

# Molecular Freedom of the Ammonium Ion. Heat Capacity and Thermodynamic Properties of Ammonium Perchlorate from 5°–350°K\*

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The heat capacity of  $\text{NH}_4\text{ClO}_4$  has been determined by adiabatic calorimetry from 5°–350°K and found to be of simple sigmate character without thermal anomalies. The heat capacity ( $C_p$ ), entropy ( $S^\circ$ ), enthalpy function  $(H^\circ - H_0^\circ)/T$ , and Gibbs energy function  $(G^\circ - G_0^\circ)/T$  evaluated at 298.15°K from these data are 30.61, 44.02, 20.24, and  $-23.78$  cal/(gfm °K). Combination of these values with aqueous  $\text{NH}_4\text{ClO}_4$  thermochemical data suggests the absence of zero-point entropy. Comparison with the heat capacity of isostructural  $\text{KClO}_4$  permits resolution of the molecular dynamics of the ammonium ions and leads to the conclusion that these ions are restricted rotators, prevented from freely rotating by comparatively low-energy barriers.

## I. INTRODUCTION

Although Janik<sup>1</sup> and others have established that the ammonium ion does not rotate freely in simple halide salts, the prospect of such motion is enhanced by an increase in the uniformity of the crystalline field to be expected in salts with high lattice symmetry containing polyatomic anions of low charge. Morfee *et al.*<sup>2</sup> have shown that the torsional oscillations of the ammonium ions in ammonium stannichloride and stannibromide have a heat capacity contribution at 300°K which is midway between that for free rotation and classical torsional oscillations; hence these ions are restricted rotators. Although both the anion and the lattice of ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ) may have less symmetrical force fields than do the stannihalides, the charge on the anion is smaller for the perchlorate. Moreover, Smith and Levy<sup>3</sup> reported that reasonable agreement could be obtained between neutron-diffraction data for ammonium perchlorate at 300°K and a theoretical model in which the ammonium ions are assumed to be freely rotating. The second moments of Ibers<sup>4</sup> for the proton-resonance absorption line in polycrystalline ammonium perchlorate were interpreted in terms of random reorientation about random or nearly random axes. Spin-lattice relaxation times were reported to be consistent with a barrier of  $2.0 \pm 0.6$  kcal/gfm hindering reorientation. In accordance with the prediction of Wert and Marx<sup>5</sup> are the more recent

studies of Richards and Schaeffer,<sup>6</sup> which seem to indicate an even lower value for the barrier (i.e., <1 kcal).

Infrared studies by Waddington<sup>7</sup> and cold neutron scattering experiments by Rush *et al.*<sup>8</sup> also strongly support these results. Less convincing evidence in favor of an ordered hydrogen-bonded arrangement of the ammonium ions has been suggested by Venkatesan<sup>9</sup> on the basis of x-ray diffraction Fourier projections. Ammonium perchlorate thus seemed to offer unusually interesting possibilities for study.

In principle, the thermal method for deducing the extent of ionic freedom simply involves comparing the heat capacities of the ammonium salt and the corresponding isostructural alkali salt. Although ideally the rubidium compound would be a favored comparison compound because its lattice dimensions most nearly coincide with those of the ammonium compound, the potassium salt should also be acceptable, as the work on the stannihalides,<sup>2</sup> tetraphenylboron,<sup>10</sup> and pentaborate hydrates<sup>11</sup> has already demonstrated. Since the contributions from both the ammonium and alkali salts to the increment  $(C_p - C_v)$ , occasioned by the anharmonicity of the vibrational modes,<sup>12</sup> are nearly the same as are the internal vibrational and torsional modes of the anions, the expression  $[C_p(\text{NH}_4\text{ClO}_4) - C_p(\text{KClO}_4) - C_{\text{int}}(\text{NH}_4^+)]$ , adjusted as it is for the almost negligible contribution from the internal vibrational modes of the ammonium ions, should represent the torsional contribution of the ammonium ions.  $C_{\text{int}}(\text{NH}_4^+)$  can be evaluated from the frequency assignment of Wagner and Hornig.<sup>13</sup>

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<sup>1</sup> J. A. Janik, in *Proceedings of the 4th Symposium on Inelastic Scattering of Neutrons, Bombay, 1964* (International Atomic Energy Agency, Vienna, 1965), p. 243.

<sup>2</sup> R. G. S. Morfee, L. A. K. Staveley, S. T. Walters, and D. L. Wigley, *J. Phys. Chem. Solids* **13**, 132 (1960).

<sup>3</sup> H. G. Smith and H. A. Levy, American Crystallographic Association Annual Meeting, Cornell University, Ithaca, N.Y., July 1959, Abstract K-6.

<sup>4</sup> J. A. Ibers, *J. Chem. Phys.* **32**, 1448 (1960).

<sup>5</sup> C. Wert and J. Marx, *Acta Met.* **1**, 113 (1953).

<sup>6</sup> R. E. Richards and T. Schaeffer, *Trans. Faraday Soc.* **57**, 210 (1961).

<sup>7</sup> T. C. Waddington, *J. Chem. Soc.* **1958**, 4340.

<sup>8</sup> J. J. Rush, T. I. Taylor, and W. W. Havens, Jr., *Bull. Am. Phys. Soc.* **6**, 261 (1961).

<sup>9</sup> K. Venkatesan, *Proc. Indian Acad. Sci.* **46A**, 134 (1957).

<sup>10</sup> T. Davies and L. A. K. Staveley, *Trans. Faraday Soc.* **53**, 19 (1957).

<sup>11</sup> G. T. Furukawa, M. L. Reilly, and J. H. Piccirelli, *J. Res. Natl. Bur. Std.* **68A**, 381 (1964).

<sup>12</sup> R. C. Lord, Jr., *J. Chem. Phys.* **9**, 700 (1941).

<sup>13</sup> E. L. Wagner and D. F. Hornig, *J. Chem. Phys.* **18**, 296 (1950).

TABLE I. Heat capacity of ammonium perchlorate\*  
( $\text{NH}_4\text{ClO}_4$ ,  $\text{gfm}=117.497 \text{ g}$ ).

$\bar{T}$	$C_p$	$\bar{T}$	$C_p$
Series I			
		79.15	16.60
		85.87	17.55
4.85	0.0569	92.79	18.32
5.77	0.103	100.50	19.05
6.72	0.156	108.77	19.77
7.63	0.227	116.79	20.43
8.53	0.324	123.81	20.98
9.42	0.429	132.26	21.59
10.33	0.543	140.78	22.17
11.32	0.692	149.31	22.73
12.39	0.874	157.87	23.25
13.51	1.092	166.49	23.77
14.71	1.352	175.34	24.27
16.04	1.663	184.44	24.79
17.55	2.037	193.53	25.29
19.28	2.501	202.55	25.78
21.36	3.084	206.11	25.94
23.68	3.758	215.18	26.43
26.21	4.499	224.30	26.89
29.05	5.323	233.44	27.35
32.08	6.196	242.37	27.82
35.25	7.093	251.19	28.27
38.65	8.019	260.00	28.72
42.56	9.056	268.78	29.15
		277.59	29.58
Series II			
41.59	8.796	286.49	30.03
45.70	9.865	295.44	30.48
50.26	11.009	304.49	30.93
55.19	12.165	313.87	31.37
60.33	13.308	323.13	31.82
66.42	14.532	331.85	32.25
72.84	15.62	340.34	32.67
		347.14	32.97

\* Units: cal, gfm, °K.

## II. EXPERIMENTAL

### A. Ammonium Perchlorate Sample

Recrystallized reagent ammonium perchlorate, manufactured by the G. Frederick Smith Chemical Co., was sieved; crystals passing a 20-mesh screen were analyzed and subsequently used for the calorimetric measurements. Analytical determinations (in weight percent) by the Kjeldahl method indicated  $15.34 \pm 0.03$  ammonium and determination by fusion with sodium carbonate and subsequent determination of chloride revealed  $84.61 \pm 0.1$  perchlorate present (theoretical:  $\text{NH}_4=15.35$  and  $\text{ClO}_4=84.86$ ). Determinations for chlorate, bromate, chloride, hypochlorite, sulfate, non-alkali metals, moisture, and water-insoluble ash were all negative and hence below the approximately 0.001% sensitivity limits. These determinations were made in accordance with military specification methods.<sup>14</sup>

### B. Calorimetric Technique

The heat capacity measurements were made in the Mark I cryostat with platinum-resistance thermometer

<sup>14</sup> J. C. Schumacher, *Perchlorates. Their Properties, Manufacture, and Uses* (Rheinhold Publ. Corp., New York, 1960), p. 110.

A-3 and calorimeter W-9 (previously described<sup>15</sup>). A quasiadiabatic technique<sup>16</sup> was employed. All potential, resistance, mass, time, and temperature measurements were referred to standards or calibrations by the National Bureau of Standards. A calorimetric sample of 73.2932-g mass was employed. Helium exchange gas (104 torr) was sealed in the sample space to facilitate thermal equilibration. The heat capacity of the calorimeter-heater-thermometer assembly was determined in a separate set of experiments and represented between 9.2 and 32.8% of the total heat capacity over the temperature range of the measurements.

## III. RESULTS

### A. Heat Capacity

The experimental heat capacity data are presented in chronological sequence in Table I so that the magnitude of the temperature increments used may usually be inferred from the adjacent mean temperatures. These data have been adjusted for curvature and are given in terms of the defined thermochemical calorie of 4.1840 J, an ice point of 273.15°K, and a gram formula mass (gfm) of 117.497. It is evident from Fig. 1 that their temperature dependence is of simple sigmate character without thermal anomalies.<sup>17,18</sup> The probable error decreases from about 4% at 5°K to 1% at 10°K and to less than 0.1% above 20°K. Smoothed values of the

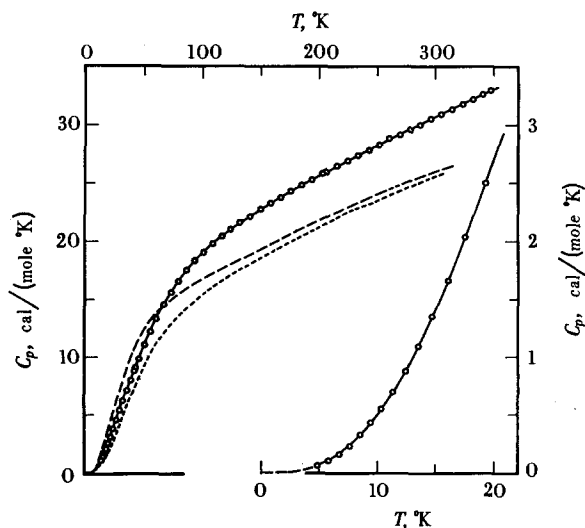


FIG. 1. The heat capacities of  $\text{NH}_4\text{ClO}_4$ ,  $\text{KClO}_4$ ,<sup>17</sup> and  $\text{CsClO}_4$ .<sup>18</sup> The  $\circ$ - $\circ$  represents the present data on  $\text{NH}_4\text{ClO}_4$ , the  $\dots$  curve and the  $---$  curve are, respectively, those of the latter two substances.

<sup>15</sup> E. Greenberg and E. F. Westrum, Jr., *J. Am. Chem. Soc.* **78**, 4526 (1956).

<sup>16</sup> E. F. Westrum, Jr., J. B. Hatcher, and D. W. Osborne, *J. Chem. Phys.* **21**, 419 (1953).

<sup>17</sup> W. M. Latimer and J. E. Ahlberg, *J. Am. Chem. Soc.* **52**, 549 (1930).

<sup>18</sup> K. S. Pitzer, W. V. Smith, and W. M. Latimer, *J. Am. Chem. Soc.* **59**, 1826 (1937).

TABLE II. Molal thermodynamic functions of ammonium perchlorate<sup>a</sup> (NH<sub>4</sub>ClO<sub>4</sub>; gfm = 117.497 g).

<i>T</i>	<i>C<sub>p</sub></i>	<i>S</i> <sup>°</sup> - <i>S</i> <sub>0</sub> <sup>°</sup>	<i>H</i> <sup>°</sup> - <i>H</i> <sub>0</sub> <sup>°</sup>	$\frac{-(G^\circ - H_0^\circ)}{T}$
5	(0.0613)	(0.0217)	(0.081)	0.006
10	0.509	0.175	1.31	0.044
15	1.416	0.538	5.94	0.142
20	2.699	1.114	16.11	0.308
25	4.148	1.870	33.19	0.543
30	5.596	2.756	57.58	0.836
35	7.006	3.725	89.10	1.179
40	8.377	4.750	127.58	1.561
45	9.697	5.814	172.78	1.974
50	10.95	6.901	224.44	2.412
60	13.23	9.104	345.65	3.344
70	15.16	11.294	487.90	4.324
80	16.73	13.424	647.6	5.329
90	18.00	15.470	821.5	6.343
100	19.03	17.422	1006.8	7.354
110	19.91	19.278	1201.6	8.354
120	20.69	21.044	1404.6	9.339
130	21.41	22.729	1615.2	10.304
140	22.10	24.341	1832.8	11.250
150	22.76	25.889	2057.1	12.174
160	23.39	27.378	2287.9	13.078
170	23.99	28.814	2524.8	13.962
180	24.55	30.201	2767.5	14.826
190	25.10	31.543	3015.8	15.671
200	25.63	32.844	3269.4	16.497
210	26.14	34.107	3528.3	17.306
220	26.66	35.335	3792.3	18.097
230	27.18	36.532	4061.5	18.873
240	27.70	37.700	4335.9	19.633
250	28.21	38.840	4615.5	20.379
260	28.72	39.957	4900.1	21.110
270	29.21	41.050	5189.7	21.829
280	29.71	42.121	5484.4	22.534
290	30.20	43.172	5783.9	23.228
300	30.70	44.205	6088.4	23.910
350	33.12	49.12	7684	27.16
273.15	29.37	41.39	5282	22.05
298.15	30.61	44.02	6032	23.78

<sup>a</sup> Units: cal, gfm, °K.

heat capacity at constant pressure are presented in Table II at selected temperatures. These have been obtained from a least-squares-fitted curve of experimental data by a high-speed digital computer program.

### B. Thermodynamic Functions

Values of the thermodynamic functions obtained by computer integration of the smoothed data are also given in Table II. The heat capacities below 5°K are extrapolated by the Debye  $T^3$  limiting law, using a  $C_p/T$  vs  $T^2$  plot. Neither isotopic mixing contributions nor nuclear spin terms are included in the entropy or Gibbs energy function, so that these are practical values suitable for equilibrium calculations. A probable error of less than 0.1% obtains above 50°K.

## IV. DISCUSSION

### A. Rotational Freedom of the Ammonium Ion

To estimate the energetics of the rotational motion of the ammonium ion from thermal data, it would be desirable to compare the heat capacities of ammonium perchlorate with isostructural alkali perchlorates on the assumption that the respective contributions from the internal and torsional oscillations of the ClO<sub>4</sub><sup>-</sup> anions and the ( $C_p - C_v$ ) increments will be nearly identical for both compounds at temperatures sufficiently high for the lattice vibrations to achieve classical values. Since the small contribution of the internal vibrational modes of the ammonium ion [ $C_{\text{int}}(\text{NH}_4^+)$ ] can be approximated from the frequency assignments of Wagner and Hornig,<sup>13</sup> the adjusted experimental difference in the heat capacities

$$\Delta C_p = C_r = [C_p(\text{NH}_4\text{ClO}_4) - C_p(\text{MClO}_4)] - C_{\text{int}}(\text{NH}_4^+),$$

can be attributed to the torsional motion of the ammonium ion. The two factors relevant in approximating the lattice heat capacity of NH<sub>4</sub>ClO<sub>4</sub> with that of an alkali perchlorate are lattice dimensions and the mass of the cation. RbClO<sub>4</sub> probably offers the best value for the former, whereas NaClO<sub>4</sub> best simulates the latter. Although heat capacity measurements on RbClO<sub>4</sub> and NaClO<sub>4</sub> are planned for other purposes, in the interim a practicable estimate can be based upon the heat capacity of isostructural KClO<sub>4</sub> (orthorhombic, *Pnma*). They are characterized by the following lattice constants:

$$\begin{aligned} &\text{for NH}_4\text{ClO}_4^9 \\ &\quad a = 9.13, \quad b = 5.79, \quad c = 7.47, \\ &\text{and} \\ &\quad \text{for KClO}_4^{10} \\ &\quad a = 8.83, \quad b = 5.65, \quad c = 7.24. \end{aligned}$$

<sup>10</sup> N. V. Mani, Proc. Indian Acad. Sci. **46A**, 143 (1957).

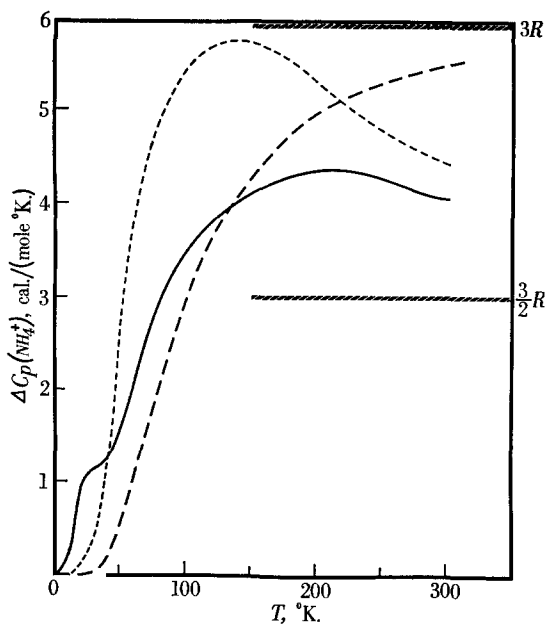


FIG. 2. The — curve is the  $\Delta C_p$  as resolved from the present heat capacity described in the text. The --- curve represents an Einstein vibrator with  $\theta_E = 300^\circ\text{K}$ , and the ... curve represents a librator with a 1.0-kcal/gfm barrier.

Each ammonium ion is surrounded by twelve oxygen atoms, six at  $2.93 \pm 0.04 \text{ \AA}$  and six at  $3.27 \pm 0.12 \text{ \AA}$ .<sup>9</sup> Four oxygen atoms of the first set may be chosen uniquely as forming weak N-H...O hydrogen bonds. In the potassium salt each cation is surrounded by twelve oxygen atoms at an average distance of 3.1  $\text{\AA}$ ; the shortest distance between oxygen and potassium atoms is 2.88  $\text{\AA}$ .<sup>18</sup> The lattice constants  $a$  and  $c$  are about 3% smaller for the potassium salt. The ionic radii of ammonium, rubidium, potassium, and sodium are 1.48, 1.48, 1.33, and 0.95  $\text{\AA}$ .<sup>20</sup>

The heat capacity of  $\text{KClO}_4$  was determined from 12° to 298°K by Latimer and Ahlberg<sup>17</sup> with a mean deviation of  $\pm 0.3\%$  except near the ice point (due to water occluded in the sample) and at the lowest temperatures. On the basis discussed, the rotational heat capacity is represented by the continuous curve of Fig. 2; the dashed curve represents an Einstein vibrator in three degrees of freedom with  $\theta_E$  equal to 300°K; the dotted curve depicts the restricted rotation of a librator (three degrees of freedom) overcoming a potential barrier of 1.0 kcal/gfm. The librational heat capacity curve is derived from the tables of Pitzer and Gwinn<sup>21</sup> with an assumed potential function of the type  $V = 0.5V_0(1 - \cos 3\phi)$  and a principal moment of inertia<sup>22</sup>

<sup>20</sup> L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structure Chemistry* (Cornell University Press, Ithaca, N.Y., 1960), 3rd ed.

<sup>21</sup> K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.* **10**, 428 (1942).

<sup>22</sup> P. S. Leung, T. I. Taylor, and W. W. Havens, Jr., *J. Chem. Phys.* **48**, 4912 (1968).

for the  $\text{NH}_4^+$  ion of  $4.826 \times 10^{-40} \text{ g cm}^2$ . The qualitative features of this plot favor the restricted-rotator model.

An early measurement of the second moment of the proton resonance (NMR) absorption line by Ibers<sup>4</sup> was interpreted as consistent with a 2.0-kcal/gfm barrier hindering the rotation of the  $\text{NH}_4^+$  ion. He stated that his barrier could be high by at most 40% if angular terms in the second moment expression are affected by protonic motion, thus allowing a barrier as low as 1.2 kcal/gfm. Richards and Schaeffer<sup>5</sup> concluded from second-moment linewidths of the NMR spectrum that the barrier is less than 1 kcal/gfm. Moreover, Ibers further deduced that ammonium perchlorate might rotate about a single axis near 20°K upon comparison with isostructural  $\text{NH}_4\text{BF}_4$  which rotates about a  $C_2$  axis at these temperatures according to the NMR (proton and fluorine) data of Pendred and Richards.<sup>23</sup> Further confirmation of this is found in the NMR data of Chiba<sup>24</sup> and that of Caron *et al.*<sup>25</sup> Stephenson *et al.*<sup>26</sup> were able to resolve the  $C_7$  for the  $\text{NH}_4^+$  and  $\text{BF}_4^-$  moieties from thermal data on  $\text{NH}_4\text{BF}_4$  and  $\text{ND}_4\text{BF}_4$  and deduced that the  $\text{NH}_4^+$  ion librates near 20°K with a barrier of 1.5 kcal/gfm. The rotational heat capacity of the  $\text{NH}_4\text{ClO}_4$  curve has a shoulder from 30° to 40°K which might be interpreted as rotation about a single axis. However, the lattice heat capacity used in deriving  $C_7$  is probably too high below 100°K, which would preclude the shoulder from rising to about the 2 cal/(gfm °K) expected for a restricted rotator. A Schottky-like shoulder of similar magnitude would also arise from the difference of two Debye functions of nearly identical characteristic temperatures (for example, if the  $\theta_D$ 's for the heat capacities of the  $\text{NH}_4\text{ClO}_4$  lattice and  $\text{KClO}_4$  differed by 50°K).

Inelastic scattering of thermal neutrons has also contributed information concerning the rotational freedom of the  $\text{NH}_4^+$  ion in  $\text{NH}_4\text{ClO}_4$ . Janik *et al.*<sup>27</sup> concluded that the  $\text{NH}_4^+$  ion at room temperature was only slightly more hindered than liquid methane on the basis of neutron scattering. Janik *et al.*<sup>28</sup> and Janik<sup>1</sup> conclude that the barrier to rotation is from 0.1 to 0.2 kcal/gfm by the same technique. Rush, Taylor, and Havens<sup>29</sup> and Rush and Taylor<sup>30</sup> deduced the barrier to rotation of the  $\text{NH}_4^+$  ion to be about 0.2 kcal/gfm from the temperature dependence of the neutron

<sup>23</sup> D. Pendred and R. E. Richards, *Trans. Faraday Soc.* **51**, 468 (1955).

<sup>24</sup> T. Chiba, *J. Chem. Phys.* **36**, 1122 (1962).

<sup>25</sup> A. P. Caron, D. J. Huettner, J. L. Ragle, D. Sherk, and T. R. Stengle, *J. Chem. Phys.* **47**, 2577 (1967).

<sup>26</sup> C. C. Stephenson, R. S. Orehtsky, and D. Smith, in *Thermodynamik Symposium in Heidelberg/Deutschland*, K. Schäfer, Ed. (AZ-Werbung-Weber Druck, Heidelberg, 1967).

<sup>27</sup> J. A. Janik, J. M. Janik, J. Mellor, and H. Palevsky, *J. Phys. Chem. Solids* **25**, 1091 (1964).

<sup>28</sup> J. M. Janik, J. A. Janik, A. Bajorek, and K. Parliński, *Phys. Status Solidi* **9**, 905 (1965).

<sup>29</sup> J. J. Rush, T. I. Taylor, and W. W. Havens, Jr., *J. Chem. Phys.* **35**, 2265 (1961); **37**, 234 (1962).

<sup>30</sup> J. J. Rush and T. I. Taylor, *J. Phys. Chem.* **68**, 2534 (1964).

scattering cross section of the hydrogen atoms. Further data of this type by Leung *et al.*<sup>22</sup> yielded a barrier of 0.4 kcal/gfm.

The heat capacity data are consistent with rotation of the  $\text{NH}_4^+$  ion against a barrier less than 1.0 kcal/mole as shown in Fig. 2.

### B. Structural and Transitional Behavior

Caron *et al.*<sup>25</sup> report that the  $a$  and  $c$  axes of  $\text{NH}_4\text{BF}_4$  expand by 10% in the range 187° to 296°K, whereas the length of the  $b$  axis remains unchanged. They report that the structure at 141°K is related to that at room temperature and is probably orthorhombic. Stammer *et al.*<sup>31,32</sup> suggest on the basis of qualitative changes in unindexed powder diffractometer scans that both  $\text{NH}_4\text{ClO}_4$  and isostructural  $\text{NH}_4\text{BF}_4$  undergo polymorphic transitions near 83°K. Neither the present heat capacity data for  $\text{NH}_4\text{ClO}_4$  nor that of Stephenson *et al.*<sup>26</sup> for  $\text{NH}_4\text{BF}_4$  lend any support to this contention. However, the rotational peak in the  $\text{NH}_4\text{BF}_4$  heat capacity curve correlates with the subtle change observed by Caron *et al.*<sup>25</sup> Similar changes in the axial lengths may obtain for  $\text{NH}_4\text{ClO}_4$  thereby making the rotational barrier temperature dependent above about 100°K, as suggested by Stephenson's analysis of the heat capacity peak for the  $\text{NH}_4^+$  ion in  $\text{NH}_4\text{BF}_4$ .

At about 513°K the orthorhombic (Phase II,  $\rho = 1.95$  g/cm<sup>3</sup>) form undergoes reversible transformation to a cubic (Phase I,  $\rho = 1.71$  g/cm<sup>3</sup>) form with the rocksalt-type structure which is presumably occasioned by the onset of relatively unrestricted rotational reorientation of the perchlorate ion.<sup>32</sup> Each alkali perchlorate (except lithium) was first shown by Vorländer and Kaascht<sup>33</sup> to undergo an enantiotropic transition to an isostructural cubic high-temperature form between 492° and 581°K. (Na = 581°K, K = 573°K, Rb = 552°K, and Cs = 492°K.) Hence, the transition temperature for the ammonium salt is seen to fall between that of rubidium and cesium as might be expected from the ionic radius. Above this temperature, exothermic decomposition ensues; a variety of products are produced.<sup>32,34,35</sup> Markowitz and Boryta<sup>36</sup> found by differential thermal analysis that  $\Delta H_t$  (II→I) =  $2.3 \pm 0.2$  kcal/gfm. More recently Krien<sup>35</sup> has found  $\Delta H_t$  to be  $2.15 \pm 0.18$  kcal/gfm by calibrated *dia* measurement. This value may be low as a consequence of thermal decomposition. The corresponding  $\Delta S_t$  of 4.4 cal/(gfm °K) is adequate

to encompass ionic reorientational rotation in an ionic lattice.<sup>37</sup>

### C. Ionic Entropy of the $\text{ClO}_4^-$ Ion

The ionic entropy of the  $\text{ClO}_4^-$  ion can be derived from the entropy of  $\text{NH}_4\text{ClO}_4(\text{c})$  [ $S_{298}^\circ = 44.02$  cal/(gfm °K)], the enthalpy of solution of  $\text{NH}_4\text{ClO}_4$  (0.80 kcal/gfm),<sup>38-40</sup> the mean activity coefficient of  $\text{NH}_4\text{ClO}_4$  ( $\gamma_{\pm} = 0.394$ ),<sup>41</sup> the solubility of  $\text{NH}_4\text{ClO}_4$  ( $m = 2.12$ ),<sup>42</sup> and the ionic entropy of  $\text{NH}_4^+$  ion [ $S_{298}^\circ[\text{NH}_4^+(\text{aq})] = 27.1$  cal/(gfm °K)]. The entropy of solution of  $\text{NH}_4\text{ClO}_4$  is 26.1 cal/(gfm °K) from the above data. This leads to a standard ionic entropy for aqueous  $\text{ClO}_4^-$  ion of  $43.0 \pm 0.2$  cal/(gfm °K). Wagman *et al.*<sup>40</sup> report 43.5 cal/(gfm °K) for this quantity.

### D. Residual Entropy and Gibbs Energy of Formation of $\text{NH}_4\text{ClO}_4$

The Gibbs energy of formation of  $\text{NH}_4\text{ClO}_4(\text{c})$  is calculable from the entropy of this research plus adjuvant undocumented data tabulated by Wagman *et al.*<sup>40</sup>:

- (1)  $\Delta H_f^\circ_{298}[\text{NH}_4\text{ClO}_4(\text{c})] = -70.58$  kcal/gfm,
- (2)  $S_{298}^\circ[\text{Cl}_2(\text{g})] = 53.288$  cal/(gfm °K),
- (3)  $S_{298}^\circ[\text{H}_2(\text{g})] = 31.208$  cal/(gfm °K),
- (4)  $S_{298}^\circ[\text{N}_2(\text{g})] = 45.77$  cal/(gfm °K),

and

- (5)  $S_{298}^\circ[\text{O}_2(\text{g})] = 49.003$  cal/(gfm °K).

The entropy of formation,  $\Delta S_f^\circ_{298}$ , of  $\text{NH}_4\text{ClO}_4(\text{c})$  is  $-165.93 \pm 0.08$  cal/(gfm °K). A value of  $-21.11$  kcal/gfm obtains for the Gibbs energy,  $\Delta G_f^\circ_{298}$ , in comparison with the value  $-21.25$  kcal/gfm presumably evaluated from data on the aqueous solution.<sup>40</sup>

The accord of the various entropies confirm the absence of residual entropy in crystalline  $\text{NH}_4\text{ClO}_4$  to within about  $\pm 0.3$  cal/(gfm °K).

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