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The heat capacities of hydroxylammonium chloride, sulfate, and phosphate

V.S. Krouk, G.J. Kabo*, A.V. Blokhin, V.V. Diky, Y.U. Paulechka

Chemistry Faculty, Research Institute for Physical Chemical Problems, Belarusian State University,
Leningradskaya 14, Minsk 220050, Belarus

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Abstract

The heat capacities of hydroxylammonium chloride, sulfate, and phosphate in the crystalline state were measured by adiabatic calorimetry between 5 and 315 K. Theoretical analyses of the experimental data for the studied compounds were made. In addition to electrostatic interactions between anionic and cationic sublattices, the existence of additional interactions such as H-bonding for hydroxylammonium phosphate was supposed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Heat capacity; Thermodynamic properties; Hydroxylammonium salts

1. Introduction

The numerous studies on the thermal behavior of ammonium salts, and also on the nature of their solid-to-solid phase transitions were reviewed in [1]. The solid-to-solid transitions in ammonium chloride, sulfate and partially in the nitrate are related to the rotation of NH_4^+ cations in the crystals of the salts [1]. Few studies of the thermodynamic properties of hydroxylammonium salts have been published, in spite of their wide use in laboratory and industrial syntheses. Caprolactam production alone consumes 6.0 million tons of hydroxylammonium sulfate per year.

The heat capacity of hydroxylammonium sulfate was reported as a C_p versus T plot in the range 303–473 K as a part of the demonstration of a new Radex calorimeter [2]. A dilatometric study on a solid-to-solid transition of hydroxylammonium perchlorate has also been reported [3]. The temperature of the transition measured on heating and cooling were 315 and 310 K, respectively. The enthalpy of the polymorphic transition (observed near 333 K) was estimated to be in the range 10.5–12.6 J g^{-1} [4]. Three phases have been reported for hydroxylammonium perchlorate, the stable orthorhombic and monoclinic phases and a metastable monoclinic phase [3]. The existence of the metastable phase was conjectured to be related to an unusually large number of H-bonds for an inorganic compound: three N–H···O bonds and one O–H···O bond per formula unit.

The vibrational spectra of hydroxylammonium chloride, bromide, iodide, nitrate, perchlorate, hydrosulfate, and deuteriosulfate have been analyzed [5]. It was found that only hydroxylammonium chloride crystallized in a monoclinic system, space group $C_{2h}^5 - P2_{1'c}/C$; unit cell parameters: $a = 6.95$ Å, $b = 5.95$ Å, $c = 7.70$ Å, $\beta = 120.8°$, $z = 4$. Like hydroxylammonium perchlorate, hydroxylammonium chloride forms many H-bonds: three N–H···Cl bonds and one O–H···Cl bond.

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* Corresponding author. Fax: +375-17-2203916.
E-mail address: kabo@bsu.by (G.J. Kabo).

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Two events were found in NMR spectra of hydroxylammonium chloride at 129 and 173 K [5]. The first was explained by NH_3-group rotation, and the second by OH-group rotation. Solid-to-solid transitions in ammonium salts are usually related to the rotation of NH_4^+ cations [1,6,7].

Reliable thermodynamic data are not available even for hydroxylamine itself. The enthalpies of combustion were reported in the late 19th and early 20th centuries [8–11] while the saturated vapor pressure and the enthalpy of sublimation were determined more recently [12]. Thermodynamic functions in the ideal gas state approximation were calculated using statistical mechanics [13]. Heat capacities of the crystalline phases and enthalpies of phase transitions have not been studied.

We report the heat capacities of three crystalline hydroxylammonium salts measured in the range 5–315 K by the adiabatic calorimetry and a theoretical interpretation of the experimental data in terms of Debye and Einstein theory.

2. Experimental

Commercial samples of hydroxylammonium sulfate and chloride were crystallized from twice distilled water and dried in a vacuum desiccator over P_2O_5. The procedure was repeated three times. Hydroxylammonium phosphate was synthesized by the substitution reaction from the chloride according to [14] and purified by triple crystallization

Table 1
Experimental molar heat capacity of hydroxylammonium chloride at the saturated vapor pressure ($R = 8.31451\ \mathrm{J\ K^{-1}\ mol^{-1}}$)

$\langle T\rangle$ (K)	$C_{s,\mathrm{m}}/R$	$\langle T\rangle$ (K)	$C_{s,\mathrm{m}}/R$	$\langle T\rangle$ (K)	$C_{s,\mathrm{m}}/R$	$\langle T\rangle$ (K)	$C_{s,\mathrm{m}}/R$
Series 1		199.46	8.635	9.49	0.03225	34.46	1.369
103.47	5.934	203.41	8.726	9.83	0.03545	35.92	1.481
106.09	6.040	207.34	8.811	10.31	0.04137	37.35	1.614
109.07	6.153	211.25	8.893	10.82	0.04857	38.73	1.731
112.39	6.296	215.15	8.961	11.36	0.05739	40.33	1.870
115.65	6.427	219.02	9.043	11.88	0.06502	42.13	2.016
118.83	6.532	222.88	9.131	12.26	0.07221	43.79	2.147
121.95	6.639	226.58	9.200	12.69	0.08124	45.58	2.297
125.01	6.747	230.95	9.266	13.09	0.08941	47.49	2.453
128.25	6.830	235.70	9.367	13.47	0.09875	49.28	2.615
131.67	6.947	240.79	9.490	13.96	0.1111	51.45	2.779
135.94	7.074	245.84	9.587	14.51	0.1233	53.96	2.980
139.58	7.172	255.88	9.762	15.09	0.1423	56.32	3.175
143.47	7.302	260.95	9.865	15.70	0.1637	58.64	3.345
147.30	7.399	266.01	9.973	16.37	0.1826	60.95	3.517
151.07	7.511	271.08	10.07	17.10	0.2126	63.23	3.678
154.78	7.605	281.11	10.27	17.90	0.2440	65.49	3.847
163.91	7.838	286.00	10.38	18.76	0.2829	67.87	4.017
168.69	7.938	290.86	10.51	19.66	0.3242	70.36	4.177
173.64	8.060	295.72	10.61	20.60	0.3745	72.75	4.327
178.05	8.164	300.58	10.74	21.78	0.4407	75.48	4.500
182.44	8.255	Series 4		22.50	0.4820	78.56	4.686
186.80	8.345	5.34	0.00548	23.42	0.5347	81.51	4.857
191.13	8.456	5.57	0.00658	24.50	0.6052	84.35	5.011
Series 2		5.86	0.00841	25.49	0.6663	87.81	5.192
151.43	7.515	6.21	0.00980	26.40	0.7295	91.84	5.412
155.08	7.615	6.53	0.01103	27.25	0.7907	95.70	5.607
158.70	7.704	6.90	0.01231	28.15	0.8551	99.41	5.776
162.27	7.798	7.30	0.01434	29.10	0.9288	102.99	5.938
Series 3		7.86	0.01767	30.25	1.025		
191.47	8.470	8.38	0.02182	31.59	1.121		
195.48	8.561	8.93	0.02632	32.99	1.249		

from water and drying in a vacuum desiccator over P_2O_5.

The purities of the samples were determined by titration of the acid formed in a chemical reaction of the hydroxylammonium salts with cyclohexanone. The purities were 99.7 mol% for the chloride, 99.4 mol% for the sulfate, and 99.0 mol% for the phosphate. The content of PO_4^{3-} anion in the phosphate was determined gravimetrically. PO_4^{3-} was precipitated by Mg^{2+} or Ba^{2+} in the presence of an ammonia buffer. The sediment was heated for conversion to $Mg_2P_2O_7$ or $Ba_2P_2O_7$. The content of the phosphate ion was found to be 99.1% of the theoretical value.

The heat capacities in the range 5–315 K were measured in a vacuum adiabatic calorimeter TAU-1 produced by VNIIFTRI (Moscow) and described earlier [15–17]. The samples of hydroxylammonium chloride (0.74586 g), sulfate (0.86759 g), and phosphate (1.05457 g) were loaded in stainless-steel containers filled with helium at $P = 5$ kPa for improved heat exchange and sealed with indium O-rings. The volumes of the two calorimetric cells were 0.6 cm^3 (for the chloride and sulfate) and 1.0 cm^3 (for the phosphate). The temperature was measured by the iron–rhodium resistance thermometers ($R_0 = 45.32$ and 101.83 Ω) located on the inner surfaces of the adiabatic shields and calibrated for ITS-90 by VNIIFTRI. Adiabatic conditions were maintained with four-junction differential thermocouples as indicators of temperature differences between the shields and the

Table 2
Experimental molar heat capacity of hydroxylammonium sulfate at the saturated vapor pressure ($R = 8.31451$ J K^{-1} mol^{-1})

$\langle T \rangle$ (K)	$C_{s,\mathrm{m}}/R$	$\langle T \rangle$ (K)	$C_{s,\mathrm{m}}/R$	$\langle T \rangle$ (K)	$C_{s,\mathrm{m}}/R$	$\langle T \rangle$ (K)	$C_{s,\mathrm{m}}/R$
Series 1		22.62	1.075	75.74	8.310	176.41	16.77
5.78	0.01491	23.68	1.196	78.55	8.626	180.14	17.02
6.05	0.01745	24.93	1.360	81.24	8.937	183.82	17.25
6.31	0.01991	26.21	1.514	83.83	9.210	187.48	17.48
6.59	0.02314	27.37	1.697	86.34	9.497	191.09	17.73
6.91	0.02597	28.43	1.820	88.77	9.747	195.04	18.02
7.28	0.02965	29.42	1.952	90.99	9.981	199.32	18.23
7.70	0.03491	30.40	2.122	93.53	10.23	203.55	18.54
8.10	0.04022	31.62	2.299	96.51	10.55	207.74	18.80
8.52	0.04719	33.01	2.484	99.40	10.82	211.89	19.07
8.97	0.05771	34.41	2.692	102.56	11.12	216.01	19.34
9.39	0.06763	35.82	2.885	105.98	11.42	220.08	19.59
9.77	0.07586	37.24	3.106	Series 2		224.11	19.85
10.14	0.08924	38.67	3.304	109.30	11.72	228.10	20.08
10.55	0.1011	40.00	3.516	112.53	12.00	232.44	20.35
11.00	0.1157	41.41	3.705	115.69	12.31	237.11	20.69
11.42	0.1330	43.03	3.928	118.70	12.50	241.75	20.98
11.81	0.1553	44.66	4.150	121.44	12.77	246.35	21.26
12.18	0.1709	46.19	4.391	124.14	12.98	250.92	21.62
12.60	0.1940	47.63	4.579	126.97	13.20	255.46	21.92
13.17	0.2232	49.11	4.816	129.94	13.39	259.97	22.19
13.76	0.2585	50.62	5.018	132.85	13.67	264.44	22.44
14.31	0.2883	52.07	5.215	135.71	13.84	269.09	22.79
14.81	0.3275	53.73	5.438	138.90	14.09	273.63	23.00
15.44	0.3703	55.60	5.748	142.40	14.40	282.67	23.63
16.18	0.4257	57.39	5.966	145.84	14.59	287.24	23.89
16.94	0.4811	59.46	6.282	149.24	14.81	292.41	24.23
17.73	0.5559	61.79	6.569	152.96	15.16	298.18	24.76
18.44	0.6315	64.01	6.838	157.01	15.44	303.91	25.12
19.09	0.6928	66.33	7.148	161.00	15.72	309.60	25.49
19.77	0.7698	68.73	7.446	164.93	15.98	315.23	25.94
20.62	0.8458	71.02	7.723	168.80	16.24		
21.63	0.9609	73.22	8.035	172.63	16.54		

calorimetric cells. The accuracy of the heat capacity measurements was proved in experiments with benzoic acid (K-1 grade, mass fraction ≥ 0.99995) [18,19] and high-purity copper (mass fraction ≥ 0.99995) [20]. The estimated uncertainty of the measured heat capacity $C_{s,\mathrm{m}}$ is $\pm 0.4\%$ in the temperature range 40–320 K. This uncertainty becomes larger at $T < 40$ K and reaches 2% near 5 K. Corrections for sublimation of the samples during the measurements were estimated to be <0.01% at 300 K and were not made.

Thermal stability of hydroxylammonium sulfate was tested with a heat bridge calorimeter [21]. Formation of a stain inside a hermetic stainless-steel container caused by decomposition of the salt was observed after heating to $T = 400$ K. Consequently, we restricted the upper temperature of the measurements to 300 K.

3. Results and discussion

The experimental values of the heat capacities of hydroxylammonium chloride, sulfate and phosphate are given in Tables 1–3, and shown in Fig. 1. The

Table 3
Experimental molar heat capacity of hydroxylammonium phosphate at the saturated vapor pressure ($R = 8.31451$ J K^{-1} mol^{-1})

$\langle T \rangle$ (K)	$C_{s,\mathrm{m}}/R$	$\langle T \rangle$ (K)	$C_{s,\mathrm{m}}/R$	$\langle T \rangle$ (K)	$C_{s,\mathrm{m}}/R$	$\langle T \rangle$ (K)	$C_{s,\mathrm{m}}/R$
Series 1		237.92	24.11	12.88	0.1559	40.83	3.427
107.87	13.30	242.44	24.37	13.21	0.1696	42.66	3.715
110.44	13.66	246.93	24.67	13.61	0.1884	44.34	4.002
113.01	13.93	251.40	24.94	14.11	0.2082	46.07	4.274
115.81	14.24	260.29	25.50	14.57	0.2296	47.84	4.577
118.83	14.59	264.69	25.83	15.12	0.2611	49.49	4.849
122.26	14.97	271.19	26.18	15.74	0.2958	51.06	5.098
124.65	15.16	275.66	26.47	16.32	0.3303	52.79	5.407
126.07	15.36	281.74	26.78	16.85	0.3645	54.69	5.725
129.94	15.74	286.60	27.06	17.35	0.4025	56.68	6.054
133.89	16.14	291.43	27.33	17.81	0.4340	58.75	6.384
137.75	16.55	296.24	27.60	18.25	0.4662	60.71	6.723
141.54	16.91	301.03	27.84	18.66	0.5024	62.77	7.069
145.25	17.23	Series 2		19.03	0.5385	64.92	7.389
148.90	17.59	5.67	0.01462	19.39	0.5686	66.98	7.726
152.50	17.90	6.07	0.01694	19.74	0.5907	69.11	8.076
156.04	18.21	6.43	0.01956	20.08	0.6271	71.31	8.390
159.53	18.51	6.75	0.02212	20.54	0.6626	73.67	8.767
163.27	18.81	7.05	0.02488	21.23	0.7235	76.18	9.144
167.25	19.12	7.44	0.02885	21.98	0.7979	78.59	9.500
171.18	19.44	7.91	0.03383	22.68	0.8711	80.94	9.831
175.36	19.75	8.34	0.03948	23.47	0.9578	83.25	10.16
179.78	20.10	8.73	0.04546	24.34	1.049	85.48	10.47
184.15	20.44	9.09	0.05100	25.16	1.144	87.93	10.81
188.47	20.75	9.43	0.05727	26.16	1.264	90.59	11.17
192.75	21.07	9.73	0.06486	27.34	1.416	93.18	11.51
196.97	21.39	10.02	0.07164	28.41	1.536	95.70	11.85
201.17	21.70	10.29	0.07922	29.40	1.692	98.43	12.17
205.62	22.00	10.54	0.08553	30.53	1.844	101.36	12.54
210.34	22.34	10.78	0.09154	31.93	2.033	104.23	12.90
215.01	22.66	11.01	0.9808	33.50	2.249	107.00	13.22
219.65	22.95	11.45	0.1101	35.06	2.486	109.71	13.57
224.25	23.28	11.65	0.1157	36.48	2.710		
228.82	23.57	11.85	0.1225	37.80	2.933		
233.38	23.85	12.41	0.1402	39.15	3.148		

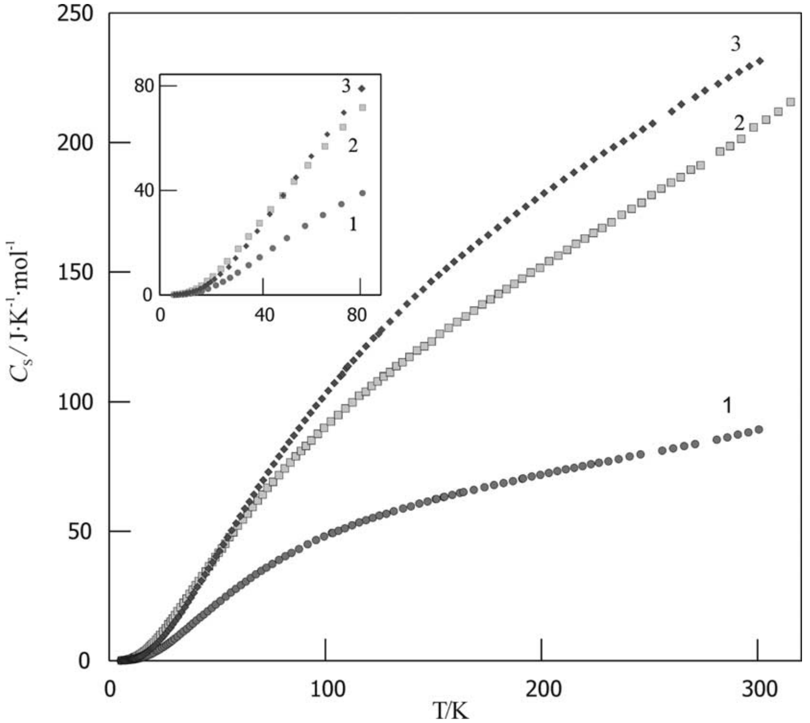

Fig. 1. Temperature dependences of the heat capacities of hydroxylammonium salts in the crystalline state. Circles (1) are for hydroxylammonium chloride; squares (2) are for hydroxylammonium sulfate and rhombuses (3) are for hydroxylammonium phosphate.

smoothed values of heat capacities, entropies, enthalpies and $\Phi^\circ_\mathrm{m} = [\Delta_0^T S^\circ_\mathrm{m} - \Delta_0^T H^\circ_\mathrm{m}]/T$ are given in Tables 4–6. Extrapolation of the heat capacities at $T < 5$ K was carried out on the basis of the Debye equation $C_{v,\mathrm{m}} = 3R \times C_{v,\mathrm{Debye}}(\Theta_\mathrm{D}/T)$, where Θ_D is the average value of the Debye characteristic temperature obtained from the experimental heat capacities near 5 K. Θ_D were found to be 183.3 K for the chloride, 143.7 K for the sulfate and 148.6 K for the phosphate.

The heat capacities of the salts showed no anomalies in the $C_p = f(T)$ curves in the temperature range studied (Fig. 1) and, therefore, no solid-to-solid transitions <300 K. The data from [2] indicate the absence of any solid-to-solid transitions in hydroxylammonium sulfate up to its melting point, 446 K. There is an essential difference between the hydroxylammonium salts and the corresponding ammonium salts, which show the existence of different crystalline phases at temperatures <300 K [6,7].

Theoretical analyses of the heat capacities for the crystalline hydroxylammonium salts were carried out using the scheme [22,23]:

$$C_p = \left[\sum C_v(E)\right]_\mathrm{int\,mol} + \left[\sum C_v(D) + \sum C_v(E)\right]_\mathrm{cryst} + [C_p - C_v] \qquad (1)$$

where $[\sum C_v(E)]_\mathrm{int\,mol}$ is the contribution of the intramolecular vibrations and $[\sum C_v(D) + \sum C_v(E)]_\mathrm{cryst}$ are the Debye and Einstein terms for the lattice vibrations. The $[C_p - C_v]$ term was included, also. The measured heat capacities, C_s, are equal to C_p within the experimental uncertainties.

The intramolecular contributions to the heat capacities were calculated from the frequencies of the normal vibrations of $\mathrm{NH_3OH^+}$, $\mathrm{SO_4{}^{2-}}$, and $\mathrm{PO_4{}^{3-}}$ ions (Table 7). The Einstein contribution of the $\mathrm{Cl^-}$ anion was based on its vibrational frequency in the hydroxylammonium chloride crystal, 208 cm^{-1} [5].

Table 4
Molar thermodynamic functions of hydroxylammonium chloride in the crystalline state

T (K)	$C_{p,\mathrm{m}}/R$	$\Delta_0^T H_\mathrm{m}^\circ/RT$	$\Delta_0^T S_\mathrm{m}^\circ/R$	Φ_m°/R
10	0.0375	0.00938	0.0126	0.00325
20	0.3432	0.08299	0.1094	0.02646
30	1.000	0.2712	0.3632	0.09189
40	1.837	0.5569	0.7641	0.2072
50	2.665	0.8961	1.263	0.3673
60	3.446	1.257	1.819	0.5624
70	4.151	1.621	2.405	0.7836
80	4.773	1.977	3.000	1.023
90	5.316	2.319	3.595	1.276
100	5.790	2.642	4.180	1.537
120	6.574	3.235	5.308	2.073
140	7.199	3.758	6.370	2.611
160	7.732	4.222	7.367	3.144
180	8.209	4.639	8.305	3.666
200	8.650	5.018	9.193	4.175
220	9.066	5.368	10.04	4.670
240	9.461	5.692	10.84	5.151
260	9.848	5.997	11.62	5.618
280	10.25	6.286	12.36	6.074
298.15	10.68	6.540	13.02	6.476
300	10.72	6.566	13.08	6.517

Table 5
Molar thermodynamic functions of hydroxylammonium sulfate in the crystalline state

T (K)	$C_{p,\mathrm{m}}/R$	$\Delta_0^T H_\mathrm{m}^\circ/RT$	$\Delta_0^T S_\mathrm{m}^\circ/R$	Φ_m°/R
10	0.08340	0.01972	0.02634	0.006495
20	0.7868	0.1950	0.2557	0.06074
30	2.052	0.5916	0.7999	0.2083
40	3.502	1.138	1.589	0.4508
50	4.923	1.753	2.523	0.7700
60	6.319	2.400	3.546	1.147
70	7.606	3.052	4.618	1.565
80	8.794	3.697	5.712	2.015
90	9.884	4.325	6.812	2.487
100	10.88	4.931	7.906	2.974
120	12.63	6.072	10.05	3.976
140	14.18	7.122	12.11	4.992
160	15.63	8.096	14.10	6.007
180	17.00	9.010	16.02	7.014
200	18.31	9.875	17.88	8.008
220	19.60	10.70	19.69	8.989
240	20.87	11.49	21.45	9.954
260	22.15	12.27	23.17	10.90
280	23.46	13.02	24.86	11.84
298.15	24.70	13.69	26.37	12.68
300	24.83	13.76	26.52	12.76
315	25.90	14.31	27.76	13.45

Table 6
Molar thermodynamic functions of hydroxylammonium phosphate in the crystalline state

T (K)	$C_{p,\mathrm{m}}/R$	$\Delta_0^T H_\mathrm{m}^\circ/RT$	$\Delta_0^T S_\mathrm{m}^\circ/R$	Φ_m°/R
10	0.07125	0.01744	0.02345	0.005893
20	0.6162	0.1513	0.2003	0.04895
30	1.760	0.4833	0.6497	0.1665
40	3.284	0.9873	1.358	0.3710
50	4.940	1.612	2.268	0.6567
60	6.597	2.305	3.316	1.011
70	8.197	3.033	4.454	1.421
80	9.702	3.774	5.648	1.874
90	11.09	4.511	6.872	2.361
100	12.38	5.234	8.108	2.874
120	14.71	6.623	10.58	3.952
140	16.75	7.927	13.00	5.072
160	18.54	9.144	15.36	6.211
180	20.13	10.28	17.63	7.354
200	21.60	11.34	19.83	8.493
220	22.97	12.33	21.95	9.620
240	24.27	13.27	24.01	10.73
260	25.50	14.17	26.00	11.83
280	26.68	15.02	27.93	12.91
298.15	27.71	15.76	29.64	13.88
300	27.81	15.83	29.81	13.98

The intramolecular Einstein terms for hydroxylammonium chloride, sulfate, and phosphate are

$$\left[\sum C_v(E)\right]_{\text{int mol}}(\mathrm{NH_2OH\cdot HCl}) = \left\{\sum_{i=1}^{12}\frac{Ru_i^2\,\mathrm{e}^{u_i}}{(\mathrm{e}^{u_i}-1)^2}\right\}_{\mathrm{NH_3OH^+}} + 3\times\frac{Ru_{\mathrm{Cl}}^2\,\mathrm{e}^{u_{\mathrm{Cl}}}}{(\mathrm{e}^{u_{\mathrm{Cl}}}-1)^2} \tag{2}$$

$$\left[\sum C_v(E)\right]_{\text{int mol}}((\mathrm{NH_2OH})_2\cdot \mathrm{H_2SO_4}) = 2\left\{\sum_{i=1}^{12}\frac{Ru_i^2\,\mathrm{e}^{u_i}}{(\mathrm{e}^{u_i}-1)^2}\right\}_{\mathrm{NH_3OH^+}} + \left\{\sum_{j=1}^{9}\frac{Ru_j^2\,\mathrm{e}^{u_j}}{(\mathrm{e}^{u_j}-1)^2}\right\}_{\mathrm{SO_4{}^{2-}}} \tag{3}$$

$$\left[\sum C_v(E)\right]_{\text{int mol}}((\mathrm{NH_2OH})_3\cdot \mathrm{H_3PO_4}) = 3\left\{\sum_{i=1}^{12}\frac{Ru_i^2\,\mathrm{e}^{u_i}}{(\mathrm{e}^{u_i}-1)^2}\right\}_{\mathrm{NH_3OH^+}} + \left\{\sum_{j=1}^{9}\frac{Ru_j^2\,\mathrm{e}^{u_j}}{(\mathrm{e}^{u_j}-1)^2}\right\}_{\mathrm{PO_4{}^{3-}}} \tag{4}$$

$u_{i(j)} = \frac{h\nu_{i(j)}}{kT}$, where $\nu_{i(j)}$ are frequencies of intramolecular vibrations in cations (i) and anions (j).

Table 7
Frequencies of normal vibrations of NH_3OH^+ cation [5], SO_4^{2-} anion [24], and PO_4^{3-} anion [24]

Cation or anion	ν (cm^{-1})	Type of vibration	ν (cm^{-1})	Type of vibration
NH_3OH^+	3157	$\nu_1(A')$	1150	$\nu_7(A')$
	3080	$\nu_2(A')$	992	$\nu_8(A')$
	3021	$\nu_3(A')$	3080	$\nu_9(A'')$
	1557	$\nu_4(A')$	1577	$\nu_{10}(A'')$
	1461	$\nu_5(A')$	1160	$\nu_{11}(A'')$
	1211	$\nu_6(A')$	550	$\nu_{12}(\tau)$
SO_4^{2-}	981	$\nu_1(A')$	1104	$\nu_3(F_2)$
	451	$\nu_2(E)$	613	$\nu_4(F_2)$
PO_4^{3-}	938	$\nu_1(A')$	1017	$\nu_3(F_2)$
	420	$\nu_2(E)$	567	$\nu_4(F_2)$

The parameters for the calculations of the lattice terms were derived using the technique proposed by Matsuo et al. [22] and Takahara et al. [23]. The number of lattice vibrations is the difference between the total number of degrees of freedom for an N-atomic molecule ($3N$) and the number of intramolecular vibrations N_{int} (6 for the chloride, 18 for the sulfate, and 24 for the phosphate).

An approximation [22],

$$[C_p - C_v] = AC_v^2T \tag{5}$$

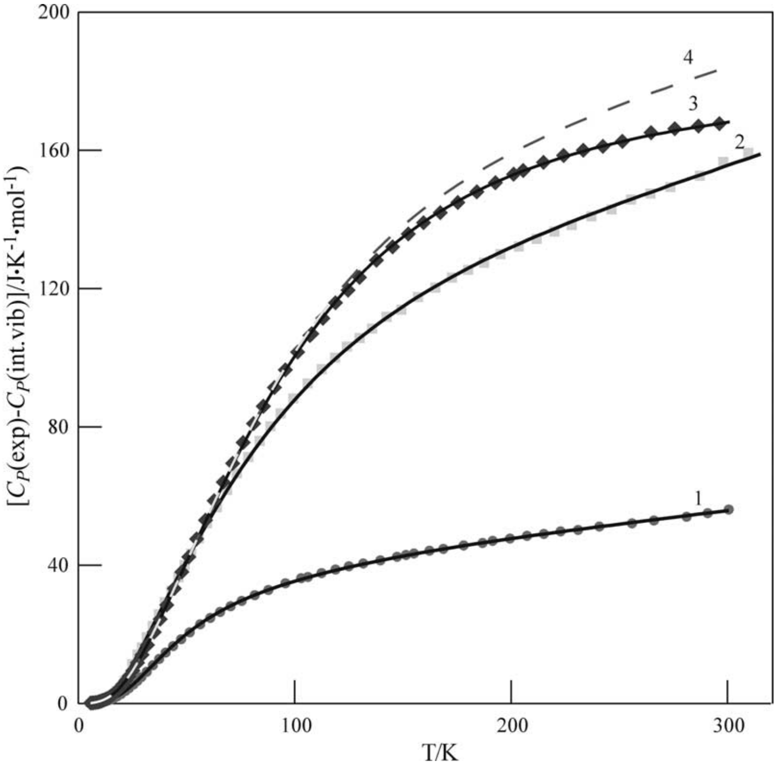

Fig. 2. Temperature dependences of the experimental (points) and calculated (lines) heat capacities after subtraction of the intramolecular contributions for hydroxylammonium chloride (1); hydroxylammonium sulfate (2) and hydroxylammonium phosphate (3). Curve (4) shows the calculated heat capacity of hydroxylammonium phosphate if $A = 1 \times 10^{-6}$ J^{-1} mol.

Table 8
The values of Debye (Θ_D) and Einstein (Θ_E) characteristic temperatures and *A* coefficients for hydroxylammonium salts in the crystalline state

Compound	Θ_D (K)	Θ_E (K)	A × 10^6 (J^{-1} mol)
Hydroxylammonium chloride	176 (3)[a]	160, 230, 630	5.0
Hydroxylammonium sulfate	174 (6), 261 (3)	319 (6), 566 (2), 622	1.83
Hydroxylammonium phosphate	175 (6)	209 (4), 366 (8), 433 (4), 2300 (2)	0

[a] Degeneracy for each mode is in brackets.

with a fitted *A* parameter was used. All the fitted parameters (Table 8) were found simultaneously by the method of least squares.

The temperature dependences of the experimental and calculated heat capacities after subtraction of the intramolecular contribution are shown in Fig. 2. The average deviation of the calculated values from the experimental ones is 0.3% in the range 20–300 K, which is comparable to the experimental uncertainty. The maximum deviation does not exceed 1.5%. However, the divergence is much larger in the low-temperature range, where it reaches 15% <15 K.

The calculated C_p values for hydroxylammonium phosphate would be substantially higher than the experimental ones, if *A* values of the same order as for the chloride and sulfate were used (Fig. 2, curve 4). Hence, the model of free vibrations for ions in the lattice does not hold for this salt. The crystal of hydroxylammonium phosphate probably has strong H-bonds between the anionic and cationic sublattices as was found for the dihydrophosphates (for example, KH_2PO_4 [25]). This is why the values of the Debye and Einstein temperatures and the *A* coefficient found for the phosphate (Table 8) are 'effective' in that they allow fitting of the experimental heat capacity data, but probably do not have any physical sense.

References

[1] N.J. Parsonage, L.A.K. Stavely, Disorder in Crystals, Vol. 2, Oxford Press, Washington, DC, 1978.
[2] Neues Sicherheitskalorimeter, Chem. Ing. Technol. 65 (1993) 506.
[3] Z.I. Grigorovich, G.N. Lubimova, Zh. Phikl. Khim. 52 (1978) 2479.
[4] J.N. Maycock, V.R.P. Verneker, in: Proceedings of the 2nd Symposium on Analytical Calorimetry, 1970, p. 291.
[5] Yu.Y. Haritonov, M.A. Saruhanov, Vibrational Spectra of Hydroxylamine and Its Co-ordinating Compounds, Tashkent, "Fan", 1971, 192 pp. (in Russian).
[6] C. Hideaki, K. Minoru, Bull. Chem. Soc. Jpn. 45 (1972) 133.
[7] H. Yoshiyuki, C. Hideaki, Bull. Chem. Soc. Jpn. 54 (1981) 901.
[8] M. Berthelot, Ann. Chim. Phys. 10 (1877) 433.
[9] M. Berthelot, Ann. Chim. Phys. 21 (1890) 384.
[10] J. Thomsen, Thermochemischer Untersuchungen. Leipzig, 1886, p. S.1.
[11] W. Swientoslawski, Zh. Rus. Fiz. Khim. Obshestva, Chem. Part 41 (1909) 608.
[12] R.A. Back, J. Betts, Canad. J. Chem. 43 (1965) 2157.
[13] M.E. Bedrina, M.A. Saruhanov, N.A. Parpiev, Uzb. Khim. Zh. 6 (1974) 29.
[14] Von G. Brauer, Handbook for Preparation of Non-Organic Compounds, Vol. 2, Moscow, Mir, 1985, 338 pp. (Russian Edition).
[15] V.I. Kosov, V.M. Malyshev, G.A. Milner, E.L. Sorkin, V.F. Shibakin, Izmeritelnaya Tekhnika 11 (1985) 56.
[16] G.J. Kabo, A.A. Kozyro, A. Marchand, V.V. Diky, V.V. Simirsky, L.S. Ivashkevich, A.P. Krasulin, V.M. Sevruk, M.L. Frenkel, J. Chem. Thermodyn. 26 (1994) 129.
[17] F. Pavese, V.M. Malyshev, Adv. Cryog. Eng. 40 (1994) 119.
[18] G.T. Furukawa, R.E. McCoskey, G.J. King, J. Res. NBS 47 (1951) 256.
[19] I.A. Vasiliev, V.M. Petrov, Thermodynamic Properties of Oxygen-Containing Organic Compounds, Leningrad, Khimiya, 1984, pp. 145–148 (in Russian).
[20] G.K. White, S.J. Collocott, J. Phys. Chem. Ref. Data 13 (1984) 1251.
[21] A.G. Kabo, V.V. Diky, Thermochim. Acta 347 (2000) 79.
[22] T. Matsuo, N. Kinami, H. Suga, Thermochim. Acta 267 (1995) 421.
[23] S. Takahara, O. Yamamuro, T. Matsuo, J. Phys. Chem. 99 (1995) 9589.
[24] A. Müller, B. Krebs, J. Mol. Spectros. 24 (1967) 180.
[25] G.C. Pimentel, A.L. McClellan. The Hydrogen Bond, Freeman, San Francisco, 1960, 462 pp.