Heat capacities and thermodynamic properties of ammonium and potassium thiocyanates from 5 to 340 K †

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The heat capacities of ammonium and potassium thiocyanates were determined by adiabatic calorimetry over the range 5 to 340 K, and associated thermodynamic functions were computed from the results. At 298.15 K, the heat capacities C_p/cal K^{-1} mol^{-1} and entropies $S°$/cal K^{-1} mol^{-1} are 29.98 and 33.52 for NH_4SCN and 21.16 and 29.70 for KSCN. In both salts, the heat capacity contribution from libration of the thiocyanate ions may be represented by two Einstein functions up to 250 K. The torsional motion of the ammonium ion increases rapidly above 100 K and contributes more than 6 cal K^{-1} to the heat capacity above 250 K. Adjuvant data on potassium thiocyanate solutions lead to $S° = (34.23 \pm 0.3)$ cal K^{-1} mol^{-1} for SCN^-(aq) at 298.15 K.

1. Introduction

Ammonium halide crystals exhibit transitions in the solid state below 300 K which are related to the orientation and motion of the ammonium ion. It was of interest to examine the heat capacity of ammonium thiocyanate crystals to establish whether similar behavior occurred for ammonium ions in an environment of rod- or pear-shaped anions. Such studies were also made on potassium thiocyanate for comparison of lattice and internal contributions from the thiocyanate ion. A further purpose of this study was to determine the thermodynamic functions for these salts and the entropy of the aqueous thiocyanate ion, as a check on the entropies of SCN^-(aq) and HNCS(g) based on studies by Brandenburg.[1]

2. Experimental

CALORIMETRIC PROCEDURES

Measurements were made by adiabatic calorimetry at temperatures between 5 and 330 K for ammonium thiocyanate and between 5 and 350 K for potassium thiocyanate, using the Mark II cryostat described elsewhere.[2] The automatic adiabatic shield

control system has also been described previously.[2] The gold-plated copper calorimeter used in this study (laboratory designation W-42) has a capacity of 93 cm^3 and has horizontal radial vanes for thermal equilibration within the sample. The calorimetric sample of ammonium thiocyanate had a mass of 66.0128 g, and its heat capacity ranged from 91.41 per cent of the total at 16.48 K to 79 per cent at 103 K and increased to 84 per cent at 330 K. Buoyancy corrections were based on a density of 1.31 g cm^{-3}. Helium at a pressure of 63 Torr at 300 K was used to facilitate equilibrium in the calorimeter. The calorimetric sample of potassium thiocyanate had a mass of 74.446 g, based on a density of 1.886 g cm^{-3} for buoyancy corrections. It was enclosed with helium gas at a pressure of 75 Torr at 300 K, and its heat capacity ranged from 82 per cent of the total at 10 K to 75 per cent at 168 K and increased gradually to 78 per cent at 350 K. A capsule-type strain-free platinum thermometer (laboratory designation A-5) located within the entrant well of the calorimeter was used for temperature measurements. All measurements of mass, temperature, resistance, potential, and time are referred to standardizations and calibrations performed at the National Bureau of Standards.

PREPARATION AND CHARACTERIZATION OF SAMPLES

Reagent grade ammonium thiocyanate (Baker Analyzed, Lot. No. 34157) was recrystallized once from 50 per cent aqueous methanol and twice from methanol. The solutions were brought to saturation at about 80 °C, then cooled to between 0 and 5 °C. The crystals were recovered in a sintered glass funnel, rinsed with cold methanol, and dried under vacuum over potassium hydroxide pellets. After a preliminary drying, the crystals were broken to uniform size in an agate mortar, dried at 60 °C for two hours, then held in a vacuum desiccator over potassium hydroxide pellets under high vacuum for ten days. The material was loaded into the calorimeter under conditions of about 48 per cent relative humidity, at which the material is not appreciably hygroscopic. Subsequent evacuation of the calorimeter and flushing with helium was expected to eliminate any traces of water absorbed from the atmosphere during loading. Examination of the heat capacity behavior of the sample near the freezing temperature of methanol indicated 0.05 mass per cent methanol entrapped in the crystals, as calculated from the excess energy absorption (1.2 cal mol^{-1}) in Series I (table 1) by attributing the excess to melting of the $CH_3OH + NH_4SCN$ eutectic at about 167 K. The excess heat capacity and entropy from this source would be negligible below 160 K, and were estimated at 0.01 cal K^{-1} mol^{-1} from 170 to 273 K, rising to 0.02 cal K^{-1} mol^{-1} at 330 K. The estimated excess enthalpy would range from 1.2 cal mol^{-1} at 170 K to 2.4 cal mol^{-1} at 273 K and to 3 cal mol^{-1} at 330 K. No adjustment for this effect was made in the tabulated results (tables 1 and 2).

Reagent grade potassium thiocyanate (Baker Analyzed) was recrystallized three times from methanol. The crystals were collected on a sintered-glass filter, rinsed with cold methanol, and given a preliminary drying under vacuum over potassium hydroxide pellets. The crystals were then broken to uniform size in an agate mortar, and dried six hours at 90 to 110 °C. They were subsequently stored under vacuum over potassium hydroxide pellets. Calorimeter loading conditions and procedures were the same as

for the ammonium thiocyanate. Examination of the heat capacity behavior of the sample near the freezing temperature of methanol showed no detectable amount (less than 0.003 per cent) of methanol entrapped in the crystals.

TABLE 1. Experimental heat capacity of ammonium thiocyanate and potassium thiocyanate

T	C_p	T	C_p	T	C_p	T	C_p
K	cal K^{-1} mol^{-1}	K	cal K^{-1} mol^{-1}	K	cal K^{-1} mol^{-1}	K	cal K^{-1} mol^{-1}
				Ammonium thiocyanate, NH$_4$SCN			
	Series I	237.88	25.57	55.92	7.709	31.44	3.461
112.36	14.78	247.80	26.35	59.67	8.288	34.43	4.031
118.45	15.43	257.46	27.07				
127.98	16.40	266.90	27.77		Series IV		Series V
137.67	17.34	276.12	28.44	5.62	0.022	61.45	8.556
146.89	18.21	285.16	29.09	6.27	0.034	64.65	9.026
156.46	19.08	294.02	29.69	6.82	0.044	68.33	9.532
166.35	20.03	302.71	30.28	7.46	0.062	72.93	10.139
175.89	20.67	311.24	30.84	8.15	0.086	78.44	10.867
185.13	21.43	320.56	31.43	8.93	0.121	84.34	11.642
194.50	22.18	330.63	32.04	9.89	0.177	90.51	12.387
204.01	22.93			10.99	0.245		
217.77	24.03		Series III	12.18	0.333		Series VI
228.25	24.82			13.48	0.459	89.36	12.257
		34.60	4.059	14.90	0.619	95.90	12.990
	Series II	35.95	4.316	16.48	0.821	102.84	13.755
172.59	20.40	38.03	4.698	18.12	1.059	110.17	14.563
182.66	21.23	39.93	5.042	19.92	1.344	117.14	15.30
192.39	22.00	42.10	5.425	21.69	1.645	124.74	16.07
201.82	22.76	44.52	5.847	23.31	1.932	133.64	16.95
210.97	23.47	46.75	6.230	25.03	2.248		
219.88	24.18	49.28	6.654	26.89	2.596		
228.57	24.85	52.50	7.175	28.99	2.990		
			Potassium thiocyanate, KSCN				
	Series I	175.49	16.98		Series III	29.17	2.969
96.06	13.009	183.87	17.28	5.53	0.015	31.80	3.578
102.37	13.435	192.85	17.59	6.46	0.024	34.81	4.289
111.96	14.040	202.41	17.93	7.39	0.036	38.57	5.155
122.14	14.622	211.81	18.25	8.41	0.057	42.95	6.117
131.91	15.13	221.06	18.56	9.26	0.083	47.46	7.052
141.34	15.59	230.17	18.85	10.08	0.114	52.26	7.957
150.49	16.00	239.89	19.16	11.02	0.150	57.50	8.843
159.41	16.37	250.20	19.50	11.96	0.198	65.00	9.967
169.61	16.77	260.34	19.82	12.91	0.260	72.57	10.876
181.05	17.19	270.33	20.15	13.94	0.343	79.37	11.609
192.22	17.57	280.18	20.50	15.06	0.441	87.02	12.340
203.15	17.96	289.87	20.85	16.23	0.576	94.98	12.940
213.86	18.32	299.42	21.21	17.54	0.744	104.63	13.584
224.37	18.66	308.82	21.61	19.02	0.957		
234.68	19.00	318.07	21.99	20.64	1.221		
		327.16	22.45	22.56	1.568		
	Series II	336.11	22.93	24.69	1.992		
167.94	16.69	344.88	23.47	26.88	2.459		

3. Results

THERMODYNAMIC PROPERTIES

The experimental heat capacities at the mean temperature of each determination are listed in chronological order in table 1 and are displayed in figure 1. These results have been adjusted for curvature and are considered to have a probable error of about
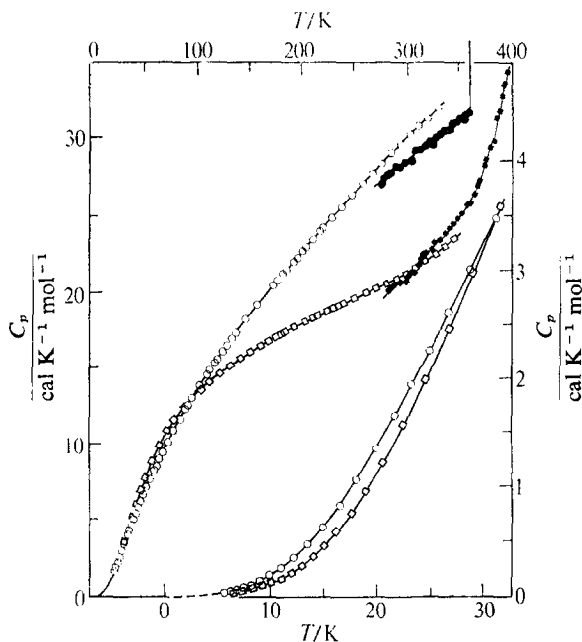

FIGURE 1. Heat capacity behavior of ammonium and potassium thiocyanates. Open circles represent experimental determinations of this research on NH_4SCN; open squares, those on KSCN. The solid circles are unpublished results of Seki[18] on NH_4SCN and the solid squares are the results of Sakiyama, Suga, and Seki on KSCN.[15] More recent measurements by Seki[34] are in much closer agreement with ours.

5 per cent at 5 K, decreasing to 1.0 per cent at 10 K and to less than 0.1 per cent above 20 K. The values are based upon cal = 4.184 J, an ice temperature of 273.15 K, and molar masses of 76.1204 and 97.1838 g mol^{-1} for ammonium and potassium thiocyanate. The smoothed heat capacities and associated thermodynamic functions presented in table 2 were obtained by digital data processing of the experimental results. The functions have a probable error of less than 0.1 per cent above 50 K. Below 6 K, the heat capacities were extrapolated using the Debye T^3 limiting law. The entropies and Gibbs functions have not been adjusted for nuclear spin and isotopic mixing contributions, and hence are practical values for use in chemical thermodynamic calculations.

ENTROPY OF AQUEOUS THIOCYANATE ION

For potassium thiocyanate, Parker[3] gives (5790 ± 50) cal mol^{-1} at 298.15 K for the enthalpy of solution, ΔH_s°, based on measurements by Partington and Soper.[4] At

TABLE 2. Thermodynamic functions of ammonium thiocyanate and potassium thiocyanate

T	C_p	S	$H' - H_0^c$	$-(G^c - H_0')/T$
$\overline{K}$	$\mathrm{cal\ K^{-1}\,mol^{-1}}$	$\mathrm{cal\ K^{-1}\,mol^{-1}}$	$\mathrm{cal\ mol^{-1}}$	$\mathrm{cal\ K^{-1}\,mol^{-1}}$
Ammonium thiocyanate				
5	0.018	0.006	0.022	0.002
10	0.179	0.052	0.399	0.012
15	0.630	0.199	2.293	0.046
20	1.357	0.475	7.167	0.116
25	2.242	0.871	16.124	0.226
30	3.185	1.363	29.68	0.373
35	4.137	1.925	47.99	0.554
40	5.054	2.538	70.99	0.763
45	5.934	3.185	98.48	0.996
50	6.771	3.854	130.26	1.248
60	8.330	5.228	205.9	1.797
70	9.760	6.621	296.4	2.386
80	11.081	8.012	400.7	3.003
90	12.312	9.389	517.8	3.636
100	13.468	10.746	646.7	4.279
110	14.560	12.082	786.9	4.928
120	15.597	13.393	937.7	5.579
130	16.588	14.681	1098.7	6.230
140	17.537	15.945	1269.3	6.879
150	18.450	17.187	1449.3	7.525
160	19.33	18.406	1638	8.167
170	20.18	19.603	1836	8.804
180	21.02	20.781	2042	9.437
190	21.83	21.939	2256	10.065
200	22.62	23.079	2478	10.687
210	23.41	24.202	2709	11.304
220	24.19	25.309	2947	11.915
230	24.96	26.401	3192	12.521
240	25.73	27.480	3446	13.122
250	26.49	28.545	3707	13.718
260	27.25	29.599	3976	14.308
270	27.99	30.642	4252	14.894
280	28.72	31.673	4535	15.475
290	29.43	32.693	4826	16.051
300	30.11	33.702	5124	16.623
310	30.76	34.70	5428	17.19
320	31.39	35.69	5739	17.75
330	32.00	36.66	6056	18.31
273.15	28.23	30.97	4340	15.08
298.15	29.98	33.52	5068	16.52
Potassium thiocyanate				
5	0.011	0.004	0.014	0.001
10	0.107	0.032	0.243	0.008
15	0.440	0.127	1.477	0.029
20	1.113	0.338	5.223	0.077
25	2.057	0.684	13.060	0.162

TABLE 2—continued

T	C_p	S	$H^\circ - H_0^\circ$	$-(G^\circ - H_0^\circ)/T$
K	cal K^{-1} mol^{-1}	cal K^{-1} mol^{-1}	cal mol^{-1}	cal K^{-1} mol^{-1}
30	3.161	1.155	26.06	0.286
35	4.333	1.731	44.80	0.451
40	5.472	2.384	69.34	0.651
45	6.545	3.091	99.41	0.882
50	7.535	3.833	134.65	1.140
60	9.241	5.363	218.8	1.716
70	10.601	6.894	318.3	2.347
80	11.680	8.383	429.9	3.009
90	12.553	9.810	551.2	3.686
100	13.286	11.172	680.5	4.367
110	13.925	12.469	816.6	5.045
120	14.501	13.705	958.8	5.715
130	15.030	14.887	1106.5	6.376
140	15.519	16.019	1259.3	7.024
150	15.972	17.106	1416.8	7.661
160	16.39	18.150	1579	8.284
170	16.78	19.156	1745	8.894
180	17.15	20.126	1914	9.491
190	17.50	21.062	2088	10.076
200	17.84	21.969	2264	10.648
210	18.18	22.848	2444	11.208
220	18.51	23.701	2628	11.756
230	18.84	24.531	2815	12.294
240	19.17	25.340	3005	12.821
250	19.50	26.129	3198	13.337
260	19.83	26.900	3395	13.844
270	20.16	27.655	3595	14.342
280	20.49	28.394	3798	14.831
290	20.85	29.119	4004	15.311
300	21.23	29.832	4215	15.783
310	21.64	30.54	4429	16.25
320	22.10	31.23	4648	16.70
330	22.60	31.92	4871	17.16
340	23.16	32.60	5100	17.60
350	23.82	33.28	5335	18.04
273.15	20.26	27.89	3658	14.50
298.15	21.16	29.70	4176	15.70

298.15 K, the solubility in water is 25.08 mol kg^{-1}, according to Seidell.[5] Robinson and Stokes[6] recalculated the activity coefficients obtained by Robinson[7] from iso-piestic measurements up to 5 mol kg^{-1}. Other vapor pressures of KSCN solutions are those of Pearce and Hopson[8] (up to 10 mol kg^{-1}) and those of Gibson and Adams[9] (4.59 to 17.328 mol kg^{-1}). The sets of vapor pressures are consistent with each other in the regions of overlap. The osmotic coefficients from the three sets of data were

combined on a smooth curve and extrapolated to 25.08 mol kg^{-1}, leading to 0.454 for the activity of water at the saturation point. This value agrees with those reported by Korvezee and Dingemans[10] (0.451, 0.46) for the activity of water in saturated KSCN solution at 298.15 K, and is consistent with the observation by Kolthoff and Lingane[11] that solid KSCN is deliquescent at 50 per cent relative humidity but is not hygroscopic at relative humidities of 45 per cent or less. Evaluation of the increments in the activity coefficients between Robinson's results and 25.08 mol kg^{-1} involved graphical evaluation of the integral in the relation derived from the Gibbs-Duhem equation:

$$-\ln \gamma_s = -\ln \gamma_1 + (\phi_1 - \phi_s) + \int_{m_1}^{m'} (1 - \phi)\mathrm{d}\ln m \tag{1}$$

in which ϕ is the osmotic coefficient, m is the molality, and γ_s and ϕ_s are the values at saturation (25.08 mol kg^{-1}). The lower limit of integration (m_1, γ_1, ϕ_1) refers to 5 mol kg^{-1} and the upper to $m' = 25.08$ mol kg^{-1}. We obtained $\gamma_s = 0.4465$, $\log_{10} \gamma_s = -0.3503$, and estimate ± 0.005 for the probable error in $\log_{10} \gamma_s$ (and also in $\log_{10} m_s$). The standard Gibbs energy of solution is then

$$\Delta G_s^\circ = -2RT \ln(m_s\gamma_s) = -(1865 \pm 30) \text{ cal mol}^{-1}. \tag{2}$$

This combines with ΔH_s° to give (29.03 ± 0.23) cal K^{-1} mol^{-1} for ΔS_s°, the standard entropy of solution. The entropy of K$^+$(aq), $(24.50$ cal K^{-1} mol^{-1}),[12] combined with the entropy of KSCN from table 4 gives for SCN$^-$(aq),

$$S^\circ(298.15 \text{ K}) = (34.23 \pm 0.3) \text{ cal K}^{-1} \text{ mol}^{-1}. \tag{3}$$

NBS Technical Note 270–3[12] lists 34.5 cal K^{-1} mol^{-1} for the entropy of SCN$^-$(aq), apparently based on the unpublished measurements by Brandenburg[1] of the enthalpy and Gibbs energy of solution of HNCS(g) and a statistical calculation of S° for HNCS(g). Recent recalculations[13] based on Brandenburg's and statistical data lead to (34.4 ± 0.35) cal K^{-1} mol^{-1}. The agreement between the two routes to S° is excellent, and firmly precludes disorder in the low temperature crystalline form of potassium thiocyanate. The value of S° for HNCS(g) is limited in accuracy by the uncertainty in one of the moments of inertia of the molecule and also by the amount of anharmonicity associated with the vibrations.

A similar calculation based on the entropy of NH$_4$SCN is not possible for lack of information on the activity coefficients for NH$_4$SCN solutions. The calculations can be reversed, however, to yield 0.35 for γ_s for NH$_4$SCN at saturation (23.66 mol kg^{-1}).[5] This value of γ_s for NH$_4$SCN bears a reasonable relation to that for KSCN, being slightly smaller as usually found for other comparisons of ammonium and potassium salts.[14]

4. Discussion

IONIC MOTION IN THE THIOCYANATES

The curves in figure 1 reveal no solid state transitions for either salt in the temperature region studied. Potassium thiocyanate is known to undergo a transition at about 413 K from orthorhombic to tetragonal symmetry with increasing temperature. Seki,[15] Watanabé,[16] and their colleagues present evidence from thermal, spectral, and X-ray studies that this is an order-disorder transition involving the orientation of

the thiocyanate ion. The transition occurs reversibly without shattering the crystal. Studies by Bridgman[17] showed that the denser low-temperature orthorhombic phase has larger coefficients of thermal expansion and compressibility than the high-temperature phase. Ammonium thiocyanate undergoes transitions at about 361 K and 392 K. The lower one is a phase transition from monoclinic to orthorhombic symmetry (and higher density) with increasing temperature. The upper transition is apparently an order-disorder transition and involves again orientation of the thio-cyanate ions.[18] Bridgman[17] stated that the orthorhombic form of NH_4SCN is isomorphous with that of KSCN. He also reported that the monoclinic NH_4SCN has a larger coefficient of thermal expansion but a smaller coefficient of compressibility than orthorhombic NH_4SCN, but gave no actual values for either salt.

Gutowsky and Pake[19] studied nuclear magnetic resonance spectra for several ammonium salts, including NH_4Cl, NH_4Br, NH_4I, and NH_4SCN, and found that the line-width changed markedly near 100 K, suggesting significant change in the torsional motion of the ammonium ions well below the temperatures of the phase transitions in the ammonium halides. Richards and Schaefer[20] in more recent n.m.r. studies found for NH_4SCN that the line-width narrows abruptly in going from 72 K to 90 K. Rush, Taylor, and their colleagues,[21,22] using subthermal neutron scattering to measure the freedom of NH_4^+ ions in a number of salts, conclude that the λ-transitions in the ammonium salts involve no abrupt change in the torsional frequency or freedom of motion of the NH_4^+ ions. Significant abrupt changes in freedom do occur at the higher temperature first-order transitions, however. We infer that, in ammonium thiocyanate, the ammonium ions gradually increase in rotational freedom beginning at about 70 K and probably have considerable freedom above 200 K. The neutron scattering studies indicate the potential barrier hindering rotation of the ammonium ion in NH_4SCN is close to 4 kcal mol^{-1}.[21,22]

X-Ray studies[16,23-25] on orthorhombic KSCN show four pairs of ions in the unit cell ($a = 6.635$ Å, $b = 6.66$ Å, $c = 7.58$ Å), with the thiocyanate ions at specified orientations in a plane perpendicular to the c-axis and the potassium ions midway between these planes. The monoclinic NH_4SCN also has four pairs of ions per unit cell ($\beta = 97.4°$, $a = 4.3$ Å, $b = 7.2$ Å, $c = 13.0$ Å),[26] arrayed in a layered structure.

Several infrared and Raman studies have been reported for KSCN,[15,27-29] and also for NH_4SCN.[18,30,31] These establish quite securely the vibrational frequencies for the SCN$^-$ ion in each salt along with those for the NH_4^+ ion. Oden and Decius[30] report torsional wavenumbers of 315, 354, and 375 cm^{-1} for the NH_4^+ ion. These agree with Tramer's observation[31] (300 to 330 cm^{-1}) and are compatible with a rotational barrier of 4 kcal mol^{-1} for the NH_4^+ ion in NH_4SCN. Savoie and Pézolet[27] showed that the two librational modes of the four SCN$^-$ ions in a unit cell would be split into eight components: four in-plane and four out-of-plane librations. Savoie and Pézo-let[27] extended the observations by Tramer[28] and report several infrared and Raman lines between 56 and 170 cm^{-1} for KSCN. A strong band at 69 to 70 cm^{-1} was attributed to the out-of-plane libration of the SCN$^-$ ion, but it is not possible to make unequivocal assignments for the other modes. For NH_4SCN, Tramer[31] observed several wavenumbers between 47 and 190 cm^{-1}, and attributed a broad band at

47 to 53 cm^{-1}, possibly a doublet, to the out-of-plane libration of the SCN$^-$ ion in that salt.

A graphical comparison of the heat capacities of the two salts is given in figure 1. There is little difference between the ammonium and potassium thiocyanate crystals up to about 100 K, but above that temperature the heat capacity of the ammonium salt increases much more rapidly. Most of the difference in heat capacities above 100 K can be attributed to the rotational heat capacity of the NH$_4^+$ ion. This observation is fully compatible with the spectral observations cited for the ammonium compound, and is borne out by detailed analyses of the heat capacities of each salt in the following sections.

ANALYSIS OF THE HEAT CAPACITY OF POTASSIUM THIOCYANATE

The observed heat capacity can be represented as the sum of several contributions, where C_{vib} arises from internal vibrations of SCN$^-$, C_L from lattice vibrations, and C_{lib} from libration of the SCN$^-$ ion:

$$C_p = (C_p - C_V) + C_{vib} + C_L + C_{lib}. \qquad (4)$$

For this analysis, the term $(C_p - C_V)$ was calculated using the relation

$$C_p - C_V = T\bar{V}\alpha^2/\beta, \qquad (5)$$

at 300 K, and from the approximate relation:

$$C_p - C_V = AC_p^2 T, \qquad (6)$$

at other temperatures. At 300 K, the molar volume $\bar{V}$ is 51.53 cm^3 mol^{-1}, and the value 2.0×10^{-4} K^{-1} was taken for the coefficient of thermal expansion, α.[15] The coefficient of isothermal compressibility, β, was estimated at 6.6×10^{-6} atm^{-1}, about the same as those for NH$_4$Cl and NH$_4$Br.[32]

The contributions C_{vib} from internal vibrations of the SCN$^-$ ion were calculated from harmonic oscillator (Einstein) functions, using 2053, 484, 470, and 748 cm^{-1} for the wavenumbers.[15,27-29] Upon calculating and subtracting the two preceding contributions from the observed heat capacity, the residue, $(C_V - C_{vib})$ or $(C_L + C_{lib})$, could be fitted fairly well by a Debye function for eight degrees of freedom, giving Θ_D ranging from 206 to 217 K over the region 10 to 170 K.

An alternative and better representation was possible by using a Debye function for six degrees of freedom for the lattice heat capacity, C_L, and by representing the librational heat capacity, C_{lib}, as the sum of two Einstein functions, assuming that one wavenumber might, on the average, represent the out-of-plane librations and another the in-plane librations. Over the region 5 to 25 K, values of Θ_D between 210 and 212 K together with a librational wavenumber $\tilde{v}'$ between 71 and 69 cm^{-1} gave a satisfactory fit. Using combinations of these parameters, the second librational wavenumber $\tilde{v}''$ was selected which best represented the term $(C_L + C_{vib})$ over the region 25 to 200 K. The values selected were: $\beta = 6.6 \times 10^{-6}$ atm^{-1} (at 300 K); $\Theta_D = 210$ K (for 6 degrees of freedom); $\tilde{v}' = 71$ cm^{-1}; $\tilde{v}'' = 160$ cm^{-1}. The lower librational wavenumber $\tilde{v}'$ corresponds closely to that identified with the out-of-plane mode.[27,28] The somewhat arbitrary selection of β governs the choice of the upper librational wavenumber $\tilde{v}''$. Thus increasing β to 7.0×10^{-6} atm^{-1} leads to 212 K, 69.5 cm^{-1}, and 153 cm^{-1} for

Θ_D, $\tilde{v}'$, and $\tilde{v}''$ with an almost equally good fit of the data. The significant result is that the librational heat capacity from the several modes for the unit cell can be represented adequately up to 250 K by the sum of two Einstein functions, one representing the lower group of frequencies and one the higher group found in the spectra.[27,28]

The contributions from the several terms for the selected parameters are shown in figure 2, together with the trend in Θ_D for the selected values of β, $\tilde{v}'$, and $\tilde{v}''$. Most of the rise in Θ_D between 200 and 250 K could be eliminated by
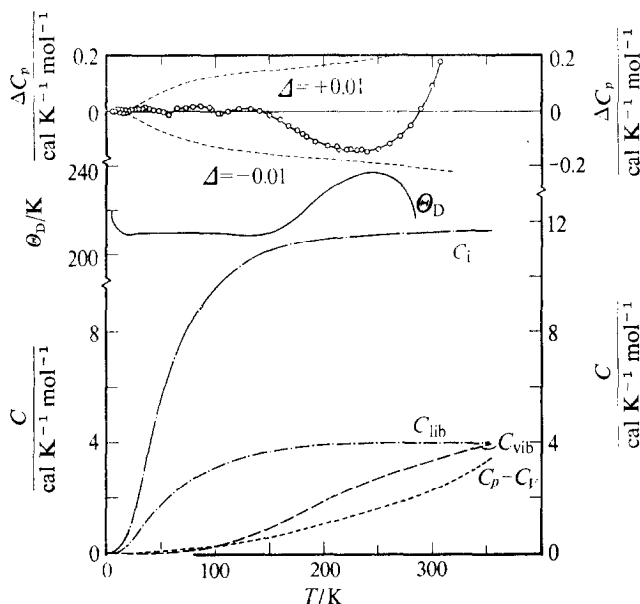
FIGURE 2. Thermal contributions from internal modes in potassium thiocyanate. The contributions calculated as described in the text are indicated at the right of each curve. Open circles represent experimental points. A percentage deviation plot is also depicted to show the quality of fit. $\Delta = \{C_p(\text{obs.}) - C_p(\text{calc.})\}/C_p(\text{obs.})$.

making β an adjustable parameter with a slightly larger value than that selected. Above 300 K, the difference, $\{C_p(\text{obs.}) - C_p(\text{calc.})\}$, strongly indicates the onset of anharmonicity in the librational modes, probably associated with a lowering of the rotational barrier due to expansion of the crystal lattice, and is part of the pre-transitional rise in heat capacity associated with the transition at 413 K.

ANALYSIS OF THE HEAT CAPACITY OF AMMONIUM THIOCYANATE

For this salt, there is an additional contribution, C_r, arising from the torsional vibration (or rotation) of the ammonium ion, together with terms from its internal vibrations. The term $(C_p - C_V)$

$$C_p = (C_p - C_V) + C_{\text{vib}} + C_L + C_{\text{lib}} + C_r, \tag{7}$$

was evaluated as for KSCN. For NH$_4$SCN we used 58.33 cm^3 mol^{-1} for $\overline{V}$, 1.45×10^{-4} K^{-1} for α,[18] and 4×10^{-6} atm^{-1} for β. In estimating the value for β, we considered the fact that α for NH$_4$SCN was less than that for KSCN, and especially

considered the observation by Bridgman[17] that the low-temperature monoclinic form of NH_4SCN has a lower compressibility than the orthorhombic crystals stable above 361 K. The selected value of β gives values of $(C_p - C_V)$ close to those for KSCN. For the internal vibrations of NH_4^+, the wavenumbers of Oden and Decius[30] ($\tilde{v}_1(1) = 3070$, $\tilde{v}_2(2) = 1677$, $\tilde{v}_3(3) = 3138$, and $\tilde{v}_4(3) = 1425$ cm^{-1}) were used. For SCN$^-$, the values ($\tilde{v}_1 = 2075$, $\tilde{v}_{2a} = 468$, $\tilde{v}_{2a} = 482$, and $\tilde{v}_3 = 755$ cm^{-1}) represented several sources.[18,30,31]

Up to 100 K, the torsional contribution, C_r, from the NH_4^+ ion was approximated by three Einstein functions, using the wavenumbers 315, 354, and 375 cm^{-1} (at 90 K) reported by Oden and Decius.[30] An equivalent representation below 100 K, but more appropriate above 100 K, was obtained by evaluating the contribution for anharmonic oscillators,[33] based on a potential barrier of 4.2 kcal mol^{-1} corresponding to a torsional wavenumber of 346 cm^{-1}.[21,22] Such a calculation can only be a first approximation for a 3-dimensional hindered rotator, but was used to help extend the range of fit for the calculated lattice and librational contributions.

After evaluating and subtracting the preceding terms from C_p(obs.), we fitted the residue $(C_L + C_{lib})$ to a Debye function for six degrees of freedom and two Einstein functions representing the librations of the SCN$^-$ ion. From 15 to 40 K, the data could be represented by (226 ± 2) K for Θ_D and (51 ± 2) cm^{-1} for $\tilde{v}'$. The value found for $\tilde{v}'$ falls very close to that reported by Tramer[31] for the out-of-plane libration of thiocyanate ion. From 5 to 12 K, the calculated heat capacities are too low by several per cent, suggesting a low-lying component in the librational frequencies or inadequacy of the Debye model in this region. From 40 to 80 K the data could be represented by (230 ± 2) K, 51 cm^{-1}, and 240 cm^{-1} for Θ_D, $\tilde{v}'$, and $\tilde{v}''$. The selection of $\tilde{v}''$ is uncertain by 30 to 40 cm^{-1}, with 210 cm^{-1} leading to 238 K for Θ_D. Tramer[31] reported a possible libration at 190 cm^{-1}. Use of this value for $\tilde{v}''$ forces Θ_D up to 240 K at 60 to 80 K. Evidently Θ_D varies considerably with temperature or the contribution from the torsional modes cannot be represented by harmonic oscillator functions even at 60 to 80 K. This latter possibility exists when the rotational barrier has a strong temperature dependence, as occurs for a barrier sensitive to changes in lattice dimensions. The correction represented by equation (5) does not entirely correct for lattice expansion in terms of the Debye model, and the approximations inherent in equation (6) may be even less valid for torsional modes. Oden and Decius[30] found torsional wavenumbers at 315, 354, and 375 cm^{-1} at 90 K, while at about 295 K Tramer found the torsional wavenumbers at 300 to 320 cm^{-1}. Similar changes in torsional wavenumbers with temperature have been observed for the ammonium halides.[22] The diminution of barrier height with increase in temperature would accentuate the gain in rotational freedom of the NH_4^+ ion above 100 K and help account for the large heat capacity contribution as a hindered rotator.

Figure 3 shows the contributions attributed to the several terms, and the trend found for Θ_D, based on 4×10^{-6} atm^{-1} for the compressibility coefficient β, and 51 and 240 cm^{-1} for $\tilde{v}'$ and $\tilde{v}''$. The contribution C_r from the torsion-rotation of the NH_4^+ ion was estimated from the relation:

$$C_p(\text{obs.}) - \{C_p - C_V + C_{vib} + C_L + C_{lib}\} (\text{calc.}) = C_r. \qquad (8)$$
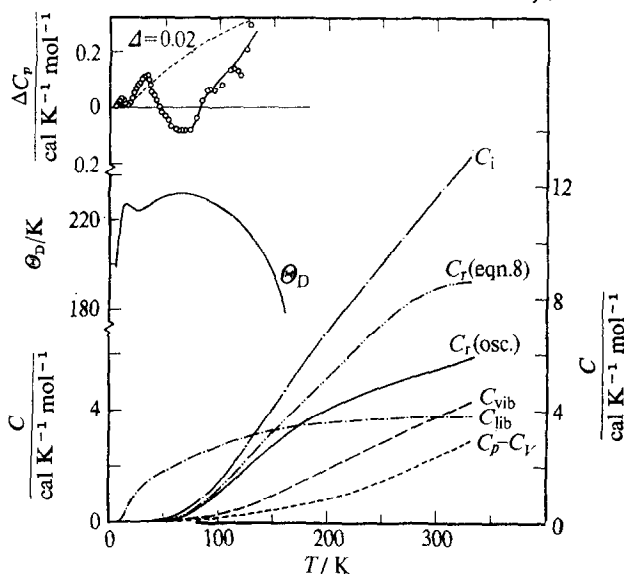
FIGURE 3. Thermal contributions from internal modes in ammonium thiocyanate. The contributions calculated as described in the text are indicated at the right of each curve. A percentage deviation plot is also depicted to show the quality of fit based on equation (7).

$$\Delta = \{C_p(\text{obs.}) - C_p(\text{calc., equation } 7)\}/C_p(\text{obs.}).$$

Above 250 K, C_{lib} was adjusted for anharmonicity by estimation from $\{C_p(\text{obs.}) - C_p(\text{calc.})\}$ for KSCN (previous section). The original selection for β (4×10^{-6} atm^{-1} at 300 K) leads to values of C_r which seem a bit large (8.4 cal K^{-1} mol^{-1} at 300 K for three degrees of freedom), but which are in good agreement with the adjusted difference between the heat capacities for NH$_4$SCN and KSCN $\{(C_p(\text{NH}_4\text{SCN}) - C_p(\text{KSCN}) - C_{\text{vib}}(\text{NH}_4^+)\}$. Increasing $(C_p - C_V)$ by 50 per cent (taking $\beta = 2.67 \times 10^{-6}$ atm^{-1} at 300 K) gives more reasonable values for C_r but suggests a rather low compressibility for NH$_4$SCN. Experimental values for β as a function of temperature would be highly desirable for more reliable resolution of the problem.

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