{-1}$	$-\{G_m^\circ(T) - H_m^\circ(0)\}/T$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
5	(0.250)	(0.0820)	(0.210)	(0.0400)
10	2.25	0.746	5.80	0.166
15	6.42	2.49	26.8	0.706
20	11.25	5.00	71.0	1.449
25	16.05	8.00	139.2	2.434
30	20.85	11.34	231.5	3.631
35	25.53	14.90	347.4	4.972
40	30.20	18.62	486.7	6.456
45	35.30	22.48	649.9	8.043
50	40.15	26.46	837.9	9.703
55	45.10	30.52	1051	11.41
60	49.50	34.63	1288	13.18
65	53.90	38.77	1546	14.99
70	58.30	42.93	1827	16.84
75	62.65	47.10	2129	18.71
80	67.15	51.29	2453	20.62
85	71.71	55.49	2801	22.55
90	76.00	59.71	3170	24.49
95	79.89	63.93	3559	26.46
100	83.75	68.14	3969	28.45
110	91.90	76.52	4848	32.44
120	99.90	84.86	5808	36.47
130	107.8	93.18	6847	40.52
140	115.8	101.5	7964	44.60
150	124.3	109.8	9164	48.69
160	132.6	118.1	10450	52.77
170	140.8	126.4	11815	56.86
180	148.1	134.6	13260	60.94
185	150.9	138.7	14005	62.99
190	152.5	142.8	14765	65.03
195	153.4	146.7	15530	67.08
200	153.4	150.6	16300	69.12
205	153.0	154.4	17065	71.15
210	151.8	158.1	17825	73.17
220	149.5	165.1	19330	77.20
230	148.2	171.7	20820	81.16
240	148.3	178.0	22300	85.07
250	149.1	184.1	23785	88.91
260	150.5	189.9	25285	92.69
270	152.3	195.7	26800	96.40
280	154.0	201.2	28330	100.0
290	155.9	206.6	29880	103.6
300	157.9	220.7	31445	115.9
310	159.7	225.9	33035	119.4
320	161.3	231.0	34560	123.0
298.15	157.5 \pm 0.2	211.0 \pm 0.3	31155 \pm 47	106.5 \pm 0.2

background heat-capacity curve from about 258 to 285 K, the excess enthalpy increase associated with the anomaly was determined. To account for the peak 0.1153 g (*i.e.* 0.59 mass per cent) of D_2O would have been fused. As a test of this attribution, several thermogravimetric analyses were made using about 11 mg of our

sample in a Mettler TA 3000. On heating each sample to about 513 K, a mass loss of 0.57 per cent occurred. When heated above this temperature the sample began to decompose and ND_3 was liberated. The mass loss of 0.57 per cent is in agreement with our attribution of D_2O as the solute.

The experimental $C_{p,m}$ values for our sample were, therefore, adjusted by subtracting the heat capacity due to the 0.1153 g of D_2O by using the results of Long and Kemp.⁽¹⁶⁾ The $C_{p,m}$ values for pure ND_4ReO_4 are also presented in table 1. The corrections amounted to 1 per cent for the region $20 \text{ K} \leq T \leq 200 \text{ K}$, up to 1.5 per cent for $200 \text{ K} \leq T \leq 260 \text{ K}$, and about 3 per cent at temperatures above those where the D_2O fused. The lower curve of figure 1 represents the $C_{p,m}$ for pure ND_4ReO_4 .

Values of the smooth heat capacities and thermodynamic quantities obtained by integration of the smoothed results for pure ND_4ReO_4 are presented at selected temperatures in table 2. The heat capacities below 8 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 $C_{p,m}T^{-3}$ in such a plot in order to use the linear portion of the curve for the extrapolation to $T \rightarrow 0$.

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